

Efficient Nanostructured Ni-based Catalysts for Electrochemical Valorization of Glycerol

MOHAMED SEIF EDDINE HOUACHE

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*Department of Chemical and Biological Engineering
Faculty of Engineering
University of Ottawa*

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Abstract

The biodiesel industry produces millions of kilograms of low-value glycerol, which must be either stored or disposed of, creating environmental concerns. Even though glycerol is utilized as a raw material within various industries its supply is still superior to the demand. Upgrading this biodiesel by-product into value-added products using electrochemical technologies is a promising approach and will make biodiesel production more environmentally friendly with added financial benefits.

Precious metals are the state-of-the-art electro-catalysts for the oxidation of organic compounds, and so are a logical choice for the electro-oxidation of glycerol. Two factors that hinder their use in this regard for commercial applications include their cost and susceptibility to poisoning by the carbonyl (CO) species formed during the electro-oxidation process. The use of inexpensive transition metals as the principal metals in a catalyst composite is thus appealing, leading to the selection of nickel (Ni). Furthermore, its high activity, anti-poison ability and long-term stability in alkaline solutions make it an attractive candidate for glycerol electrooxidation reaction (GEOR).

The main thrust of this work is to develop a deeper understanding of the factors involved in controlling the selectivity of the product reaction without 3 carbon cleavage on non-precious metal surfaces.

To overcome a trial-and-error approach, we took advantage of modern synthesis and characterization techniques for metal alloy nanoparticles and advances in rapid identifications and quantifications of products based on infrared spectroscopy. These tools were expected to provide the foundation for the detailed understanding of GEOR mechanism hence would pave the way for the rational design of catalysts to produce specific high value-added chemicals.

We carried out extensive research to determine the effect of size, morphology, shape, support, experimental conditions and catalyst preparation methods on the catalytic performance of Ni. The thesis aims to demonstrate how the selectivity of unsupported Ni nanoparticles for GEOR can be improved via interaction of Ni with low noble and transition metals content. Enhanced selectivity towards C3 and C2 products such as glycerate, lactate, oxalate and tartronate, was achieved by simply adding less than 20 atomic percent of any of bismuth (Bi), Pd or Au onto Ni nanoparticles. Furthermore, the composition effect of carbon supported $\text{Ni}_x\text{M}_{1-x}$ ($\text{M} = \text{Bi}, \text{Pd}$ and Au) nanomaterials were

combined with Pt/C and commercial silver nanoparticles for cathodic hydrogen production and CO₂ electro-reduction, respectively. These rich-phase of Ni(OH)₂ catalysts were highly active and selective towards C-C bond breaking products leading to 100% selectivity of formate after 1 hr electrolysis and 100% conversion of glycerol after 24 hr at +1.55 V. Lastly, the first principles calculations based on the density functional theory (DFT) insights provided an explanation to understand the electronic structure, magnetism and reactivity of our catalysts. Core@shell (M_m@Ni_n) nanoparticles of 13-, 54- and 55-atoms with different elements concentrations matched the experimental results and assisted us with a better understanding of some of the microscopic phenomena involved with the reactivity of bimetallic nanoparticles.

Résumé

L'industrie du biodiesel produit des millions de kilogrammes de glycérol de faible valeur, qui doivent être stockés ou éliminés, ce qui crée des problèmes environnementaux. Même si le glycérol est utilisé comme matière première dans diverses industries, son offre est toujours supérieure à la demande. La valorisation de ce sous-produit de biodiesel en produits à valeur ajoutée à l'aide de technologies électrochimiques est une approche prometteuse et rendra la production de biodiesel plus respectueuse de l'environnement avec des avantages financiers supplémentaires. Les métaux précieux sont les électrocatalyseurs de pointe pour l'oxydation de composés organiques, et sont donc un choix logique pour l'électro-oxydation du glycérol. Deux facteurs qui entravent leur utilisation à cet égard pour des applications commerciales comprennent leur coût et leur sensibilité à l'empoisonnement par les espèces carbonyle (CO) formée durant le processus d'électro-oxydation. L'utilisation de métaux de transition bon marché comme métaux principaux dans un composite catalytique est donc intéressante, ainsi conduisant au choix du nickel (Ni). En outre, sa haute activité, sa capacité anti-poison et sa stabilité à long terme dans les solutions alcalines en font de lui un élément attractif pour la réaction d'électrooxydation du glycérol (REOG).

L'objectif principal de ce travail est de développer une compréhension plus approfondie des facteurs impliqués dans le contrôle de la sélectivité de la réaction du produit sans clivage 3 carbone sur les surfaces de métaux non précieux. Pour surmonter une approche par essais et erreurs, nous avons profité des techniques modernes de synthèse et de caractérisation des nanoparticules d'alliages métalliques et des progrès dans les identifications et quantifications rapides de produits basées sur la spectroscopie infrarouge. Ces outils devaient fournir les bases d'une compréhension détaillée du mécanisme GEOR et ouvriraient ainsi la voie à la conception rationnelle de catalyseurs pour produire des produits chimiques spécifiques à haute valeur ajoutée. Nous avons mené des recherches approfondies pour déterminer l'effet de la taille, de la morphologie, de la forme, du support, des conditions expérimentales et des méthodes de préparation du catalyseur sur les performances catalytiques du Ni. La thèse vise à démontrer comment la sélectivité des nanoparticules de Ni non supportées pour GEOR peut être améliorée via l'interaction du Ni avec une faible teneur en métaux nobles et de transition. Une sélectivité améliorée envers les produits C3 et C2 tels que le glycérate, le lactate, l'oxalate et le tartronate, a été obtenue en ajoutant simplement moins de 20 pour

cent atomique de l'un de bismuth (Bi), Pd ou Au sur des nanoparticules de Ni. En outre, l'effet de la composition des nanomatériaux $\text{Ni}_x\text{M}_{1-x}$ ($\text{M} = \text{Bi}, \text{Pd}$ et Au) supportés par du carbone ont été combinés avec du Pt / C et des nanoparticules d'argent commerciales pour la production d'hydrogène cathodique et l'électro-réduction du CO_2 , respectivement. Ces catalyseurs en phase riche en $\text{Ni}(\text{OH})_2$ étaient très actifs et sélectifs vis-à-vis des produits de rupture de la liaison C-C conduisant à une sélectivité de 100% du formiate après 1 heure d'électrolyse et à 100% de conversion du glycérol après 24 heures à +1,55 V. Enfin, les calculs du premier principes basés sur les connaissances de la théorie fonctionnelle de la densité (DFT) ont fourni une explication pour comprendre la structure électronique, le magnétisme et la réactivité de nos catalyseurs. Les nanoparticules Core @ shell ($\text{M}_m @ \text{N}_n$) de 13, 54 et 55 atomes avec différentes concentrations d'éléments correspondaient aux résultats expérimentaux et nous ont aidés à mieux comprendre certains des phénomènes microscopiques impliqués dans la réactivité des nanoparticules bimétalliques.

Co-Authorship Statement

I hereby declare that I am the first author of all the chapters written in this thesis.

I acknowledge the supervision of Prof. Elena Baranova on the work described in this thesis, her editorial comments in each chapter, and scientific guidance in performing lab experiments at the University of Ottawa.

Chapter 1, 2 and 9 are solely written by me under the editorial comments of Prof. Elena Baranova.

Chapter 3 is a manuscript published in a peer-reviewed academic journal. The electrochemical measurements were all carried out by myself with the assistance of co-op student Emily Cossar. The spectrochemical measurements and SEM images were all performed by myself. XPS analyses were conducted by Dr. Spyridon Ntais. Data analysis was performed by myself with the assistance of Prof. Baranova. The manuscript was written solely by myself with editorial comments provided by Prof. Baranova.

Chapter 4 is a manuscript submitted in a peer-reviewed academic journal. The synthesis of different shapes of Ni catalysts and the electrochemical measurements were solely done by myself. The spectrochemical measurements and XRD analyses were all performed by myself. The physicochemical characterizations were conducted by Reza Safari at McMaster University. The DFT calculations and its analyses were obtained by Dr. Mario Sandoval and his colleagues at Universidad Nacional del Sur in Argentina and Instituto Andaluz de Ciencias de la Tierra in Spain. The manuscript was written solely by myself with the assistance of Dr. Mario (Universidad Nacional del Sur) with editorial comments provided by Prof. Gianluigi Botton (McMaster), Prof. Paula Jasen, Estela González, Prof. Alfredo Juan (Universidad Nacional del Sur) and Prof. Baranova. They are all co-authors on the manuscript.

Chapter 5 is a manuscript published in a peer-reviewed academic journal. The synthesis of $\text{Ni}_x\text{Pd}_{1-x}$ catalysts and electrochemical measurements were all carried out by myself with the assistance of co-op students Kara Hughes and Abdulgadir Ahmed. The spectrochemical measurements and XRD analyses were all performed by myself. The physicochemical characterizations were taken by Reza Safari and Hanshuo Liu at McMaster University. Data analysis was performed by myself with the assistance of Prof.

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Chapter 6 is a manuscript published in a peer-reviewed academic journal. The synthesis of $\text{Ni}_x\text{Bi}_{1-x}$ catalysts was solely done by me. The electrochemical measurements were all carried out by myself with the assistance of co-op students Kara Hughes. The spectrochemical measurements, XRD analyses, constructing GEOR electrolysis cell and HPLC tests were all performed by myself. The physicochemical characterizations were conducted by Reza Safari at McMaster University. Data analysis was performed by myself with the assistance of Prof. Baranova. The manuscript was written solely by myself with editorial comments provided by Prof. Gianluigi Botton (McMaster) and Prof. Baranova. They are both co-authors on the manuscript.

Chapter 7 is a manuscript submitted in a peer-reviewed academic journal. The synthesis of $\text{Ni}_x\text{M}_{1-x}$ ($\text{M} = \text{Pd}$ and Au) catalysts was solely done by me. The electrochemical measurements were all carried out by myself with the assistance of MSc student Asma Shubair. The XRD analyses and HPLC measurements were all performed by myself. The physicochemical characterizations were conducted by Reza Safari at McMaster University. The DFT calculations and its analyses were obtained by Dr. Mario Sandoval at Universidad Nacional del Sur in Argentina. The manuscript was written solely by myself with the assistance of Dr. Mario (Universidad Nacional del Sur) with editorial comments provided by Prof. Gianluigi Botton (McMaster), Prof. Paula Jasen, Estela González (Universidad Nacional del Sur) and Prof. Baranova. They are all co-authors on the manuscript.

Chapter 8 is a manuscript submitted in a peer-reviewed academic journal. The synthesis of carbon-supported $\text{Ni}_x\text{M}_{1-x}$ ($\text{M} = \text{Pd}$, Au and Bi) catalysts was solely done by me. The electrochemical measurements were all carried out by myself with the assistance of PhD student Thibault Rafaïdeen at the university of Poitiers in France. The FTIR measurements, XRD analyses, HPLC and NMR tests were all performed by myself. The physicochemical characterizations were conducted by Reza Safari at McMaster University. The electrochemical reduction of CO_2 experiments was obtained by Uzoma Nwabara at University of Illinois at Urbana-Champaign in USA. The manuscript was written solely by myself with the assistance of Uzoma (University of Illinois) with

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Dedication

I would like to dedicate this thesis to my parents, my wife, my siblings (and their family), my parent-in-law and my sister-in-law (and her family) for their infinite and selfless love they have shown to me. My highest appreciation goes to my parents, whom paved the way for our move to Canada, simply with the hope of providing a better outlook for the future of their family. Thank you, without your sacrifices I would have never reached this moment. I am forever indebted to my beloved wife who showed selflessness and unconditional love towards me, her sacrifice will always be unparalleled. To my babies Lynda and Adam who taught me a different kind of love and responsibility. To every person who supported me and helped guide me on this journey.

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Nomenclature

List of Acronyms and Abbreviations

ALD	Atomic layer deposited
BE	Binding energy
CA	Chronoamperometry
CaF ₂	Calcium fluoride
CCE	Carbon-ceramic electrode
CE	Counter electrode
CNT	Carbon nanotube
CV	Cyclic voltammetry
DAFCs	Direct alcohol fuel cells
DEMS	Differential electrochemical mass spectrometry
DFAFCs	Direct formic acid fuel cells
DFT	Density functional theory
DGFCs	Direct glycerol fuel cells
Dh	Decahedral
DHA	Dihydroxyacetone
ECSA	Electro-active surface area
EDS	Energy dispersive x-ray spectroscopy
EELS	Electron energy loss spectroscopy
EIS	Electrochemical impedance spectroscopy
EMIRS	Electro-modulated infrared reflectance spectroscopy
EXAFS	Extended x-ray absorption fine structure
EF	Fermi level
FA	formic acid
FTIR	Fourier transform infrared spectroscopy
FWHM	Full width at half maximum
GA	Glycolic acid
GC	Glassy carbon
GEOR	Glycerol electrooxidation reaction
GGA	Generalized gradient approximation
GLA	Glyceric acid
GLAD	Glyceraldehyde
GNRs	Graphene nanoribbons
GNS	Graphene nanosheets
GONRs	Graphene oxide nanoribbons
HAADF	High-angle annular dark-field
HC	Hydrocarbons
HER	Hydrogen evolution
Hg/HgO	Mercury-mercury oxide reference electrode
HPA	Hydroxypyruvic acid
HPLC	High performance liquid chromatography
IC	Ion chromatography
Ih	Icosahedral
IR	Infrared
KOH	Potassium hydroxide
LA	Lactic acid
LN-MCTN	Nitrogen cooled mercury cadmium telluride detector

LSV	Linear sweep voltammetry
MESOX	Mesoxalic acid
MSE	Mercury-mercurous sulphate reference electrode
MWCNTs	Multi-walled carbon nanotubes
NaBH ₄	Sodium borohydride salt
NMR	Nuclear magnetic resonance
NPs	Nanoparticles
NPSS	Nano-porous stainless steel
OER	Oxygen evolution reaction
OX	Oxalic acid
PAW	projector augmented wave
PBE	Perdew, burke and erzenhorf functional
PGM	Platinum group metal
PEDOT	Poly(3,4-ethylenedioxythiophene)
PMA-50 XL	Photo-elastic modulator accessory/chamber
PMC	Phenanthroline modified carbon
PM-IRRAS	Polarization modulation infrared reflection absorption spectroscopy
PVP	Polyvinylpyrrolidone
RE	Reference electrode
RHE	Reversible hydrogen electrode
R.F(bulk)	Reflectance factor for bulk species
R.F(surf)	Reflectance factor for surface species
rGO	Reduced graphene oxide
RT	Room temperature
SAED	Selected area electron diffraction
SEM	Scanning electron microscopy
STEM	Scanning transmission electron microscopy
TA	Tartronic acid
TEM	Transmission electron microscopy
TGA	Thermogravimetric Analysis
VASP	Vienna ab-initio simulation package
WE	Working electrode
WF	Work function
XRD	X-Ray diffraction
XPS	X-ray photoelectron microscopy
θ	Bragg angle (radians)
λ	X-ray wavelength

Chapter 1

1.1 Introduction

In a world of rising climate change, populations and resource pressures, Canada must play a leading role to face escalating challenges related to deteriorating reserves of non-renewable energy sources, greenhouse gas production, environmental pollution, and related societal issues. Since 2010, Canada has had a federal mandate requiring 5% of the national gasoline pool to be renewable. Renewable fuels, like biodiesel production, are a key initiative in supporting our commitment to reducing Canada's total greenhouse gas emissions by 30% over the coming decades. Biodiesel production is reached 375 million liters in 2019, an increase of 22% over 2015 levels based on Canada Biofuels Annual report (2019). Biodiesel is derived from vegetable oils or animal and/or waste fats through a transesterification reaction. This process generates 10 wt.% of glycerol as a by-product. The biodiesel industry produces millions of kilograms of low-value glycerol, which must be either stored or disposed of, creating environmental concerns. Glycerol thermal combustion for energy production is not a solution, as the process generates toxic substances, such as acrolein.¹

Even though glycerol is utilized as a raw material within various industries such as pharmaceuticals, food, tobacco products and cosmetics, its supply is still superior to the demand. Thus, making the overproduction of glycerol a global challenge that should be effectively addressed in a timely manner. Upgrading this biodiesel by-product into value-added products using electrochemical technologies is a more promising approach, and will make biodiesel production more environmentally friendly with added financial benefits. Electrochemical oxidation of glycerol to value-added products without three-carbon (C-C-C) cleavage with concurrent cathodic production of hydrogen in an electrolytic cell attracted significant attention in recent years.² The electrochemical partial oxidation of glycerol in alkaline media consists of complex reaction pathways³ and produces a large number of useful intermediates, such as glycerate, tartronate, oxalate, hydroxypyruvate, glycolate, dihydroxyacetone, mesoxalate and formate ions. A mixture of these products during the glycerol electrooxidation reaction (GEOR) has been

observed and reported in the literature.⁴ Some of these oxygenated species have industrial uses, from heavy metal complexing agents to polymer precursors or drug delivery agents. All three-carbon electro-oxidation products are more valuable than glycerol. A number of recent studies showed GEOR on noble metals such as platinum (Pt), palladium (Pd) and gold (Au)⁵⁻¹¹, which have satisfactory activity but low selectivity towards desired products. Furthermore, to make the GEOR practically viable, novel inexpensive and selective catalysts are necessary and this has led to the selection of nickel (Ni). Ni is one of the most commonly used non-noble metal catalysts and has been applied in numerous electrochemical systems. However, it suffers from the high overpotentials compared to Pt group metals. These possible applications are due to their properties, such as good stability in alkaline media, a large surface area and a high-power capacity. They can be easily converted to nickel oxyhydroxide nanoparticles with good cyclability. Thus, research on these materials is very essential and can advance electrochemical energy technologies. The main thrust of this work is to study how to control the selectivity of the product reaction. Modification of Ni catalyst with other metals, guided by strategies used in previous work on related systems such as (i) bismuth (Bi) to suppress carbon double bond cleavage and give selectivity to 1,3-dihydroxy-2-propanone at low potentials;¹² (ii) gold (Au) to reduce activity, but also increase selectivity to higher oxidation products, such as hydroxypyruvate;¹³ and (iii) cobalt (Co) to shift the $\text{Ni}^{2+/3+}$ transitions to lower potentials, which leads to less oxidized products.¹⁴ Understanding how this $\text{Ni}^{2+/3+}$ transition is influenced by structure and additives will be key to optimizing the selectivity of Ni towards glycerol electro-oxidation.

1.2 Research objectives

The primary objective of this research is the identification of an active and stable Bi-based electrocatalyst that can affect the selective electro-oxidation of glycerol to the value-added products without C-C-C cleavage.

The basis of this thesis is a fundamental hypothesis which goes as follows:

“Understanding how this $\text{Ni}^{2+/3+}$ transition is influenced by structure and additives will be key to optimizing the selectivity of Ni towards glycerol electro-oxidation”.

To fulfill the overall objective of this thesis, the following detailed objectives are listed below:

- Synthesis stable and efficient Ni-based electro-catalysts with low noble and post-transition metal content ($\text{Ni}_x\text{Pd}_{1-x}$, $\text{Ni}_x\text{Au}_{1-x}$, and $\text{Ni}_x\text{Bi}_{1-x}$, $x = 100-80$ at. %) and high selectivity towards three-carbon glycerol oxidation products. To study the effect of particle size, surface and bulk structure, as well as the composition of nanoparticles on their catalytic activity and stability against poisoning.
- Study the physicochemical characterizations of the fabricated nanostructured catalysts to obtain information about morphology, particle size as well as surface and bulk structure. To establish a structure-to-property correlation for the best performing catalysts that lead to high catalytic activity, stability and selectivity to desired products.
- Investigation of electro-catalytic activity and stability for GEOR in an alkaline media.
- Monitor the in-situ and ex-situ formation of products during glycerol electro-oxidation as a precursor for a mechanistic understanding of the reaction pathway using polarization modulation infrared reflection absorption spectroscopy (PM-IRRAS), high-performance liquid chromatography (HPLC) and nuclear magnetic resonance (NMR).
- Design and construct an electrolysis cell that comprises the best performing Ni-based electro-catalyst for simultaneous GEOR with cathodic hydrogen production or CO_2 electro-reduction.
- Density functional theory (DFT) calculations to understand the electronic structure, magnetism and reactivity of our catalysts.

1.3 Thesis structure and organization

This thesis has been divided into nine main chapters ordered as follow:

Chapters 3 to 8 each represent an independent article published in or submitted to a peer-reviewed academic journal. Due to this structure, some repetition of ideas and elements (i.e. experimental methodology) was inevitable. The literature cited is included in the form of separate bibliographies at the end of each individual chapter.

Chapter 1 a general introduction to this dissertation is given along with the objectives and motivations behind this work.

- Chapter 2** a comprehensive literature review with a special focus on glycerol electrochemical oxidation research. The main emphasize is made on catalyst selection, design and characterization for application in the GEOR, along with recent theoretical developments, based on DFT calculations.
- Chapter 3** describes the detailed investigation of the electrochemical treatment to improve the catalytic activity of polycrystalline bulk nickel towards GEOR.
- Chapter 4** represents an investigation of the effect of different structures of Ni microstructure of GEOR by combining electron microscopy, electrochemistry and in-situ infrared spectroscopy techniques. Using the Vienna ab-initio simulation package (VASP) and density functional theory (DFT), we modeled the surfaces of β -Ni(OH)₂ and β -NiOOH systems as well as their different cleavage planes with different possible terminations.
- Chapter 5** deals with electrochemical valorization of glycerol on mono-and bi-metallic Ni_xPd_{1-x} in alkaline solution. It also proposes direct vs indirect mechanism of electron transfer on Ni/NiOOH surface and confirmation that this is an active phase for GEOR.
- Chapter 6** represents the utilization of inexpensive Ni_xBi_{1-x} nanoparticles for selective oxidation of glycerol to C3 and C2 products by adding small quantities of Bi adatom (≤ 10 at.%).
- Chapter 7** This chapter comes as a direct comparison study between Ni_xPd_{1-x} and Ni_xAu_{1-x} core-shell like nanoparticles synthesised with facile co-reduction method towards GEOR. A further step was taken to compute the excess energy, strain, electronic structure, Bader charge and work function for the Core@shell (M_m@Ni_n) nanoparticles of 13-, 54- and 55-atoms with different elements concentrations. The model's findings were directly related to the experimental work.

Chapter 8 the last chapter is about co-electrolysis of GEOR on a carbon supported $\text{Ni}_x\text{M}_{1-x}$ ($\text{M} = \text{Bi}, \text{Pd}$ and Au) nanomaterials with Pt/C and Ag NPs for cathodic H_2 production and CO_2 electro-reduction, respectively.

Chapter 9 A synthesis conclusion of all the research data described in the previous chapters, including the future research perspectives related to this work.

Appendices The appendices at the end include supplementary information for Chapters 3, 4, 5, 6, 7 and 8, as well as a list of the publications, conference meetings and poster presentations related to this work.

I hope you will enjoy walking through the path of my journey in the past four years of the project. Welcome on-board and enjoy the reading.

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Chapter 2

Background and Literature Review

2 Study on Catalyst Selection for Electrochemical Valorization of Glycerol

Based on the paper:

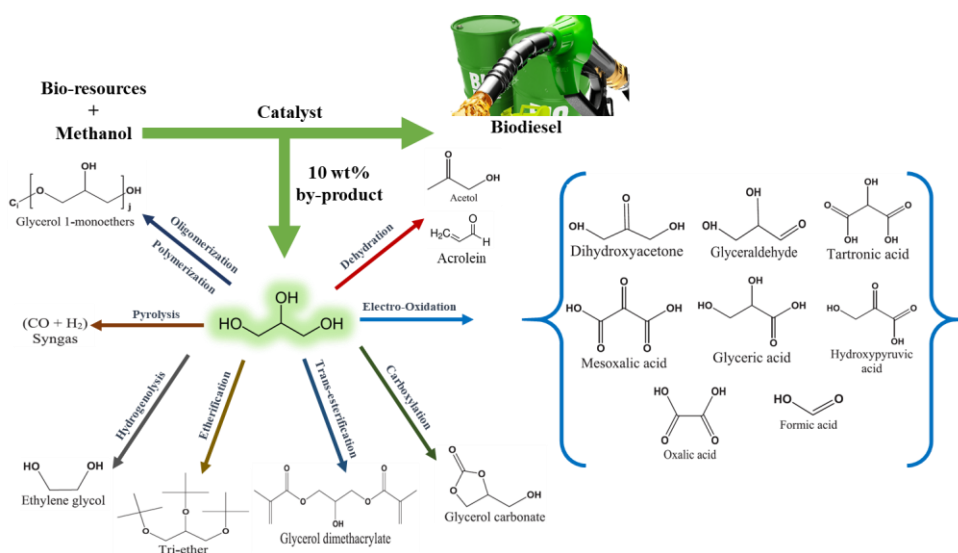
Houache M. S. E., Hughes K., Baranova E. A., Sustainable Energy & Fuels, 2019, 3, 1892-1915.

2.1 Introduction

2.1.1 Sustainable use of glycerol surplus

In a world of rising populations, climate change and natural resources depletion, the quest for clean, renewable and widely available energy sources becomes constantly more urgent.¹⁻³ It is clear now that there is an urgent need to reduce our dependency on a single fuel source. Biofuels are the best means for cleaner and renewable energy supply, which allows complementing oil supply or completely substitute it, while protecting the environment. For instance, biodiesel production is a key factor in showing our commitment to reduce total greenhouse gas and carbon dioxide (CO₂) emissions over the coming decades. Biodiesel is a mixture of mono-alkyl esters derived from natural resources, making biodiesel fuel biodegradable, renewable, often locally available. Furthermore, biodiesel has lower sulphur content and produces less hydrocarbons (HC) and carbon monoxide (CO).⁴ Biomass generated from animal fats and plant lipids are common sources of biodiesel. Based on United States Environmental Protection Agency (US EPA) study, the utilization of biodiesel can reduce 70% HC, 78% CO₂ emissions and 50% particulate matters in exhaust emissions compared to traditional diesel fuels.⁵ The most common way to produce biodiesel is via or base- or acid-catalyzed transesterification of edible/non-edible vegetable oils and fats (triglycerides) with alcohol (methanol) to yield fatty acid alkyl esters (i.e. biodiesel) and glycerol as illustrated in schematic 2.1.⁶ This process generates 10 wt.% of glycerol as a by-product. The biodiesel industry generates hundreds of millions of kilograms of low-value glycerol, which must be either disposed or stored of, creating environmental concerns. Thermal combustion of glycerol for energy

production is not a solution, as the process produces acrolein as toxic substance.⁷ Because of the relative abundance of glycerol, it is imperative that practical and efficient utilization is found for it in order to maintain the viability of biodiesel. Despite applications of glycerol⁸⁻¹¹, there still exists an imbalance between the large supply and the inadequate demand. Thus, in the last decade several studies have been carried out to find ways of glycerol valorization into useful products. Fortunately, glycerol is a highly rich in functionalities with three -OH groups that makes it a suitable candidate for the conversion into value-added chemicals.¹² A diverse array of processes including glycerol reforming (photo-¹³, thermo-¹⁴⁻¹⁶ and electro-catalytic¹⁷), hydrogenolysis^{18,19}, dehydration^{20,21}, esterification^{22,23}, etherification²⁴, pyrolysis^{25,26}, carboxylation²⁷, oligomerization and polymerization²⁸ have been studied (scheme 2.1). The variety of value-added chemicals ranging from glyceric acid, dihydroxyacetone and lactic acid, acrylic acid²¹, to 1,3-propanediol and 1,2-propanediol.^{18,19}



Scheme 2.1. Transesterification reaction shown for biodiesel and glycerol production followed by different catalytic conversion of glycerol into value-added chemicals.

However, several of these processes have drawbacks, such as a lack of sufficient yield and selectivity. Some systems require high running-cost production processes “e.g., high pressure (P) and temperature (T)” or require a long reaction time, hindering them from being commercially feasible.²⁹ To address these disadvantages and to facilitate the commercial transformation of glycerol to more valuable chemicals, clean electrochemical technologies have been assessed as an alternative approach. This is because of its straight forward operation, low T and P. Furthermore, the use of renewable electricity makes the

route environmentally friendly. In this context, the electrooxidation process is one the promising routes to obtain high value tartronic acid (TA), dihydroxyacetone (DHA), glyceraldehyde (GLAD), glyceric acid (GLA) and hydroxypyruvic acid (HPA). The products may utilize as heavy metal complexing agents for the control of water pollution,^{30,31} for the synthesis of biocompatible compounds used for food additives, or in detergent industry. Tartronic acid, mesoxalic acid (MESOX) and glyceric acid are mostly converted into many market products such as emulsifiers or biodegradable polymers.³² Additionally, TA also serves as a drug-delivery agent, in order to enhance the tetracycline antibiotic absorption into blood.¹⁷ DHA is expansively utilized in the cosmetic as a safe skin tanning agent and used as a versatile building block for the organic synthesis of a variety of fine chemicals.^{33,34} Glycolic acid (GA) serves as personal care products and as versatile cleaning agent, e.g., rust removal and degreasing agent.³⁵ While MESOX is utilized as a precursor in organic synthesis for anti-HIV agent³⁶ and diabetes treatment.³⁵ All three-carbon electrooxidation products have a higher price than glycerol sometimes in a ratio of 500 in the case of the hydroxypyruvate.³⁷ Production of formic acid (FA) is of interest as well³⁸⁻⁴⁰, due to the use of formic acid as hydrogen (H₂) carrier to catalytically release H₂ on demand or as fuel in DFAFCs.⁴¹⁻⁴³ Analysis of glycerol reaction products is complex because of the various possible glycerol electrooxidation products that can be generated. Sometimes the reported reaction pathways and products are conflicting; even on the similar system being studied. This could be due to several reasons such as, different catalyst types, differences in concentration of reactants and limitations of the analytical techniques used. Glycerol electrooxidation (GEOR) products have been analyzed by numerous techniques, such as ion chromatography (IC), nuclear magnetic resonance (NMR) spectroscopy,⁴⁴ in-situ electro-modulated infrared reflectance spectroscopy (EMIRS),⁴⁵ in-situ Fourier transform infrared spectroscopy (FTIR),⁴⁶ differential electrochemical mass spectrometry (DEMS),⁴⁷ high performance liquid chromatography (HPLC)⁴⁸ and PM-IRRAS.⁴⁹ Over the last eight years, the number of research papers on GEOR has increased, with a rapid increase occurring after 2010 as indicated in Figure 2.1. The purpose of this review is to present advances in glycerol electrooxidation during the last five years. For earlier contributions to this field, we kindly refer the reader to the following other reviews.^{16,17} The focus here is to highlight the critical strategies in the catalyst development and applications to enhance the catalyst's performance in terms of selectivity, stability and activity. In addition, recent theoretical developments, based on density functional theory (DFT) calculations, will be addressed

as this tool is effective to unravel the catalyst functionality-reaction selectivity and activity relationship.

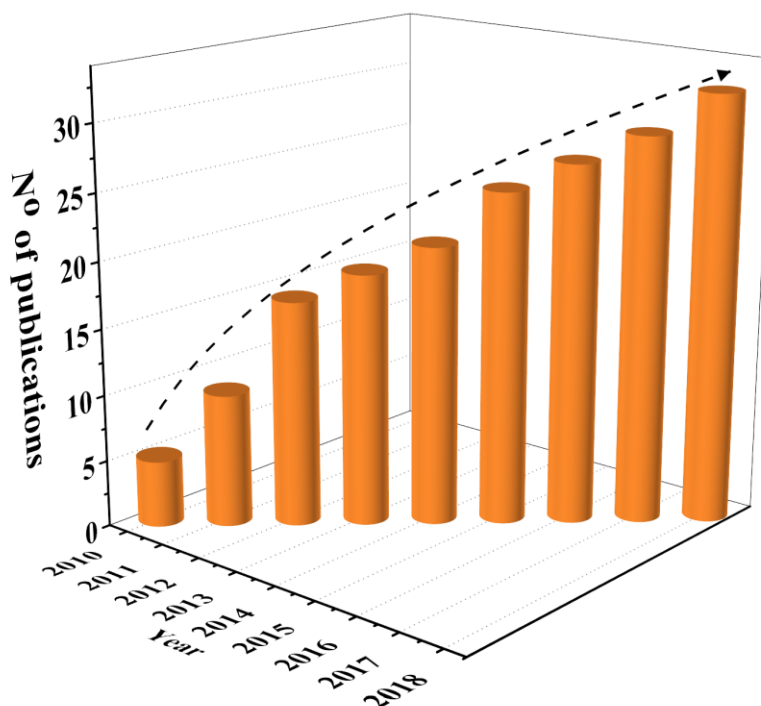


Figure 2.1. Increasing number of research papers on glycerol electrooxidation (data as of December 2018, Scopus).

2.1.2 Electrochemical conversion of glycerol

Typically, alcohol electrochemical valorization is a multistep process which involves the adsorption of alcohol, inter-atomic bonds cleavage, charge transfer, reactions between the oxygenated species and the alcohol fragments and product desorption.⁵³ Therefore, the anode efficiency is dependent on the: (i) interaction between the catalyst surface and alcohol molecules, (ii) interaction between the resulting adsorbed alcohol fragments and the catalyst surface, and (iii) surface oxides formation. In this context, the reaction mechanism, the product distribution obtained and the degree of glycerol conversion relies significantly on (i) the glycerol concentration, (ii) the geometric and electronic properties of the electrodes and (iii) the working conditions of the electrochemical conversion process (e.g., solution pH, temperature and electrolyte solution).⁵³

Electrochemical reactors can be utilized in two different configurations: "fuel cell" and "electrolysis", as shown in Figure 2.2. The "fuel cell" configuration generates valuable products and cogenerates electrical energy through direct oxidation reaction of

glycerol at the anode and oxygen reduction at the cathode. The "electrolysis" configuration generates valuable products at the anode with concurrent cathodic production of hydrogen (H_2) and could be combined with/or CO_2 electroreduction.

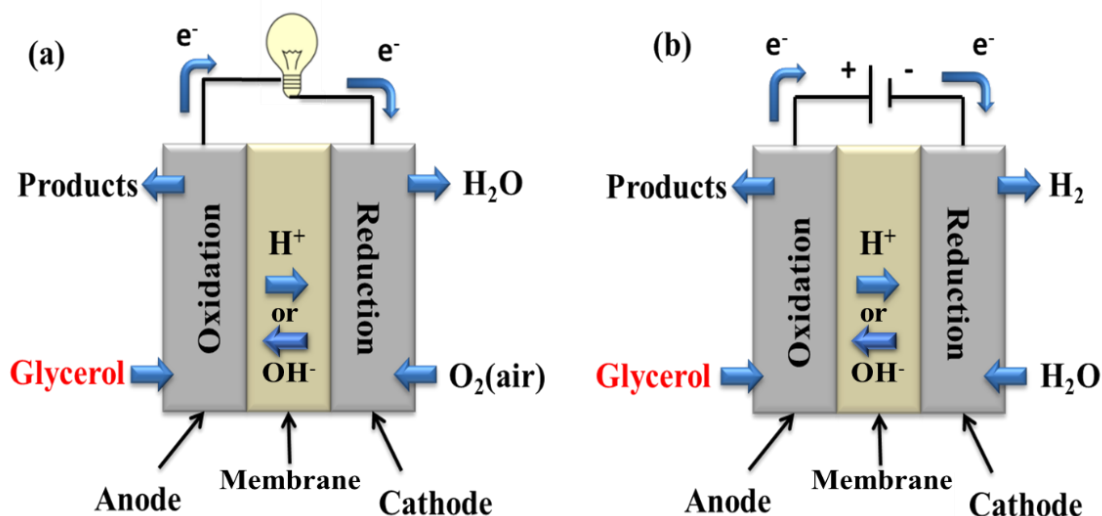


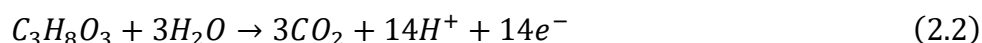
Figure 2.2. Working principle of a) fuel cell and b) electrolysis cell.¹⁷

Water Electrolysis is an alternative process to steam reforming of hydrocarbons that allows generation of clean H_2 . It is interesting to compare the electrochemical production of H_2 from water and glycerol electrolysis from a thermodynamic point of view. In classical water electrolysis, gaseous or liquid water is fed to the anodic compartment, oxidizing to generate oxygen and protons:



$$\Delta H_r^0 = 286 \text{ kJ} \cdot \text{mol}^{-1} \quad \Delta G_r^0 = 237 \text{ kJ} \cdot \text{mol}^{-1}$$

Similarly, glycerol is oxidized in the anodic compartment of the electrolysis cell, generating carbon dioxide and protons:



With the thermodynamic data under standard conditions:

$$\begin{aligned} \Delta H_r^0 &= 3\Delta H_f^0(CO_2)_{gas} - 3\Delta H_f^0(H_2O)_{liq} - \Delta H_f^0(Glycerol)_{liq} \\ &= 3(-393.5) - 3(-285.8) - (-665.9) = 342.8 \text{ kJ} \cdot \text{mol}^{-1} \end{aligned}$$

$$\begin{aligned}\Delta G_r^0 &= 3\Delta G_f^0(CO_2)_{gas} - 3\Delta G_f^0(H_2O)_{liq} - \Delta G_f^0(Glycerol)_{liq} \\ &= 3(-394.4) + 3(237.2) + (475.5) = 3.9 \text{ kJ.mol}^{-1}\end{aligned}$$

Both reaction enthalpies show the need for an external energy input ($\Delta G > 0$), provided by an external electric power source. The minimum standard theoretical voltage U_{cell}^0 to activate the reaction can be calculated from ΔG_r^0 : $U_{cell}^0 = \Delta G_r^0 / n.F$, with n the number of electrons involved in the reaction and F the Faraday constant. Therefore, $U_{cell}^0 = 1.23V$ for water electrolysis ($n=2$) and $U_{cell}^0 = 0.003V$ ($n=14$) for glycerol electrolysis.¹⁷ The thermodynamic data demonstrates that the use of alcohols and in particular glycerol at the anode of electrolysis cell could be energetically more interesting than the oxidation of water for the H_2 production.

Although there are still limited research studies on GEOR reported in literature, the knowledge has extended significantly during the last half decade which reflected the importance of value-added chemicals such as TA, GLYCA DHA and MESOX from a bio-renewable waste. Most of GEOR reports have been studied in the alkaline media but only few in neutral (base-free) or acidic media.

2.1.3 Electrocatalysis

The nature of the anodic electro-catalysts towards GEOR will be governed by two main aspects: the catalyst selectivity in order to attain the desired reaction products at maximum yield and high catalytic activity at the lowest potential domain possible to reduce the electrical energy consumption. In order to meet these goals, two main strategies could be employed as illustrated in Figure 2.3. (i) Increasing the intrinsic activity of each active site. (ii) Increasing the active sites number on a given electrode, i.e. through improved catalyst structuring to expose more active sites per mass or increased surface area.⁵⁴ Therefore, the precise control of these parameters i.e. different catalyst supports, geometry, morphology and surface composition will have an impact on the adsorption of glycerol and will induce an increase catalytic activity and may also prompt a change in the catalyst selectivity of the anode electrode materials. Similarly, bimetallic also prompt changes in the electronic configuration compared to monometallic due to changes in electron transfer for the GEOR. Quantitative and qualitative analysis

of GEOR products on various catalysts platinum (Pt), palladium (Pd), gold (Au) and nickel (Ni) - based catalysts have been summarized in Table 2.1.

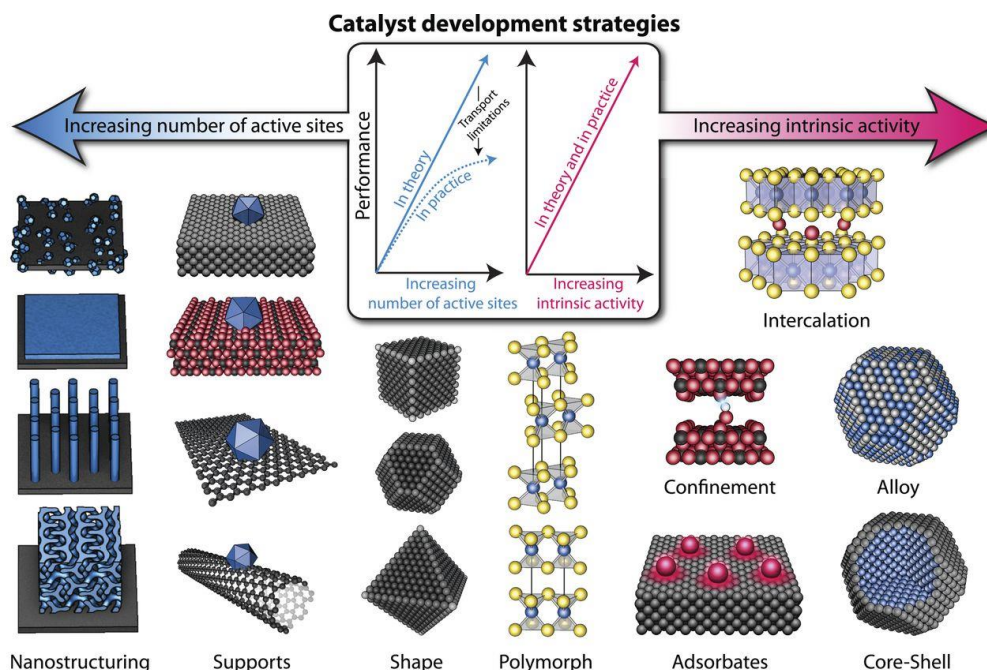


Figure 2.3. Schematic of various catalyst development strategies that control the catalytic performance. (Reproduced with permission.⁵⁴ Copyright© 2017, Science)

2.2 Catalyst development for glycerol electrooxidation

2.2.1 Platinum-based catalysts

2.2.1.1 Platinum group in alkaline media

Platinum has been widely studied as a catalyst for the GEOR, because of its high activity and excellent stability in both acidic and alkaline media. The electrochemical behaviour of monometallic Pt and the effect of different morphologies, support, and promoters have been shown in several studies. Wang *et al.*⁵⁵, fabricated an amorphous structure with ultra-dispersed Pt nanoparticles (NPs) (0.36 nm) loaded on nitrogen functionalised carbon (AU-Pt/PMC) via severe etching process for GEOR. They demonstrated that the use of amorphous ultra-dispersed structure led to remarkable enhancements in the electrocatalytic activity (5.1 times) and stability (24.3 times) compared with commercial Pt/C. They attributed catalytic improvements to the superimposed effect between strong metal-support interactions and Pt clusters.⁵⁵ In another work⁵⁶, an approach of using platinum loaded carbon nanotube (Pt/CNT) synthesized by a microwave induced reaction was proposed for glycerol oxidation.

Pt/CNT showed six-fold increase in the current density compared to Pt/C followed with negative shift of onset potential by 120 mV. This was attributed to the presence of CNT, which improved the durability of Pt and increased the electro-active surface area (ECSA). In another study ⁵⁷, the promotional role of the metal oxide support (tert-butylamine-modified $\text{CeO}_2 \cdot x\text{H}_2\text{O}$ nanoparticles with abundant OH groups) on Pt/CNT was discussed for GEOR. The obtained results illustrated that the OH groups on $\text{CeO}_2 \cdot x\text{H}_2\text{O}$ NPs were the main factors for the promotion of the catalytic stability and activity of Pt/CNTs, by stripping poisonous intermediates from Pt nanoparticles. Additionally, this support also accelerated the deprotonation and dehydrogenation of glycerol.⁵⁷

Many efforts were directed towards the fabrication and application of bi-metallic Pt-based electrocatalysts. There are various reports on Pt-M (M = Pd,^{58,59} Au,⁶⁰⁻⁶⁵ Ru,⁶⁶⁻⁷⁰ Ag,^{71,72} Bi,⁷³ Sb,^{70,74} Cu,^{58,75} Co,⁷⁵ Sn,^{68,70,76} and Ni,^{59,68,69}). In most cases bimetallic catalysts outperformed monometallic Pt for GEOR. Some of these works that are also summarized in Table 2.1. *Prasanna et al.*⁷⁶, prepared a novel ternary polymer- CNT composite by application of three monomers (hexachlorocyclotri phosphazene (CP), 2,2'-benzidinedisulfonic acid (BZD) and amine terminated cyclophosphazane (ATCP) as support for Pt and Pt-Sn NPs for GEOR. Figure 2.4 illustrates the schematic presentations for the Pt and Pt-Sn NPs deposited on ATCP-CP-BZD-CNT composites. The obtained results highlighted that Pt-Sn/ATCP-CP-BZD-CNT and Pt/ATCP-CPBZD- CNT had higher oxidation current (38.89 mA/mg and 26.59 mA/mg) at lower onset potential (-0.74V and -0.64 V vs. SCE) than the commercial Pt/C. Additionally, the synthesized bimetallic sample was employed as the anode, achieving 70% formate, 17% glyceraldehyde and 13% glycolate in 0.5 M glycerol in alkaline media.⁷⁶ In the recent study ⁵⁸, the Cu filled nano-porous stainless steel (NPSS) electrode was decorated with Pd and Pt (Pt-Pd/Cu/NPSS). The synthesized sample gave four times higher activity at a lower onset potential (-0.54 V) compared to Pt/Cu/NPSS and Pd/Cu/NPSS samples.⁵⁸ Pt-Pd/Cu/NPSS also exhibited high electroactive surface area (ECSA) ~ 1.3 times and more poisoning tolerance than the other two single decorated samples. In another work,⁶⁸ $\text{Pt}_{50}@\text{M}_{50}$ nano-catalysts (M = Ru, Sn or Ni) loaded on multi-walled carbon nanotubes (CNT) were prepared by the electrostatically assisted co-reduction method and were reported with a spherical shape of ~ 3 nm in size. In terms of electrochemical performance, the Pt@Ni/CNTs displayed the highest mass activity and lowest onset potential in the presence of glycerol (275 mA $\text{mg}^{-1}_{\text{Pt}}$ and -492 mV vs. Hg/HgO). In glycerol electro-

conversion experiments, Pt@Ni/CNTs had an exponential-like decay, in which a plateau was achieved after 6 h and 60% glycerol conversion. While for Pt@Ru/CNTs reaching 40% oxidation after 12 h electrolysis.⁶⁸ However, despite the increased glycerol consumption obtained with Pt@Ni/CNTs, a lower amount of products formed. This phenomenon was attributed to the electrolysis curve profile, in which steady state was achieved after 6 h, preventing further oxidation of the products.⁶⁸

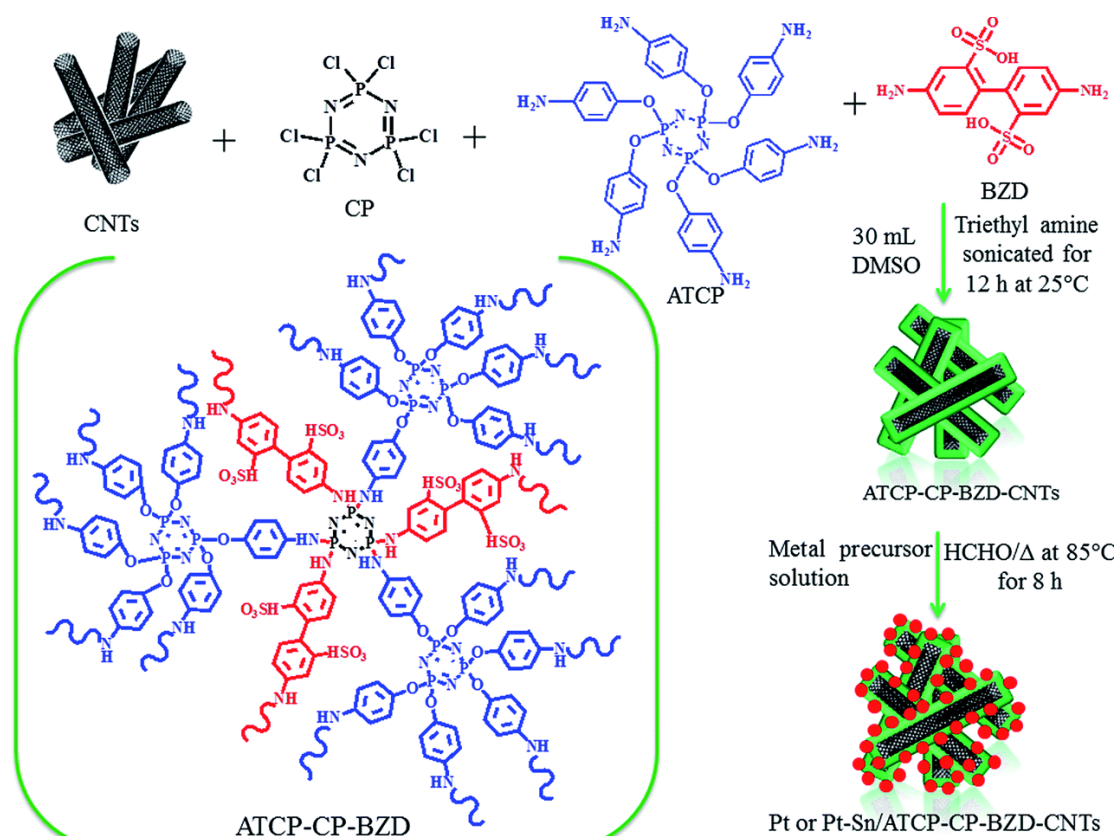


Figure 2.4. Schematic representations for the preparation of ATPC–CP–BZD–CNT composite and platinum and platinum–tin nanoparticles deposited ATPC–CP–BZD–CNT composites. (Reproduced with permission.⁷⁶ Copyright© 2014, Electrochemistry Communications)

In the recent study,⁵⁹ the authors used single-step solvothermal technique to synthesize bimetallic and trimetallic alloy NPs involving Pt, Pd, and Ni supported on a reduced graphene oxide (rGO).⁵⁹ The mass activity of different electrocatalysts toward GEOR was generally found to be in the order of Pt₇₀Pd₂₄Ni₆/rGO > Pt₇₃Pd₂₇/rGO > Pt₇₄Ni₂₆/rGO > Pd₆₈Ni₂₆/rGO > Pt/C. Particularly, Pt₇₀Pd₂₄Ni₆/rGO showed a 5.37 A mg⁻¹ mass activity, which was ~5 times higher than commercial Pt/C. They attributed the enhancement to the oxophilic nature of Ni, which acted as the co-catalyst. Based on their XPS analysis, Ni in the trimetallic alloys provided the hydroxyl group, which in turn

accelerated the oxidation of the intermediate carbonaceous species formed on the catalyst surface and prompted adsorbed CO removal.⁵⁹ A series of graphene nanosheets (GNS) supported Pt, PtNi, PtRu, PtRh, PtRuNi and PtRhNi catalysts were prepared using a polyol reduction process and investigated for GEOR.⁶⁹ Electrochemical measurements indicated that the PtRhNi/GNS and PtRh/GNS displayed better activity in terms of higher current densities (5.58 and 4.47 mA cm⁻²) and lower onset potentials (-0.719 V and -0.71V vs.SCE), which were 22 and 18 times higher than Pt/GNS catalyst, respectively. The rise of the performance was ascribed to the synergistic interactions of the different metal atoms, where Pt dehydrogenated glycerol, Ni provided oxygen containing species, while Rh stabilised the metal-glycerol complex and facilitated C-C bond cleavage. Furthermore, a quantitative analysis (HPLC) attested that GEOR was highly selective towards oxalate at -0.4V on PtRh/GNS (~28.2%) and PtRhNi/GNS (37.6%) catalysts. Compared with the PtRhNi/GNS, the PtRuNi/GNS exhibited a better selectivity of C3 products.⁶⁹ Another ternary catalysts, based on Pt_(1-2x)Ru_xSn_xO_y/Ti combination, were developed by thermal decomposition of polymeric precursors.⁷⁰ The glycerol oxidation increased significantly in the presence of RuO₂ and SnO₂ due to the larger surface area and ability to donate large amount of OH⁻ species. The Pt_{0.8}Ru_{0.1}Sn_{0.1}O_y/Ti catalyst showed approximately 170 mV lower overpotential than Pt O_y/Ti samples.⁷⁰ Furthermore, in another study,⁶⁶ bimetallic nanoparticles supported on carbon Pt_xCu_{x-1} (100:0, 90:10, 70:30, 50:50, and 0:100) were synthesised using borohydride reduction method for GEOR. The electrochemical measurements for glycerol in direct glycerol fuel cell (DGFC) (90 °C) singled out Pt₉₀Cu₁₀/C as the most active electrocatalyst in all the potential range studies, especially when compared to the PtCu/C and Pt/C electrocatalysts. Their beneficial effect was ascribed to the superficial defects, geometric effects as well as an electronic effect on the Pt surface caused by the presence of Cu.⁶⁶ A novel class of ternary hexagonal PtCuCo nanostructures were reported for ethylene glycol (EG) and glycerol electrooxidation.⁷⁵ The optimized PtCuCo (with atomic ratios of 51.7:23.2:25.1) displayed a significant enhancement in the catalytic activities of (3519.9 and 4926.4 mA.mg⁻¹) for the electrooxidation of glycerol and EG, respectively, outperforming the PtCu, PtCo, as well as Pt/C catalysts. The enhanced performance was attributed to the electronic effects among Pt, Cu and Co as well as the unique hexagonal nanostructure.⁶⁶ Electrooxidation of glycerol over PtAg nanotubes (PtAgNTs) prepared using partial galvanic exchange of Pt on Ag NT, showed a promotional role of Ag.⁷² Unfortunately, no product analysis was reported. In alkaline media, the PtAgNTs

demonstrated a 3-fold higher mass activity compared to commercial Pt black and 50% improvement in activity compared to PtNTs and Pt/C as shown in Figure 2.5. *Garcia et al.*⁷¹, studied the promotional effect of bimetallic PtAg NPs in combination with an alternative catalyst support MnO_x/C, comparatively to the conventional carbon black. They reported that PtAg/C displayed 2-fold increase in the activity compared to monometallic followed with negative shift of onset potential to 79 mV towards GEOR. This enhancement is more pronounced for PtAg/MnO_x/C, in which the addition of MnO_x further promoted the activity of Pt as a source of oxygenated species required by GEOR, leading to an optimum catalytic surface. Additionally, PtAg/MnO_x/C, PtAg/C and Pt/C attained maximum power density of 102.8, 77 and 59.4 mW cm⁻², respectively at 90 °C and ambient pressure. Based on their in-situ FTIR results, all used catalysts favored the formation of 1-C atom products and breaking the C-C-C bonds of glycerol.⁷¹

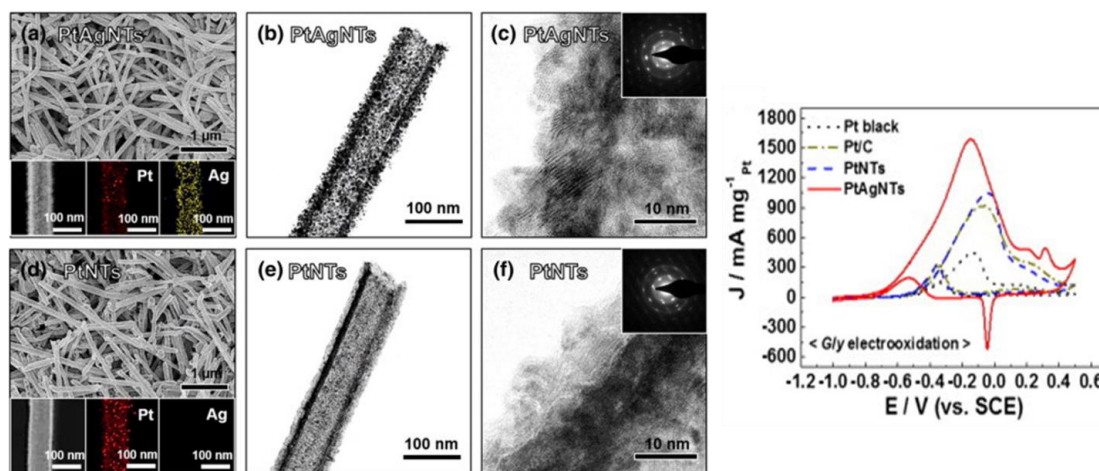


Figure 2.5. (a, d) SEM, (b, e) TEM, and (c, f) HRTEM images of PtAgNTs and PtNTs. The insets of a, d and c, f show HAADF-STEM images with corresponding elemental maps and SAED patterns, respectively. CV in 0.5 M NaOH + 0.5 M glycerol (scan rate: 50 mV s⁻¹). (Reproduced with permission.⁷² Copyright© 2017, Journal of Power Sources)

The effect of adding bismuth (Bi) to Pt/C catalysts was studied for GEOR in alkaline media.⁷³ Addition of 10% of Bi led to higher activity, while the onset potential was approximately 200 mV lower than monometallic Pt. Pt₉Bi₁/C was also evaluated in an direct electrolysis cell, generating hydrogen at the rate of 0.11 and 0.23 Nm^{H₂} 3 h⁻¹ m⁻² in (2M NaOH + 2M glycerol) with an electrical energy consumption of 1.3 or 1.65 kWh (Nm^{H₂} 3)⁻¹ at 0.55 or 0.7 V, respectively. Remarkably, their system followed the Faraday law electrolysis and saved 66% and 57% energy compared with the traditional water electrolysis.⁷³ Moreover, in-situ FTIR measurements showed that Pt₉Bi₁/C avoided

the C-C bond cleavage, thus increasing the selectivity towards C3 compounds. At high potentials, dihydroxyacetone and glyceraldehyde acted as reaction intermediates to the formation of carboxylates, while at lower potentials, glyceraldehyde is the main reaction product.⁷³ In a report done by *Li et al.*⁶⁵, two monometallic (Pd/C and Pt/C) and bimetallic (Pd-Au (wt 4:1)/C and Pt-Au (wt 4:1)/C) catalysts for GEOR was studied. Addition of gold to monometallic, the values of onset potential were 139 and 133 mV more negative on Pt-Au/C and Pd-Au/C than that on the Pt/C and Pd/C. In addition, the onset potential value for GEOR on Pt-Au /C electrode was 160 mV more negative than that on Pd-Au/C electrode. The current density values (at V=-0.3V) on Pd-Au (wt 4:1)/C and Pt-Au/C electrodes were 6.2 and 4.6 times higher than monometallic electrodes.⁶⁵

2.2.1.2 Platinum group in acidic media

Several studies have been conducted using Pt and Pt-based materials in acidic media, because Pt is one of the few materials that showed promising catalytic activity and stability towards GEOR. The influence of different carbon and graphene supports (carbon Vulcan, MWCNTs, GONR, GNR) on GEOR on Pt was reported.⁷⁷ It was found that the supports did not influence the shift of the onset potential towards lower values. The obtained results suggested that the onset potential was limited by the dissociative adsorption step. However, the current density of Pt/GNR was higher than the other catalysts, a finding corroborated by *Teles et al.*⁷⁸ The effect of interaction between Pt and three different carbon-based supports (Pt/C, Pt/ poly-aniline (PANI) and Pt/porous-PANI) was investigated.⁷⁹ It was found that Pt/porous PANI catalyst prepared by attapulgite (ATP) as the sacrificial template had the best catalytic activity.⁷⁹ When the reaction time of the template removal was 11 h and the ratio of $m_{\text{Au}}/m_{\text{ATP}}$ was 1:3, the Pt/porous PANI hybrid nano-structure showed an outstanding activity ~5 times higher than Pt/PANI toward GEOR.

In the recent study, several groups reported fabrication of bimetallic catalysts for GEOR. *Pupo et al.*⁸⁰, prepared core-shell catalysts ($\text{Rh}_x\text{@Pt}_y$ and $\text{Sn}_x\text{@Pt}_y$) using chemical reduction method. Based on their characterization results, the core-shell nanoparticles were homogeneously distributed on the carbon black surface. High Pt content led to lower overpotential (120 mV for Rh@Pt_3 and 130 mV for Sn@Pt_3) and higher current densities towards glycerol electrooxidation. Thus, the authors attributed the catalytic improvements to the electronic interaction between Pt and the core metal.⁸⁰

Recently, another study reported a preparation of a series of binary PtRu/C catalysts with different atomic ratios (from 7:3 to 3:7) for GEOR with an average particle size of approximately 2 nm.⁸¹ The electrochemical measurements showed more enhanced catalytic activities for the GEOR on the bimetallic PtRu/C catalysts than for the Pt/C catalyst in acidic media. The Pt₅Ru₅ turned out to be the optimal ratio as it had 40% higher activity compared to mono-metallic. In the electrocatalytic batch reactor, the PtRu/C catalyst produced more oxidized products, such as glycolic acid, at higher glycerol conversion than the Pt/C catalyst.

The effect of the modification of platinum surfaces by metals from p-group on the electrooxidation of glycerol has also been mostly studied (Bi^{82,83}, Sb⁸³⁻⁸⁶, Sn^{80,87-89} and Pb^{90,91}). The following will highlight a number of these studies that have been investigated. A novel concept recently reported by *Bu et al.*⁹¹, fabricated a new class of porous PtPb/Pt nanoplates (NPs) and porous PtPb/Pt octahedra (OTs) with different compositions using a facile chemical etching method. Due to the alloy effect and highly open (3D) structure, the porous PtPb/Pt NCs exhibit enhanced performances toward GEOR with the optimized porous Pt₃Pb nanoplates exhibiting superior activities of (1.46 mA cm⁻² and 1.00 A mg⁻¹_{Pt}) than the commercial Pt/C (0.30 mA cm⁻² and 0.20 A mg⁻¹_{Pt}). In addition, Pt₃Pb NPs also exhibited ultra-stable features after long-term durability with only 34.2% (0.66 A mg⁻¹_{Pt}) mass activity loss after 5000 cycles, whereas only 4.5% (0.009 A mg⁻¹_{Pt}) for commercial Pt/C. Similarly, another group synthesized Pb_x@Pt_y/C core-shell (CS) nanostructures (with molar ratios of 1:3, 1:2, 1:1 and 2:1) for GEOR.⁹⁰ Microscopy results indicated that CS nanoparticles were well-dispersed on carbon support, with spherical shapes and small particle sizes (2.6–3.9 nm). The Pb@Pt₃/C (5.08 mA cm⁻²) turned out to be the optimal ratio as it had ~197% higher current density activity compared to mono-metallic Pt/C (2.58 mA cm⁻²). After 3,000 potential cycles, Pb@Pt₃/C lost only ~28% of activity with respect to Pt mass.⁹⁰ Furthermore, in another study, the intermetallic nanostructured PtSb/C was evaluated as an anode for GEOR in both acidic and alkaline media.⁸⁵ The authors highlighted that PtSb/C performed 50% better than commercially available Pt/C nanoparticle in both environments. Based on the in-situ FTIR measurements, carboxylic acid was the main route through which glycerol oxidation starts at 0.4V and at 0.6V CO₂ was detected in acidic media. Whereas, in alkaline media, glycolate and glyoxalate formation took place at 0.4V. At 0.5V, the IR absorption band (1580 cm⁻¹) ascribed to glycolate, glyoxal, glyoxalate and formate. Also,

at 0.5 V, the band (1400 cm^{-1}) assigned to glycerate, glycolate and carbonate. At 0.6V, glycolate emerged as a band at (1080 cm^{-1}).⁸⁵ In 2012 *Koper et al.*⁹², demonstrated 100% selectivity to dihydroxyacetone (DHA) over a carbon supported Pt electrode. This due to the addition of Bi, which blocks certain sites of Pt that were active for primary glycerol oxidation, the applied current was key for attaining secondary glycerol oxidation, leading to DHA selectivity. Nevertheless, the author's findings had a major drawback, which was that the quantitative dihydroxyacetone selectivity can only be attained at low conversions (<1%) and reduces remarkably at higher conversion such that the overall yield of DHA wouldn't exceed 1%.⁹² In a later study, similar group investigated the effect of other adatoms (Sn, In and Pb) on the selectivity and activity of Pt/C.⁸⁶ These promoters enhanced the catalytic activity of the catalyst, however, unlike Bismuth- didn't promote the selectivity toward DHA. High selectivities and yields toward DHA were also studied by *Lee et al.*⁸³, who employed a PtSb/C catalyst in acidic media, and a conversion of 90% at a glycerol yield of 61% was attained. They further confirmed that the selectivity can be controlled by the applied potential, where higher anodic potentials promote carbon bond cleavage and thus the formation of C_1 and C_2 products.⁸³

2.2.2 Palladium-based catalysts

From the survey of the literature, it is clear that palladium is the strongest competitor to platinum catalysts for GEOR. Specifically, Pd-based catalysts illustrate high activity for GEOR in alkaline media and have been extensively investigated in the last 5 years. There are studies which have looked at Pd/C nanoparticles for GEOR in alkaline solution.⁹³ Figure 2.6 presents the polarization curves in 0.1 M glycerol + 0.3 M KOH on a Pd electrode prepared by electrodeposition on carbon paper (CP). One can observe two oxidation waves in the forward and reverse scan of the electrode potential. The forward oxidation wave represents chemisorbed species of adsorbed alcohol whereas the reverse peak, at lower potentials, represents the desorption zone of hydrogen from a palladium surface. The onset potential is shifted towards higher potential in comparison to Pt/CP ($\sim 130\text{ mV}$). Nevertheless, Pd/CP is an optimal candidate for fuel cell applications as it shows higher current density and excellent poisoning tolerance for this reaction.⁹³

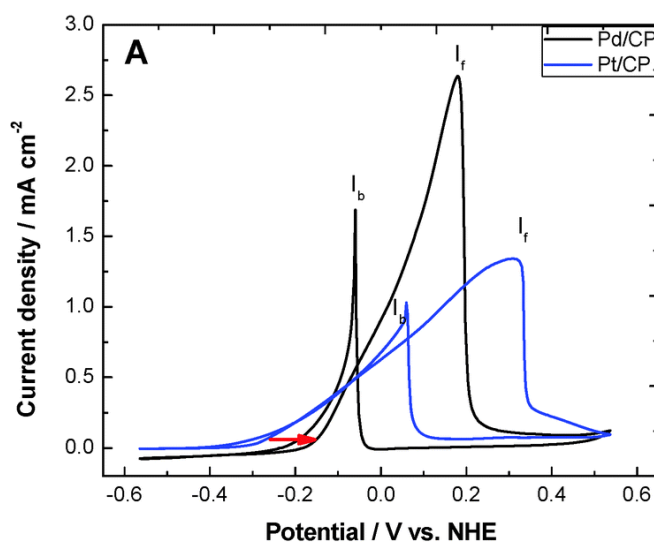


Figure 2.6. Electrocatalytic evaluation of Pd and Pt electrodeposited on carbon paper for the oxidation (0.1 M glycerol in 0.3 M KOH). Scan rate: 20 mV s⁻¹. The red arrow indicates the potential shift related to the presence of electrocatalyst. (Reproduced with permission.⁹³ Copyright© 2012, J. Electrochem. Soc.)

The effect of the catalyst support on Pd catalytic activity has been investigated in several studies. For instance, *Xiaofei and Pei* have proposed to use immobilized Pd nanoparticles in a nano-sized carbide supported on carbon aerogel (Pd@WC-Mo₂C/C).⁹⁴ Their approach allowed the preparation of nanoparticles with smaller particle size distribution, higher surface area and enhanced electrochemical activity and durability for GEOR, almost twice compared to Pd/C. They attributed catalytic improvements to the synergetic effects between the Pd nanoparticles and the (*hcp*) structure of binary carbides in the presence of tungsten and molybdenum active phases.⁹⁴ The catalytic behaviour of palladium decorated on nanoporous stainless steel (NPSS) using pulsed electrodeposition is shown in Figure 2.7.⁹⁵ Pd/Cu/NPSS showed a 350% higher mass activity compared to Pd/NPSS followed with negative shift of onset potential to 100 mV towards GEOR. This due to the presence of both nanopores NPSS and Cu which improved the durability of Pd and increased the electroactive surface area (ECSA).

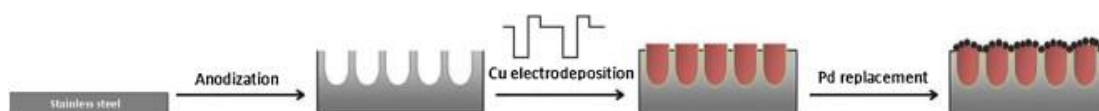


Figure 2.7. Schematic illustration of the procedure for preparing NPSS/Cu/Pd electrode. (Reproduced with permission.⁹⁵ Copyright© 2018, Sci. China Mater.)

Pd core-shell nano-catalyst (FeCo@Fe@Pd/C) was investigated for electrooxidation of EG, glycerol and ethanol.⁹⁶ In comparison, the best results were reported for EG oxidation due to its faster electrocatalytic rate constant when compared to the ethanol (4-fold) and glycerol (2-fold). The study highlighted that during the alcohol oxidation processes, Pd core-shell nano-catalyst was very stable against generated carbonaceous poisoning. This behavior was ascribed to its higher EASA, smaller nanoparticles size, and the positive strain effect on its active surface due to the incorporation of the Pd lattice on its core alloy.⁹⁶ Similarly, *Fashedemi et al.*⁹⁷, synthesized ternary core-shell nano-catalyst (FeCo@Fe@Pd) loaded on multi-walled carbon nanotubes bearing carboxylic (MWCNT-COOH) and sulfonic acid (MWCNT-SO₃H) via the “microwave-induced top-down nanostructuring and decoration”.⁹⁷ FeCo@Fe@Pd/MWCNT-COOH showed smaller particle size (~7.4 nm), evenly loading on the support, large ECSA and enhanced electrocatalytic activity for EG and glycerol in alkaline media. However, both Pd/MWCNT-COOH and FeCo@Fe@Pd/MWCNT-COOH exhibited significant selectivity to oxidize glycerol to carbonate, reaching 47% and 73%, respectively. Moreover, the oxidation products were diverse compared to EG, including tartronate, glycolate, glycerate, formate and oxalate.⁹⁷ The use of octylphenoxypolyethoxyethanol (NP-40) in fabricating Pd nanospheres supported on reduced graphene oxide (RGO) were synthesised.⁹⁸ Their approach showed 9.4 and 6.3 times increase in mass activity compared to Pd/C catalyst for EG and glycerol electro-oxidation, respectively. The performance of Pd/RGO was attributed to the high active surface area and the higher resistance to adsorbed CO. The synthesis and catalytic performance of nanohybrid materials composed of Pd decorated with and without manganese dioxide (Pd-MnO₂) highlighted that onion-like carbon (OLC) support significantly (150 %) promoted the reaction.⁹⁹ The improved performance was ascribed to the increase of surface area and to the synergistic effects of the nanohybrid materials enhanced by the intrinsic physio-chemical properties of OLC.⁹⁹ In another work,¹⁰⁰ palladium supported on reduced graphene oxide (RGO) + phosphotungstic acid (HPW) composite materials prepared via a photoreduction process showed high catalytic activity for GEOR. It was reported that Pd/HPW/RGO-4 equals to 5:4 as the most promising mixture ratio for ethylene glycol and glycerol oxidation.¹⁰⁰ Furthermore, Pd nanoparticles electrodeposited on poly(3,4 ethylenedioxythiophene) (PEDOT) coated carbon paper electrode were also investigated for GEOR.¹⁰¹ Addition of phosphorus and Ni oxide promoters to Pd/C was investigated¹⁰² The promoted electrocatalysts were

superior to Pd/C, Pd-Ni/C and Pd-NiOx/C as demonstrated in CV, Tafel plot, and impedance spectroscopy experiments. The influence and promotional role of mesoporous silica (SiO₂) deposited on Pd in GEOR was also reported.¹⁰³ It was found that well-ordered mesoporous cage-like arrangement of silica enhanced the current density by two times if compared to commercialized Pd/C.

A study of DGFCs built with, bis (dibenzylidene acetone) palladium Pd (DBA)₂ anode catalyst showed a maximum power density of 24 mW cm⁻² when the fuel cell was fed with 5 wt. % aqueous solutions of glycerol in 2 M aqueous KOH.¹⁰⁴ The results demonstrated the higher performance by Pd (DBA)₂ catalyst due to higher tolerance against poisoning by intermediates/products of GEOR. The morphology of Pd catalyst was shown to influence both EOR and GEOR.¹⁰⁵ Palladium nanoparticles with well-defined trigonal bipyramidal or tetrahedral nanocrystals showed higher current densities and durability compared to spherical Pd/C towards ethanol and glycerol electrooxidation in alkaline media.¹⁰⁵

Many efforts were directed towards the fabrication and application of bi-metallic Pd-based electrocatalysts. For instance, several Pd-M catalysts, where M = Pt,¹⁰⁶ Au,¹⁰⁷⁻¹¹⁰ Ru,^{111,112} Ag,¹¹³⁻¹¹⁷ Rh,¹¹⁸ Bi,¹¹⁹⁻¹²¹ Sn,¹²²⁻¹²⁴ Cu,¹²⁵⁻¹²⁹ Co,¹³⁰ Mo,¹³¹ In,¹³² and Ni¹³³⁻¹³⁵ have been reported recently. In most cases bimetallic catalysts outperformed monometallic Pd for GEOR as summarized in Table 2.1.

In the recent study, Pd₇Ru₃ nanoparticles supported on carbon were fabricated using the microwave-assisted heating method.¹¹¹ It was found that addition of 30 at.% Ru to Pd not only reduced the onset oxidation potential for GEOR but also generated higher current densities at lower potentials compared to Pd/C by itself. Using in-situ infrared spectroscopy and HPLC analysis it was shown that PdRu/C gave mainly glycerate.¹¹¹ Similarly, another report studied PdRu-PEDOT/C catalysts with various Pd:Ru atomic ratios synthesized by one step electrodeposition.¹¹² It was reported that Pd₅Ru-PEDOT/C shaped as nanoflowers exhibited the highest activity and stability which was about 5 times higher than Pd/C. The high current densities were due to the presence of high-energy surface sites on Pd₅Ru-PEDOT/C favourable for OH⁻ adsorption. Figure 2.8 shows the proposed bi-functional mechanism of Pd₅Ru-PEDOT/C catalyst. The following observations were highlighted: (a) glycerol undertakes adsorption and dehydrogenation on Pd active sites; (b) water dissociatively adsorbs on the Ru sites to

form oxygen containing species at low potential; (c) formation of glyceric acid and glycolic acid on the Pd surface and (d) formation of carbonate due to C-C bond cleavage followed by combination of CO_{ad} with OH_{ad} .¹¹²

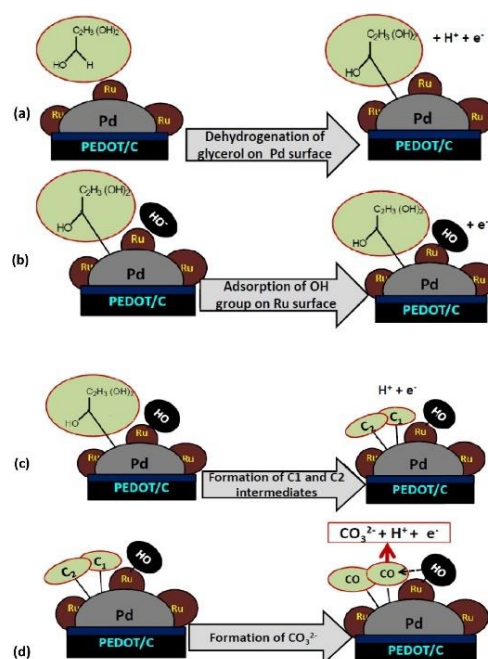


Figure 2.8. Schematic representation of glycerol oxidation on Pd_5Ru -PEDOT/C electrode. C1= glyceric acid and C2=glycolic acid. (Reproduced with permission.¹¹² Copyright© 2017, Nanoscale Research Letters)

Electrooxidation of glycerol on Pd-Rh (atomic ratio of 78:22) electrodeposits were reported in alkaline media.¹¹⁸ Using FTIR, carbonate was identified as the main product of GEOR along with glycerate, glycolate and oxalate. The results confirmed that the presence of Rh helped to enhance the low ability of Pd to break C–C bonds in the strongly alkaline medium. Additionally, the PdRh catalyst was strongly dependable on the concentration of hydroxyl groups as CO_2 was generated at high potential in low pH. This is due to the consumption of OH^- inside the thin cavity forcing the reaction to proceed through the production of carbon dioxide, instead of carbonate.¹¹⁸ Fabrication of Pd-Co alloy nanoparticles electrodeposited on gold surface (Pd-CO/Au) have been described by *Rostami et al.*¹³⁰ They reported that SEM image of Pd- Co_3 /Au exist as clusters and cauliflower like nanostructures with an average size of 44 nm. The addition of Co enhanced the steady state of current density by twice and lowered the onset potential by 80 mV than that of Pd/Au in 1M KOH +1M glycerol. They ascribed the enhancement of the reaction kinetic to the alloying of Pd with Co followed by lattice compression, which resulted in shifting the d-band center energy. Their claim has been

described by DFT calculation in other reports.^{136,137} Serov *et al.*¹³², coupled a sacrificial support method with the thermal reduction of metal precursors to prepare unsupported uniformly-distributed PdIn catalysts with ratios of 3:1, 1:1, and 1:3. They reported negative onset potential shift of ~ 130 mV and almost 5 times increased peak current density for GEOR on PdIn₃ compared to Pd. Unfortunately, no product analysis was reported. The bimetallic PdPt nanowire networks (NNWs) with tunable composition were synthesized in an aqueous solution using sodium borohydride as reducing agent.¹⁰⁶ It was reported that PdPt NNWS had higher current density (0.046 A cm^{-2}) than that of conventional Pt/C (0.023 A cm^{-2}).¹⁰⁶ Recent study reported a promising catalytic activity of PdAg and PdAg₃ supported on carbon nanotube (CNT) for GEOR.¹¹³ This is in agreement with the fuel cell studies conducted on PdAg/CNT.¹¹⁴ PdAg/CNT was the most efficient anode for alcohol oxidation (AOR) in passive air breathing DFC achieving a maximum power densities of 135.1, 202.3, 245.5 and 276.2 mW cm^{-2} for methanol, ethanol, ethylene glycol and glycerol, respectively at 80°C and ambient pressure as shown in Figure 2.9.¹¹⁴

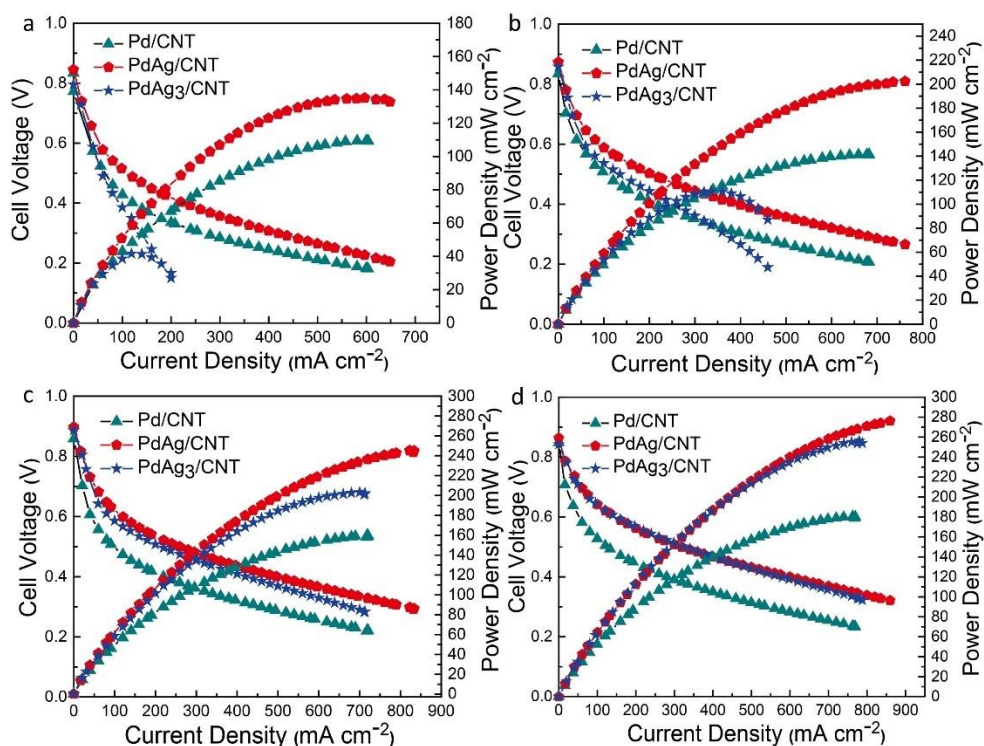


Figure 2.9. Polarization and power density curves of direct alcohol AEMFCs with different anode catalysts (Pd/CNT, PdAg/CNT and PdAg₃/CNT, $0.5 \text{ mg}_{\text{Pd}} \text{ cm}^{-2}$) at optimized operating conditions. AEM: Tokuyama A901; cathode catalyst: Fe-based catalyst (Acta 4020), $3.0 \text{ mg}_{\text{catalyst}} \text{ cm}^{-2}$; anode fuel: 6.0 M KOH + 3.0 M (a) methanol, (b) ethanol, (c) ethylene glycol and (d) glycerol, 4.0 ml min^{-1} ; cathode fuel: 200 sccm O₂,

ambient pressure; temperature (anode fuel/cathode fuel/cell): 25/80/80 °C. (Reproduced with permission.¹¹⁴ Copyright© 2014, Electrochemistry Communications)

Furthermore, quantitative analysis attested that GEOR is selective towards oxalate at 32 %, 22.8% and 8.6% on PdAg₃/CNT, PdAg/CNT and Pd/CNT respectively at 60 °C, attributing that silver facilitated the C-C bond cleavage of glycerol to C₂ (oxalate) and lowers glycerol conversion.¹¹⁴ Under the same conditions, the half-cell system test showed that the PdAg/CNT was twice higher in mass activity than Pd/CNT, which could be ascribed to the following reasons: (i) the particle size of alloyed catalyst was smaller by ~ 6.5 times than mono-metallic, resulting in a high ECSA (ii) the presence of silver could accelerate the reaction rate of alcohol electrooxidation reaction, and (iii) the 3D structured of CNT support enhanced the mass transport of hydroxide ions and alcohol molecules, hence improved the electrical conductivity, as well as the mechanical and the thermal stabilities.^{113,114}

Holade et al.^{116,117}, prepared carbon supported bimetallic nanoparticles of Pd_xNi_{x-1} and Pd_xAg_{x-1} (x = 1,0.9,0.8,0.7,0.6 and 0.5) using “Bromide Anion Exchange” method. They reported that the alloying bimetallic catalysts were primarily mix of Pd metal, Ni oxides, Ag metal and small traces of AgBr. It was found that addition of 10–50 at.% Ni or Ag to Pd not only lowered the onset oxidation potential for GEOR but also produced higher current densities at lower potentials compared to monometallic Pd/C. In particular, authors singled out Pd₅₀Ni₅₀/C and Pd₆₀Ag₄₀/C which gave up to 25% and 62.5% higher mass activity, respectively, when compared to Pd/C that followed a negative shift of onset potential to 150 mV. Their studies were also supplemented with quantitative and qualitative analysis combining in-situ FTIR and HPLC measurements, confirming glyceraldehyde as a reaction intermediate and the main products are tartronate, oxalate, glycolate and glycerate ions after 4 hours electrolysis.^{116,117} *Coutanceau et al.*¹²⁰, reported the enhancement of GEOR activity on Pd/C by simple decoration of Bi₂O₃ and Bi(OH)₃ clusters on the surface. Based on their in-situ FTIR, Pd₉Bi/C didn't affect the selectivity of glycerol electrooxidation favoring carboxylate formation, while the onset potential for GEOR remained high comparing to Pt₉Bi/C and Pd_{4.5}Pt_{4.5}Bi/C catalysts. *Zalineeva et al.*¹¹⁹, synthesised controlled size and shape of Pd nanoparticles and modified their surfaces by Bi adsorption using colloidal method.^{138,139} They noted that the performance of Pd-nanospheres (Pd-NS), Pd-nanocubes (Pd-NC) and Pd- nanooctahedrons (Pd-NO) have similar selectivity towards glycerate at low potentials, while hydroxypyruvate,

dicarboxylates carbonate and CO_2 at high potentials for GEOR in alkaline media. Modification of Pd-NS and Pd-NC by Bi coverage led to a change in GEOR mechanism with the formation of hydroxyacetone at low potentials.¹¹⁹ Serov *et al.*¹²⁶, used a sacrificial support method in combination with the thermal reduction of metal precursors to prepare unsupported uniformly-distributed Pd:Cu catalysts with ratios of 1:3, 1:1, and 3:1. They found that PdCu and Pd₃Cu electrocatalysts showed improved GEOR activity and lower onset potential, which they ascribed to the presence of surface Cu and Cu₂O sites favouring adsorbed OH⁻ species as confirmed by their DFT calculations. Also, they investigated the product distribution of glycerol using in-situ Infrared Reflection Adsorption Spectroscopy (IRRAS), confirming CO₂ production at 0.6 V vs. RHE.¹²⁶ Furthermore, in another study, alloy catalyst Pd₃Cu supported on a novel nitrogen-doped meso-porous-carbon (NMC) was prepared by the polyol reduction method, which showed improved durability, lower activation energy and better current density (1.67 A mg⁻¹) of 2.5 times higher than Pd/C (0.67 A mg⁻¹) for GEOR.¹²⁵ Similarly, a metal salt (sodium hypophosphite) reduction synthesis of PdCu/C led to its superior catalytic performance in polyalcohol oxidation in alkaline medium.¹²⁸ The composition-optimized Pd₈₃Cu₁₇ catalysts showed 3 times higher reaction rate and 32% greater power density in DGFC testing compared to Pd/C. A series of active Pd₁Sn_x with high atomic ratio ($\geq 50\%$) were prepared using a sacrificial support method in combination with the thermal reduction process.^{140,141} Among various PtSn compositions, Pd₁Sn₁ catalyst showed 10 times greater current density and 150 mV lower onset potential for GEOR compared to mono-metallic Pd.^{140,141} The electrochemical studies in combination with in-situ FTIR measurements confirmed that Pd-Sn structure leads to the formation of C3 carboxylate compounds with no evidence of the formation of signatures for CO_{ads}, CO₃²⁻ and CO₂ at $\sim 1950\text{ cm}^{-1}$, 1410 cm^{-1} and 2343 cm^{-1} , respectively.¹⁴⁰

Ternary PdAuSn materials were fabricated using electron beam irradiation reduction method by adding Au and Sn as co-catalysts.¹⁴² The results showed that PdAuSn/C with Pd:Au:Sn atomic ratio of 50:40:10 had the two times higher activity than Pd/C. However, the stability of ternary catalysts was lower than bimetallic compositions during GEOR. Pd₅Au₄Sn/C demonstrated the highest power density of 51 mWcm⁻² and degradation rate of 210 $\mu\text{V h}^{-1}$ in 120 hours experiment in a single alkaline DGFC at 85 °C. This promoting role of Sn and Au was attributed to a bifunctional mechanism, where Sn and Au adsorb

and enhance the concentration of OH^- species in proximity to Pd, favoring the oxidation of glycerol on Pd surfaces.¹⁴²

2.2.3 Gold-based catalysts

Based on the literature reports, gold is the second strongest competitor to platinum catalysts for GEOR. Specifically, Au-based catalysts display high activity for GEOR in alkaline media; hence, it has been extensively investigated in recent studies. The behaviour for monometallic gold and the effects of different morphologies, supports and promoters was mostly studied in alkaline solutions. For instance, *Padayachee et al.*¹⁴³ investigated the effect of particle size on the GEOR using Au NPs supported on carbon. Several approaches were initially tested in an attempt to attain Au NPs with varying average gold diameters: (i) utilizing different reducing agents (NaBH_4 , THPC and citrate), (ii) altering the Au: reducing agent molar ratio, (iii) and adjusting the Au loading on the catalysts. The best mass activity and lower onset potential were reported for Au/C (≤ 4.7 nm) due to its surface area effects when compared to Au/C (≥ 43 nm). The study highlighted that the drop in onset potential (~ 100 mV) was due to predominance of Au(110) facets on the surface, while the deactivation of larger particles was attributed to high proportion of Au(111) or lower gold surface area.¹⁴³ *Qi et al.*¹⁴⁴, optimised the reaction environment to selectively produce tartronate on two Au/C electrocatalysts synthesized via a nanocapsule method (Au/C-NC) and aqueous- phase reduction method (Au/C-AQ). The anode potential was adjusted to < 0.45 V. RHE to avoid over oxidation of the secondary hydroxyl group and C-C bond cleavage, thereby oxidizing two primary hydroxyl groups and promoting the tartronate selectivity. The authors claimed that the glycerol conversion ratio of Au/C-NC (89.2%) was slightly lower than Au/C-AQ (95.6%), however the TA yields were negligible (61.8% Au/C-NC and 61.2% of Au/C-AQ). Meanwhile, by decreasing the thickness of the electrode, increasing the flowrate and operating temperature could enhance the reaction kinetics and accelerate the desorption rate of produced tartronate from active sites.¹⁴⁴ Similarly, other report was able to influence the selectivity towards tartronate or mesoxalate by modifying the anode potentials.¹⁴⁵ Changing the potential from 0.35 V to 0.65 V vs. RHE, the mesoxalate yield enhanced significantly from 0% to 57%, whereas the tartronate yield dropped (~ 3 times) from 79% to 26%. The obtained results attest that oxidizing glycerol to glycolate was dominant at ≥ 0.9 V, resulting in the C-C bond cleavage.¹⁴⁵ In the recent study,¹⁴⁶ the authors presented a novel concept in GEOR ; using capillary electrophoresis on Au foil

(8 cm²) to determine glycerol products (neutral diols and carboxylates).¹⁴⁶ They reported the best strategies to separate neutral diols and carboxylates were using capillary complexation with borate and electroosmotic flow (counter-EOF and reverse EOF modes), respectively. All the experiments were coupled with dual capacitively coupled contactless conductivity detectors (C⁴D); which reduced the time required for separation under counter-EOF mode and showed the interaction of some anionic species with the flow modifier used in the reverse EOF mode.¹⁴⁶ After 16 h of electrolysis, 87% of the glycerol was converted to glyceraldehyde and DHA (as intermediates), and to formate, glycerate, hydroxypyruvate and glycolate (as products). The process of using capillary electrophoresis to separate glycerol, DHA and glyceraldehyde was found to take one-fifth of the time compared to HPLC.¹⁴⁶ Next, urchin-like Au nanocrystals were synthesized via facile one-step electrodeposition with addition of FeCl₃ which served as catalyst and growth directing agent.¹⁴⁷ The addition of Fe (III) enhanced the steady state of current density by ~2.8 times and lowered the onset potential by 7 mV than that of the polycrystalline Au NPs in 0.5M KOH + 0.1M glycerol. They ascribed the enhancement of the reaction kinetic to the special structures of the urchin-like Au NPs with larger surface-to-volume ratio and high ECSA sites; providing good electron-conducting tunnels.¹⁴⁷ Additionally, the exposed facets of the Au structures were another vital factor, since the urchin-like Au nanocrystals were preferentially growing along the (111) planes, which tended to be more favourable for GEOR.

The effect of the catalyst support on Au NPs activity has been shown in several studies. For instance, a series of Au NPs on various supports (poly (m-aminophenol) (PmAP) wrapped graphene (Au-P4P/rGO), extended poly (4-vinylpyridine) functionalized graphene (Au-P4P/G), P4P functionalized reduced graphene oxide (Au-PmAP/G) and carbon black (Au-CB) were fabricated.¹⁴⁸ The activity enhancement was ascribed to the lowest d-band center, facilitated desorption of glycerate from Au surface and hindered further decomposition of GLA into other products. Hence, at 0.2 V vs. Hg/HgO, Au-P4P/G electrocatalyst achieved 68.6% of glycerate and the ratio between C3 products and others (C1 + C2) was 4.92 compared to Au-CB with just 0.96.¹⁴⁸ In another study, Au-CeO₂/C (1:3:1) electrocatalyst was synthesised in aqueous solution using sodium borohydride as reducing agent followed with intermittence microwave irradiation method for CeO₂/C powders.¹⁴⁹ The authors reported that the addition of CeO₂ to Au/C electrocatalyst enhanced the catalytic performance for GEOR. Hence, the value

of onset potential was ~ 190 mV shifted negatively and close to that on E-TEK Pt/C. The current densities over Au/C and Au-CeO₂/C were 20.4 and 75.4 mA cm⁻² (~ 3.7 times higher) and the current densities at -0.3 V.SCE were 1.8 and 7.1 mA cm⁻² (~ 4 times higher), respectively. The obtained results indicated that Au-CeO₂/C had great anti-poisoning effect on CO and was more stable catalyst than ETEK Pt/C for GEOR in the presence of CO.¹⁴⁹ *Li et al.*¹⁵⁰, fabricated Au (1 1 1)/SiO₂ cavity/ITO electrode via electrodepositing Au NPs at the bottom of the SiO₂ cavities in direct contact with the tin oxide (ITO) electrodes followed by annealing the electrodes at 700 °C, forming single gold particles dominated by the (111) facet as shown in Figure 2.10. The electrode exhibited satisfactory electrocatalytic activity towards GEOR in alkaline media. This phenomenon was mostly attributed to the porous structure which created an ideal environment for the reaction.

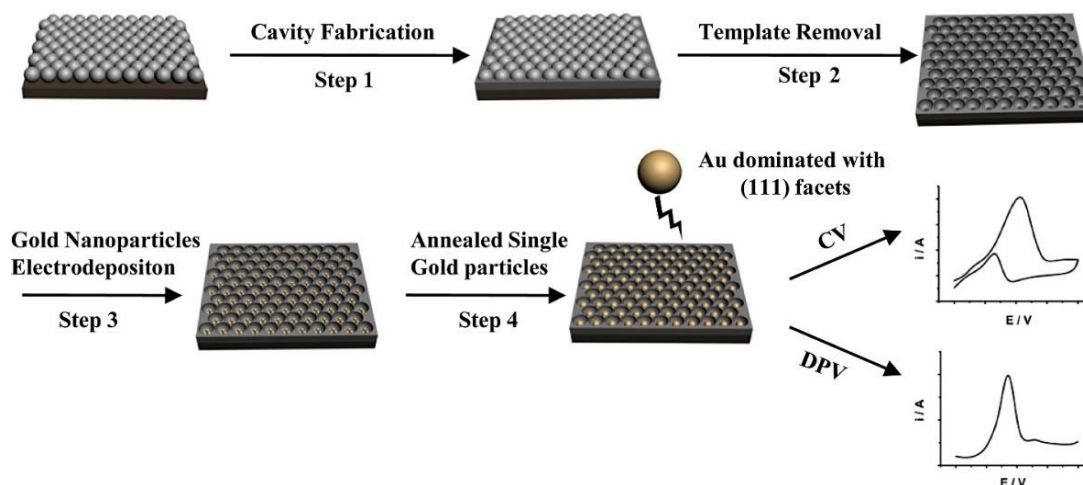


Figure 2.10. Schematic illustration of the preparation steps for fabrication of single gold particles in highly ordered SiO₂ cavities as electrodes and the process of electrochemical detecting method for glycerol. (Reproduced with permission.¹⁵⁰ Copyright© 2018, Talanta)

Interestingly, each cavity of the SiO₂ behaved as an independent electrochemical cell in which the glycerol molecules were trapped, creating a microenvironment beneficial to catalyze GEOR. Subsequently, another study¹⁵¹, reported GEOR activity enhancement on pre-deposited MnO₂ on Au/C electrocatalyst via electroless deposition process. Au₉MnO₂/C showed promising catalytic activity for glycerol electrooxidation resulting in 12-fold higher mass activity than those reported in literature. This was attributed to Au incorporation in MnO₂ that prevented Au agglomeration.

Many efforts were directed towards the fabrication and application of Au-based bi-metallic electrocatalysts as shown by various reports on Au-M (M = Cu,^{152,153} Pd,¹⁵⁴ and Ag,¹⁵⁵⁻¹⁵⁸). In most cases bimetallic catalysts outperformed monometallic Au for GEOR. Some of these studies are summarized in Table 2.1.

The fabrication of 2D porous AuCu triangular nanoprisms using facile wet-chemical method have been reported.¹⁵² The mass activity increased as follows: Au (573 mA mg_{Au}⁻¹) < Au₂Cu₁ (1245 mA mg_{Au}⁻¹) < Au₁Cu₂ (1752 mA mg_{Au}⁻¹) < Au₁Cu₁ (2263 mA mg_{Au}⁻¹). The porous 2D Au₁Cu₁ triangular nanoprism catalysts exhibited the highest mass activity among AuCu catalysts towards GEOR in alkaline media, as well as higher than commercial Pt/C (685, 47 mA mg⁻¹) and Pd/C (556,37 mA mg⁻¹), respectively. The results indicated that these 2D porous triangular nanoprisms (AuCu) showed promising prospects for application as anode electrocatalysts for DGFC.¹⁵² Similarly, *Thia et al.*¹⁵³, demonstrated that the electrodeposition of Cu species onto Au/C enhanced the C3 selectivity during GEOR and the resulting bimetallic catalysts were primarily a mix of Au metal, Cu oxides and Cu metal. The selectivity modification was attributed to the presence of an Au⁺ species that was produced by an interaction between electro-deposited Cu₂O and Au. The presence of Au⁺ enhanced the selectivity to tartronate and glycerate and suppressed carbon bond cleavage to formate and glycolate. However, when Au⁺ amount decreased, the formation of thick Cu and/or CuO₂ layers were formed over Au/C; preventing the diffusion of initially oxidised products and causing them to be oxidised further to glycolate and formate.¹⁵³

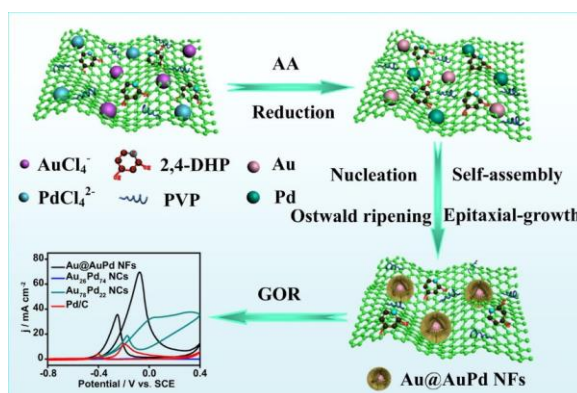


Figure 2.11. Schematic illustration of the formation mechanism of Au@AuPd NFs/rGO. (Reproduced with permission.¹⁵⁴ Copyright© 2014, Sensors and Actuators, B: Chemical)

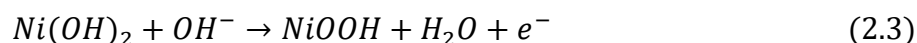
In a recent study¹⁵⁴, the authors synthesised dendritic core-shell Au@AuPd nanoflowers loaded on reduced graphene oxide (Au@AuPd NFs/rGO) with the assistance

of 2,4-DHP as (stabilizer and structure-director) and PVP as (dispersing agent) using the one-pot wet chemical method as illustrated in Figure 2.11.¹⁵⁴ The synthesized branched architectures exhibited enlarged ECSA, enhanced catalytic properties, improved stability and durability toward GEOR in alkaline solution compared to Au₇₈Pd₂₂NCs/rGO, Au₂₆Pd₇₄ NCs/rGO and commercial Pd/C electrocatalyst. This phenomenon was attributed to the special alloy core-shell nanostructures and the synergistic effects of the bimetals.

*Gomes et al.*¹⁵⁵ and *Garcia et al.*¹⁵⁶ studied the bimetallic catalyst (Au-Ag/C) and highlighted that Ag addition had led to glycerol electrooxidation at lower overpotentials. Silver also altered the GEOR reaction pathway by cleaving the C-C bond leading to formate formation. The effect of silver on the activity of the binary Au-Ag/C electrocatalyst was attributed to Ag segregation on the catalyst surface and resulting electronic interaction between Au and Ag.¹⁵⁵ Similarly, *Thia et al.*¹⁵⁷ examined 3D porous Au structure with residual amounts of Ag within its pores to tune the GEOR pathway towards formate (59.31%) and glycolate (34.72%). The surface modification of Ag NPs loaded on reduced graphene oxide (RGO) with low content of Au and the activity of Au-modified Ag/RGO (Au_x-Ag/RGO) electrocatalysts have been investigated.¹⁵⁸ Polarization measurements in alkaline media highlighted that the Au/RGO catalyst showed almost similar current density as Au_x-Ag/RGO per geometric area of glassy carbon electrode, whereas Ag/RGO displayed no activity. In terms of the Au mass specific activity, the Au_x-Ag/RGO catalysts had great advantages over Au/RGO.¹⁵⁸

2.2.4 Non-Pt group metal catalysts

Majority of GEOR studies have been focused on expensive, noble metals such as Pt, Pd and Au (Table 2.1) and only few reports dealt with non-precious metals, e.g., Ni, Ag and Co₂O₃. Nickel was reported to be an efficient catalyst for oxidation of various organic compounds in alkaline medium such as methanol¹⁵⁹, ethanol¹⁶⁰, urea¹⁶¹ and ammonia.¹⁶² It has been proposed^{163,164} that Ni(OH)₂/NiOOH transition is critical in the electrooxidation of glycerol:



where, nickel oxyhydroxide is the active surface phase that is required to oxidize glycerol. This indicates that Ni-based electro-catalysts have high overpotential, i.e., above 1.2 V

vs. RHE, however show good stability and robustness. *Oliveira et al.*^{163,165} prepared Ni-based electrocatalysts (CoNi, FeNi, FeCoNi) for GEOR in alkaline media. Their results revealed that the presence of Fe and Co in the binary and ternary Ni-based materials were advantageous for GEOR due to the formation of oxide and hydroxides.¹⁶³ The in-situ FTIR measurement showed the presence of CO₂ and hydroxypyruvate ion as the reaction products. Substantial amount of CO₂ was generated with NiCo/C electrocatalyst that was attributed to the presence of Co, which enhanced the C-C-C bond cleavage of the glycerol molecules. The HPLC analysis showed that the main reaction products were formate, while tartrate, glycolate, oxalate and glycerate were also detected. Furthermore, FeCoNi/C and Ni/C displayed the best conversion ratio of glycerol to formate and glycolate, CoNi/C demonstrated (17.9%) as the highest glycerol conversion ratio.¹⁶⁵ The authors further extended their study by varying various reaction parameters such as, temperature, scan rate, NaOH and glycerol concentration in order to investigate their influence on Ni oxyhydroxide species (β -NiOOH) and as a result on glycerol conversion.¹⁶⁶ Carbonate and oxalate were the main products at lower glycerol concentrations, while at higher concentrations, formate prevailed. Recently, *Houache et al.*⁴⁹, reported that the activity of the bulk Ni electrode could be enhanced for GEOR after applying a sin-wave treatment of Ni electrode in the presence of ascorbic acid. The treated-Ni surface gave a six-folds increase in surface area and nine times enhanced catalytic activity. The in-situ PM-IRRAS measurements showed that the main products were carbonyl, carboxylate ions and glyceraldehyde. Both treated and as-prepared Ni surfaces had identical spectra features, demonstrating that the sinusoidal wave treatment affected the reaction rate but did not alter the selectivity. These product distributions demonstrate a rapid formation of glycerate ions acting as both reaction intermediate and product for the formation of smaller molecules after C-C-C bond cleavage.⁴⁹ The use of the homogenous precursor solution of Ni-based catalysts using polyvinylpyrrolidone (PVP) and sodium tartrate was reported for the preparation of an anode for GEOR and a cathode for hydrogen evolution (HER).¹⁶⁷ In another study,¹⁶⁸ a comparison of the atomic layer deposited (ALD) TiO₂ on Ni/C to uncoated Ni/C catalyst was reported. It was found that the conversion of glycerol was higher on TiO₂-Ni/C than on Ni/C, respectively at 27.5% and 20.4%. The catalytic activity of ALD(TiO₂)-Ni/C towards GEOR was enhanced by 2.4 times due to abundant formation of Ni(OH)₂. Furthermore, DFT calculations were in correlation with experiment confirming that TiO₂ coating affected the adsorption/desorption of glycerol. In a recent study¹⁶⁹, Ni, Ni-Cu and NiCo NPs were

loaded on modified carbon-ceramic electrode (CCE). It was shown that the NiCo/CCE had 2 times higher electrocatalytic activity and 180 mV shift to lower onset potential than mono-metallic Ni.

Addition of Ni to noble metal catalysts ($\text{Pt}_2\text{Ni}_1/\text{C}^{170}$, $\text{Pd}_{60}\text{Ni}_{40}/\text{C}^{171}$ and Au/Ni core/shell on polystyrene (PS) spheres¹⁷²) led to considerable reaction rate increase due to the modification of the geometric and electronic structure of bimetallic materials in comparison with monometallic Pt/C, Pd/C and Au/PS. Therefore, the Ni co-catalyst served as a promoter and was able to minimize markedly the Pt, Pd and Au amount without significantly reducing the activity.

Recently, a series of C3 saturated alcohols have been electro-oxidized on Co_3O_4 electrode.¹⁷³ It was found that current activity increased in the following order: glycerol > 1,2-propanediol > 1,3-propanediol > 1-propanol > 2-propanol. The NMR studies illustrated that the carbon bond cleavage occurred faster from alcohols having adjacent OH^- group and that formate was the major product of GEOR. Furthermore, an application of silver bulk electrode to GEOR was reported.¹⁷⁴ The study showed that glycerol electrooxidation on Ag is pH dependent and the oxidation current density increases significantly as the pH shifts from ca. 11 to 14. Based on their HPLC analysis, glycolic, glyceric and formic acids were the main products.

Table 2.1. Comparison of performance reported in the open literature.

Detection technique: HPLC					
Catalyst	Synthesis	Electrolyte	Conditions	Selectivity	Ref.
Pt/C	Modified polyol method in ethylene glycol	2 M glycerol + 0.5 M H ₂ SO ₄	CA – 1.1 V vs. SHE; 7 h; 60°C	GLAD: 42.1%, GLA: 57.8%, GA: 0.5%	81
PtRu/C				DHA: 35%, GLAD: 17.1%, GLA: 11.1%, GA: 17.2%	
Pt/C	Modified colloidal method	0.1 M glycerol + 0.5 M H ₂ SO ₄	CA – ~0.4 V vs. SHE; 10 h; 60 °C	DHA: ~5%, GLAD: ~90%, GLA: ~5%	83
PtBi/C				DHA: ~53%, GLAD: ~31%, GLA: ~5%	
PtSb/C				DHA: ~58%, GLAD: ~30%, GLA: ~12%	
Pt/C			CA – ~0.6 V vs. SHE; 10 h; 60 °C	DHA: ~2%, GLAD: ~76%, GLA: ~8%	
PtBi/C				DHA: ~58%, GLAD: ~20%, GLA: ~8%	
PtSb/C				DHA: ~64%, GLAD: ~26%, GLA: ~9 %	
Pt/C			CA – ~0.8 V vs. SHE; 10 h; 60 °C	DHA: ~2%, GLAD: ~50%, GLA: ~20%, HPA: ~2%, TA: ~2%	
PtBi/C				DHA: ~15%, GLAD: ~49%, GLA: ~18%, HPA: ~2%, TA: ~2%, GA: ~4%	
PtSb/C				DHA: ~67%, GLAD: ~20%, GLA: ~7%, HPA: ~2%, TA: ~2%	
Pt/C			CA – ~1 V vs. SHE; 10 h; 60 °C	DHA: ~4%, GLAD: ~25%, GLA: ~22%, GA: ~13%	
PtBi/C				DHA: ~4%, GLAD: ~50%, GLA: ~19%, GA: ~2%, HPA: ~2%, TA: ~2%	

PtSb/C				DHA: ~42%, GLAD: ~22%, GLA: ~11%, GA: ~6%, %, HPA: ~2%,	
Pt ₉ Bi/C	Water-in oil microemulsion method - NaBH ₄ reducing agent	2 M glycerol + 0.5 M NaOH	CA – 0.55 V vs. RHE, 4 h	GLAD: 79.6%, GLA: 10.2%, HPA: 4.1%, TA: 6.1%	73
			CA – 0.7 V vs. RHE, 4 h	GLAD: 58.3%, GLA: 23.6%, HPA: 7.2%, TA: 10.9%	
Pt/ATCP-CP-BZD-CNT	Formaldehyde reduction method	0.5 M glycerol + 0.5 M KOH	26.59 mA current; 4 h	GLAD: 20%, GA: 14%, FA: 66%	76
Pt-Sn/ATCP-CP-BZD-CNT			38.89 mA current; 4 h	GLAD: 17%, GA: 13%, FA: 70%	
Pt/GNS	One pot polyol-assisted reduction method	0.5 M glycerol + 0.5 M KOH	CA – -0.4 V vs. SCE; 2 h	OXA: ~20%, GA: ~37%, GLAD: ~30%, GLA:~13%	69
PtNi/GNS				OXA: ~12%, GA: ~42%, GLAD: ~6%, GLA:~40%	
PtRu/GNS				OXA: ~17%, GA: ~20%, GLAD: ~33%, GLA:~30%	
PtRhNi/GNS				OXA: ~37%, GA: ~22%, GLAD: ~6%, GLA:~35%	
Pt/GNS				OXA: ~13%, GA: ~56%, GLAD: ~13%, GLA:~18%	
PtNi/GNS			CA – -0.1 V vs. SCE; 2 h	OXA: ~8%, GA: 32%, GLAD: ~8%, GLA:~52%	
PtRu/GNS				OXA: ~12%, GA: ~33%, GLAD: ~16%, GLA:~39%	
PtRhNi/GNS				OXA: ~24%, GA: 22%, GLAD: ~34%, GLA:~20%	
Pt/GNS			CA – 0.2 V vs. SCE; 2 h	OXA: ~12%, GA: ~67%, GLAD: ~6%, GLA:~15%	
PtNi/GNS				OXA: ~12%, GA: ~30%, GLAD: ~30%, GLA:~28%	
PtRu/GNS				OXA: ~17%, GA: ~49%, GLAD: ~3%, GLA:~31%	
PtRhNi/GNS				OXA: ~17%, GA: ~42%, GLAD: ~28%, GLA:~13%	

Pd/CNT	Modified aqueous-phase reduction method	1 M glycerol + 4 M KOH	CA – 0.1 V vs. SHE; 2 h 50°C	OXA: ~25.3%, GA:~ 8.5%, TA: ~39.5%, MESOXA: ~3.8% GLA: ~21.7%, LA: ~1.2 %	113
PdAg/CNT				OXA: 35.9%, GA: 20.9%, TA: ~26.4%, MESOXA: ~1.5%, GLA: ~14.2%, LA: ~1.1%	
PdAg ₃ /CNT				OXA: ~39.2%, GLA: ~37.9%, TA: ~13.7%, GLA: ~8.8%, LA: ~0.3%	
Pd/CNT	Aqueous-phase reduction method	1 M glycerol + 6 M KOH	CA – 0.2 V vs. SHE; 2 h 60°C	OXA: ~10.5%, GA:~ 1.5%, TA: ~41%, MESOXA: ~26% GLA: ~12%, LA: ~10 %	121
PdAg/CNT				OXA: 28%, GA: 1%, TA: ~38%, MESOXA: ~24%, GLA: ~9%, LA: ~10%	
PdAg ₃ /CNT			CA – 0.2 V vs. SHE; 2 h 80°C	OXA: ~35%, GA: ~1%, TA: ~29%, MESOXA: ~24% , GLA: ~8.8%, LA: ~10%	
PdAg/CNT				OXA: ~31.5%, GA: ~0.5%, TA: ~39%, MESOXA: ~20%, GLA: ~9%, LA: ~10%	
			CA – 0.2 V vs. SHE; 4 h 80°C	OXA: ~40.5%, GA: ~0.5%, TA: ~44%, MESOXA: ~10%, GLA: ~5%, LA: ~10%	
Pd/C Pd ₉₀ Ni ₁₀ /C Pd ₇₀ Ni ₃₀ /C Pd ₆₀ Ni ₄₀ /C Pd ₅₀ Ni ₅₀ /C Pd ₉₀ Ag ₁₀ /C Pd ₇₀ Ag ₃₀ /C Pd ₅₀ Ag ₅₀ /C	Bromide Anion Exchange	0.1 M glycerol + 0.1 M NaOH	CA – 0.8 V vs. RHE; 4 h	OXA, TA, GLA, GA, FA	115 & 117
AuAg sheet	Etching process in concentrated nitric acid solution.	0.5 M glycerol + 0.5 M NaOH	CA – 0.1 V vs. Ag/AgCl; 2 h	FA: 59.31%, GA: 34.72%	157

Au/C-AQ	Aqueous phase method	1 M glycerol	CA – 0.1 V vs. RHE; 12 h	TA 61.2%	144
Au/C-NC	Organic phase nano-capsule method	+ 8 M KOH	CA – 0.1 V vs. RHE; 12 h	TA 61.8%	
Au/C	Modified solution-phase based nanocapsule method	1 M glycerol + 2 M KOH	CA – 0.35 V vs. RHE; 1 h	GLA: ~15%, TA: ~80%, OXA: ~5%	145
			CA – 0.45 V vs. RHE; 1 h	GLA: ~7%, TA: ~75%, OXA: ~3%, MESOXA: ~15%	
			CA – 0.55 V vs. RHE; 1 h	GLA: ~13%, TA: ~40%, OXA: ~2%, MESOXA: ~45%	
			CA – 0.65 V vs. RHE; 1 h	GLA: ~16%, TA: ~21%, OXA: ~3%, MESOXA: ~60%	
			CA – 0.7 V vs. RHE; 1 h	GLA: ~10%, TA: ~20%, OXA: ~10%, MESOXA: ~60%	
Au/C	Water-in oil microemulsion method - NaBH ₄ reducing agent followed by Cu electro-deposition	0.5 M glycerol + 0.5 M NaOH	CA – 0.1 V vs. Ag/AgCl; 2 h	TA: 7.68%, GLA: 22.06%, OXA: 3.08%, GA: 43.98%, FA: 23.2%	153
Cu _{+0.3/30} -Au/C				TA: 17.56%, GLA: 28.89%, OXA: 16%, GA: 12.69%, FA: 24.87%	
Cu _{+0.1/30} -Au/C				TA: 11.93%, GLA: 27.07%, OXA: 8.23%, GA: 20.73%, FA: 32.04%	
Cu _{+0.015/30} -Au/C				TA: 14.55%, GLA: 39.03%, OXA: 3.77%, GA: 17.59%, FA: 25.06%	
Cu _{-0.1/30} -Au/C				TA: 12.35%, GLA: 34.73%, OXA: 7.65%, GA: 20.07%, FA: 25.21%	
Cu _{-0.3/30} -Au/C				TA: 7.95%, GLA: 26.86%, OXA: 4.51%, GA: 25.85%, FA: 34.83%	
Au-CB	Water-in oil microemulsion method - NaBH ₄ reducing agent followed by support dispersion mixed under sonication	0.5 M glycerol + 0.5 M NaOH	CA – 0.2 V vs. Hg/HgO; 2 h	GLA: 34.5%, GA: 12.7%, TA: ~15%, OXA: ~15%, FA : ~23%	148
Au-PmAP/G				GLA: 42.2%, GA: 17.8%, TA: ~13%, OXA: ~2%, FA : ~25%	
Au-P4P/rGO				GLA: 57.4%, GA: 11.3%, TA: ~8%, OXA: ~10%, FA : ~8%	
Au-P4P/G				GLA: 68.6%, GA: 7%, TA: ~15%, FA : ~8%	

Au-CB	Water-in oil microemulsion method - NaBH ₄ reducing agent followed by support dispersion mixed under sonication	0.5 M glycerol + 0.5 M NaOH	CA – 0.6 V vs. Hg/HgO; 2 h	GLA: 15%, GA: 40%, TA: ~2%, OXA: ~3%, FA : ~40%	168
Au-PmAP/G				GLA: 15%, GA: 40%, TA: ~2%, OXA: ~3%, FA : ~40%	
Au-P4P/rGO				GLA: 45%, GA: 30%, TA: ~8%, OXA: ~7%, FA : ~10%	
Au-P4P/G				GLA: 55%, GA: 20%, TA: ~3%, OXA: ~2%, FA : ~15%	
Au-CB			CA – 1 V vs. Hg/HgO; 2 h	GLA: 10%, GA: 45%, TA: ~2%, OXA: ~3%, FA : ~40%	
Au-PmAP/G				GLA: 12%, GA: 45%, TA: ~1%, OXA: ~2%, FA : ~40%	
Au-P4P/rGO				GLA: 40%, GA: 40%, TA: ~6%, OXA: ~1%, FA : ~13%	
Au-P4P/G				GLA: 44%, GA: 35%, TA: ~3%, OXA: ~3%, FA : ~15%	
Ni/C	Commercial	0.1 M glycerol + 0.1 M KOH	CA – 0.7 V vs. Hg/HgO; 3 h	DHA: 1.5% GLAD: 3.1%, GLA: 29.8%, HPA: 17.9%, GA: 28.2%, OXA: 4.1%,	168
ALD (TiO ₂)-Ni/C	Commercial/TiO ₂ deposition			DHA: 4%, GLAD: 0.9%, HPA: 10.1%, TA, 3.7%, GLA: 24%, OXA: 4.8%, FA: 1.4%	
Ni/C	Impregnation/ Reduction method	0.1 M glycerol + 0.1 M NaOH	CA – 1.6 V vs. RHE; 8 h	FA: 32.2%, GA: 11.5%, GLA: 0.5 mM	165
NiCo/C				FA: 7.5%, GA: 4.5%, GLA: 0.25 mM	
NiFe/C				FA: 4%, GA: 3.7%, GLA: 0.1 mM	
NiFeCO/C				FA: 34.1%, GA: 10.3%, GLA: 0.2 mM	
Ni/C			CA – 1.6 V & 1.9 vs. RHE; 8 h	GLA, GA, FA, OXA, TA	163
Bulk Ag	Commercial	0.1 M glycerol + 1 M NaOH	CA – 1.125 V vs. RHE; 14 h	FA, GA, GLA	174

Detection technique: FTIR

Catalyst	Synthesis	Electrolyte	Conditions	Selectivity	Ref.
Pt(111)	Commercial	0.2 M glycerol + 0.5 M H ₂ SO ₄	LSV – 0.1 – 0.95V vs. RHE, 1 mV/s	DHA, GA, glyoxylate, MESOXA, TA	175
Pt/C	Polyol method with PVP	0.25 M glycerol + 0.1 HClO ₄	LSV – 0.05 – 1.45 V vs. RHE, 1 mV/s	GLAD, GLA and CO ₂	103
PtSb/C		0.15 M glycerol + 0.15 M NaOH/HClO ₄	LSV – 0.1 – 1 V vs. RHE, 1 mV/s	glyoxal, FA, g.yOXA, GA, GLA, glycoaldehyde	77
Pt(1 1 1)/Bi _{ir}	Commercial, modified by Bi using irreversible adsorption technique	0.1 M glycerol + 0.1 M HClO ₄	LSV – 0.1 – 0.9 V vs. RHE, 1 mV/s	CO ₂ , aldehydes, ketones, carboxylic acid and DHA	82
Pt(1 00)/Bi _{ir}				CO, CO ₂ , aldehydes, ketones and carboxylic acid	
Pt(111)	Commercial	0.1 M glycerol + 0.1 M NaOH	LSV – 0.1 – 0.9 V vs. RHE, 1 mV/s	carboxylates and acyl are main intermediates	176
Pt ₉ Bi/C	Water-in oil microemulsion method - NaBH ₄ reducing agent		LSV – 0.1 - 1.2 V vs. RHE	GLAD, DHA	73
Pt/C PtAg/C PtAg/MnO _x /C	Water-in oil microemulsion method - NaBH ₄ reducing agent	1 M glycerol + 1 M KOH	LSV – 0.1 – 1.4 V vs. RHE, 1 mV/s	GLAD, DHA, GLA, glyoxylate, HPA, FA	71
Pt ₉ Au/C Pt ₇ Au ₃ /C PtAu/C	Borohydride reduction method	1 M glycerol + 1 M KOH	LSV – 0.05 – 0.5 V vs. RHE	GLA, TA, DHA, HPA, FA, carbonate, GA, glyoxylate	64
Pd ₇₁ Ru ₂₉ /C	Microwave assisted heating method	0.5 M glycerol + 1 M KOH	CA – 0.7 V vs. RHE, 4 h	TA, DHA, GLA, GLAD	111
Pd ₃ Cu	Sacrificial support method	0.1 M glycerol + 1 M KOH	LSV – 0.2 – 1.23 V vs. RHE, 1 mV/s	CO ₂	126
PdSn			LSV – 0 – 0.9 V vs. RHE, 1 mV/s	GLAD/GLA,DHA,carboxylate	122

Pd-NP	Colloidal method - Ascorbic acid reducing agent	0.1 M glycerol + 0.1 M NaOH	LSV - 0.1 - 1 V vs. RHE, 1 mV/s	DHA, GLAD, GLA, HPA	119
Pd ₉ Bi/C Pd ₄₅ Pt ₄₅ Bi/C	Water-in oil microemulsion method - NaBH ₄ reducing agent	0.1 M glycerol + 0.1 M NaOH	LSV – 0.05 - 1.15 V vs. RHE, 1 mV/s	GLA, DHA, GLAD	120
PdRh	Electrochemical reduction	0.1 M glycerol + 0.1 M KOH	LSV – 0.05 - 1.3 V vs. RHE, 1 mV/s	GLAD, GLA, GA OXA and carbonate	118
Pd/C Pd ₇₀ Ni ₃₀ /C Pd ₆₀ Ni ₄₀ /C	Bromide Anion Exchange	0.1 M glycerol + 0.1 M NaOH	CA – 0.8 V vs. RHE, 1 h	GLAD, GLA and GA	117
Au/C Au ₇₅ Ag ₂₅ /C Au ₅₀ Ag ₅₀ /C Au ₂₅ Ag ₇₅ /C	Reducing metal precursors in glycerol NaOH	0.1 M glycerol + 0.1 NaOH	LSV – 0.1 - 1.6 V vs. RHE, every 0.1 V	GLA, GA, DHA, HPA, MESOXA, OXA, TA, glyoxylate, malonate, pyruvate, GLAD	155
Ni/C			CA –1.5 V vs. RHE, 2 h	FA, carboxylates, OXA	166
NiCo/C NiFe/C NiFeCO/C	Impregnation/ Reduction method	0.1 M glycerol + 0.1 M NaOH	CA – 1.6 V vs. RHE; 4 h	GA, OXA, GLA, TA, FA	165
Ni/C NiCo/C			LSV – 0.6 - 1.9 V vs. RHE, 1 mV/s	GLA, GA, FA. OXA, TA, MESOXA	163
Detection technique: PM-IRRAS					
Catalyst	Synthesis method	Electrolyte	Conditions	Selectivity	Ref.
Bulk Ni	Commercial	0.1 M glycerol + 1 M NaOH	CA – 0.42, 0.44, 0.52 and 0.54 V vs. Hg/HgO; 30 min	GLAD, carbonyl species, carboxylates	49
Detection technique: NMR					
Catalyst	Synthesis	Electrolyte	Conditions	Selectivity	Ref.
Pd/MWCNT-COOH FeCO@Fe@Pd/MWCNT-COOH	Microwave-induced synthesis	5 wt% glycerol + 2 M KOH	102 mA; 3.32 h	TA, 15%, GLA: 14%, GA: 14% OXA: 9%, FA: 3%, carbonate:47%	97
			102 mA; 4.68 h	TA, 7%, GLA: 3%, GA: 7% OXA: 7%, FA: 3%, carbonate:73%	
Co ₃ O ₄	Electrodeposition / annealing in air	0.5 M glycerol + 1 M KOH	0.6 V vs. Hg/HgO; 24 h	FA	173

2.3 Glycerol electrooxidation mechanism

The integration of quantum mechanical calculations using the density functional theory (DFT) and experimental electrochemical and the state of the art in-situ analytical techniques is necessary to provide strategies for rational design of catalysts for GEOR. The understanding GEOR mechanism is important for desired product selectivity and reaction optimization. The synergy between theoretical simulations and experiment has been reported in order to visualize the reaction paths. Glycerol electrooxidation mechanism has many pathways that will depend on the catalyst properties. Recently, three research groups reported an experimental and computational approach for understanding the mechanism of glycerol oxidation on Pt and Au single crystal electrodes. The combined DFT calculations on Pt (100) and Pt (111) and electrochemical experiments as well as spectroscopy showed that GEOR is highly structure sensitive on Pt surfaces.¹⁷⁷ Figure 2.12 illustrates two proposed GEOR pathways that are governed by the initial bonding mode of the dehydrogenated glycerol adsorbate. On Pt(100), the dehydrogenated glycerol binds through one double Pt=C bond, yielding only glyceraldehyde, whereas on Pt (111) electrode it binds through two adjacent single Pt-C bond, yielding an enediol intermediate (i.e., glyceraldehyde and dihydroxyacetone). Moreover, cyclic voltammetry and FTIR experiments suggested the existence of inactive intermediate, CO, which is highly resistant to oxidation.¹⁷⁷

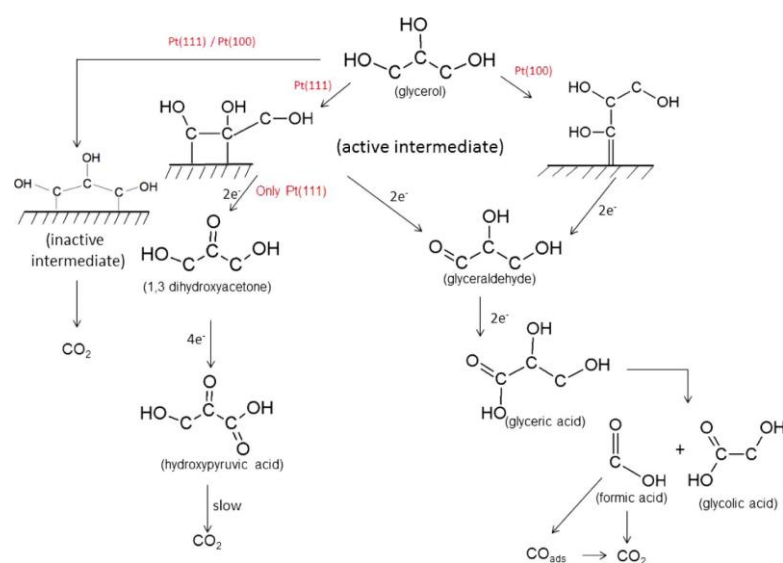


Figure 2.12. Schematic of glycerol oxidation mechanism on Pt(111) and Pt(100) electrodes in acidic solution. (Reproduced with permission.¹⁷⁷ Copyright© 2016, ACS Catalysis)

Furthermore, *Fernandez et al.*¹⁷⁸, reported the mechanism for GEOR on the well-ordered and disturbed Pt(100) single crystal electrodes in acidic solution using cyclic voltammetry and in-situ infrared spectroscopy. They stated that GEOR onset potential on Pt (100) is dependent on the defects present on the surface. On the well-ordered Pt surface, the glycerol oxidation starts at 0.1V vs. RHE in comparison to 0.8V vs. RHE for highly disordered surface. DFT calculations supported by qualitative analysis showed the presence of CO and carbonyl absorption bands, which are strongly adsorbed on low-coordinated Pt sites if compared to ordered surfaces. The authors ascribed this phenomenon to the Pt-CO bond breaking which is the GEOR rate determining step.

Electrochemical and DFT studies of GEOR on Au electrode were reported recently.¹⁷⁹ It was found that in acidic medium glycerol oxidation start occurring at measurable extent below 1.0 V vs. RHE, in contrast to previously reported studies.^{180,181} On gold, GEOR activity varied significantly based on electrolyte choice, where HClO₄ provided better results than H₂SO₄ because of the competitive adsorption of sulphate over perchlorate ions.^{182,183} Combining the DFT calculations on Au (111) and experiment, it was demonstrated that the most favorable GEOR pathway is dehydrogenation of the secondary carbon at 0.39 V vs. RHE, leading to formation of dihydroxyacetone, hence at the same potential 2,3-dihydroxy-2-propenal was formed by primary carbon dehydrogenation as shown in Figure 2.13. At 0.5V and 0.6V, CO and glyceraldehyde were produced, respectively. These data were in satisfactory agreement with the experimental data at ~0.5 V.¹⁷⁷

Based on the reviewed literature regarding GEOR mechanism it is clear that there are still a lot of questions that remain to be addressed in order to guide the design of efficient and selective catalysts for selective glycerol electrooxidation. In particular, an elucidation of glycerol oxidation mechanism on non-Pt group metal catalysts is important for practical utilization of GEOR. Understanding the mechanism is a top priority for the successful electrochemical valorization of glycerol. A breakthrough in this effort will increase the overall GEOR efficiency, making it a strong competitor to catalytic partial oxidation. Efforts in the fundamental understanding of the reaction mechanism are necessary to pave the way for the rational design of selective and stable catalysts.

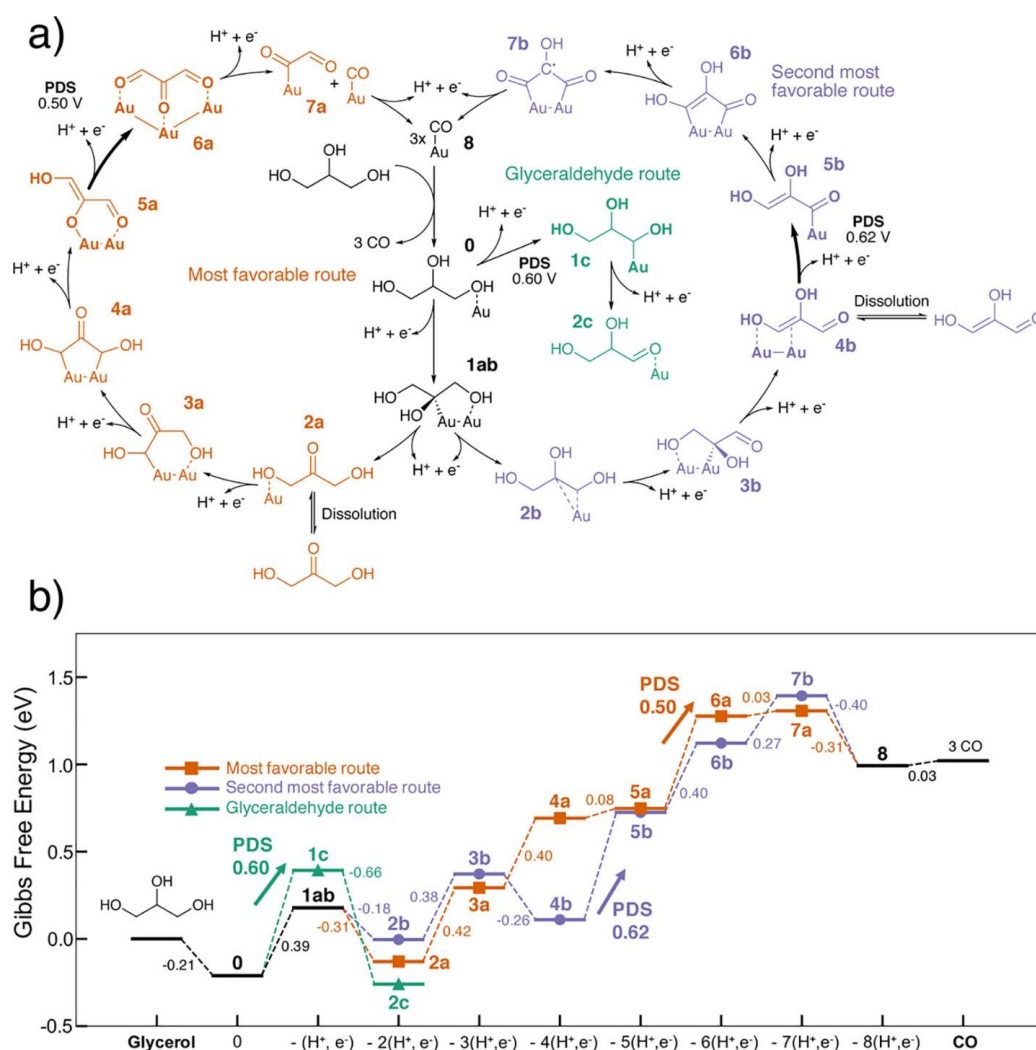


Figure 2.13. Catalytic routes of glycerol dehydrogenation on Au(111), presented as (a) catalytic cycles and (b) energy landscape. The two most favorable complete dehydrogenation routes to CO are marked in red with squares and blue with circles, respectively, while a path ending in adsorbed glyceraldehyde is shown in green with triangles. PDSs are marked for each route. (Reproduced with permission.¹⁷⁹ Copyright© 2018, The Journal of Physical Chemistry C)

2.4 Conclusion and outlook

From the overview of the literature presented here, it is clear that there is a growing worldwide attention in the development of advanced electrocatalysts for glycerol electrooxidation. In the past five years, tremendous efforts have been devoted to developing GEOR catalysts from both the fundamental understanding of the reaction using DFT approach to the application of the modern in-situ analytical techniques for identification and quantification of the reaction products. The application of carbon supports, polymer supports or the combination of polymers and other supports, have attracted considerable attention in the last five years. The main reasons for this are the

cost reduction of catalyst preparation, and the use of more environmentally friendly materials by using cheap materials in synthesizing selective and active electrocatalyst for GEOR.

HPLC analyses, nuclear magnetic resonance spectroscopy and in-situ infrared spectroscopy measurements of GEOR products have illustrated that the product distribution can be influenced by the applied potential, as well as the nature, structure and composition of the electrode material, which can be tuned through various synthesis approaches. All these insights forecast the possibility to control the selectivity of given products and to enhance catalytic activity in glycerol electrooxidation reaction. To complement these experimental techniques is the integration of quantum mechanical calculations using the density functional theory (DFT) for atomic insights to facilitate the screening of the best electrocatalysts for experimental testing. The synergy between theoretical simulations and experiment for the past five years has provided good understanding of GEOR mechanism on Pt and Au single crystal electrodes. However, we are still in early stage and many questions have to be addressed in order to guide the design of selective and efficient catalysts for selective GEOR. In particular, an elucidation of glycerol oxidation mechanism on non-Pt group metal catalysts. A breakthrough in this effort will enhance the overall GEOR efficiency, making it a strong competitor to hetero-catalytic partial oxidation.

Majority of GEOR studies have been carried out in an alkaline media with only a few in acidic solutions. Platinum is one of the few materials that showed promising catalytic activity and stability towards GEOR in acidic media with onset potential at 0.4V vs. RHE. Addition of p-group (Bi, Sb, Pb, Sn and In) elements promoted the catalytic activity significantly and shifted the overpotential at lower values with different selectivities ranges from carbon cleavage and formation of C_1 and C_2 products with (Sn, In and Pb) and DHA with (Bi and Sb). Whereas in alkaline media, addition of 10% of Bi led to higher activity, while the onset potential was approximately 200 mV lower than monometallic Pt/C. Moreover, in-situ FTIR measurements showed that Pt_9Bi_1/C avoided the C-C bond cleavage, thus increasing the selectivity towards C_3 compounds. At high potentials, dihydroxyacetone and glyceraldehyde acted as reaction intermediates to the formation of carboxylates, while at lower potentials, glyceraldehyde is the main reaction product. Decoration of Pd/C by Bi_2O_3 and $Bi(OH)_3$ clusters on the surface didn't affect

the selectivity of glycerol electrooxidation favoring carboxylate formation, while the onset potential for GEOR remained high comparing to Pt₉Bi/C catalysts. Similarly, different Pd morphologies ranging from nanocubes, nanospheres and nanooctahedrons have similar selectivity towards glycerate at low potentials, while hydroxypyruvate, dicarboxylates carbonate and CO₂ at high potentials for GEOR in alkaline media. Gold is also active and anti-poisoning by adsorbed species, making it more selective towards C₃ compounds. Based on literature, Au/C has the highest selective material to tartronate and mesoxalate comparing to other catalysts reaching 79% and 60% in 1M glycerol at 0.35V and 0.7 V vs. RHE for 1 h at 50 °C, respectively. Nevertheless, majority of glycerol electro-oxidation studies were focused on expensive and noble metals such as Pt, Pd and Au (94%) of analyzed literature since 2013 in this study. Whereas only 6% of publications report application of Ni-based electro-catalysts. Since glycerol is not reduced at the cathode, Ni-based materials are highly suitable for membraneless GEOR technology with concurrent cathodic production of H₂. However, Ni-based electro-catalysts have high overpotential, i.e., above 1.2 V vs. RHE, despite showing good stability and robustness. Carbonate and oxalate were the main products on Ni/C at lower glycerol concentrations, while at higher concentrations, formate prevailed with low selectivity into C₃ products.

As there is high production costs associated with the petrochemical industry, GEOR products would open new markets for cost-efficient production of fuels. One of the vital factors in realizing this goal is searching for a suitable alternative to noble metal-based catalysts. It was found that some non-precious Pt group metal catalysts have shown promising results, however, results are still not up to industrial scale standards. Nonetheless, some of the reported novel catalysts hold promise to be valuable catalysts if the selectivity toward single products can be altered. The cost assessment of GEOR should kept in mind when investigating promising materials as it is linked to the catalyst cost, stability and selective product formation.

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Chapter 3

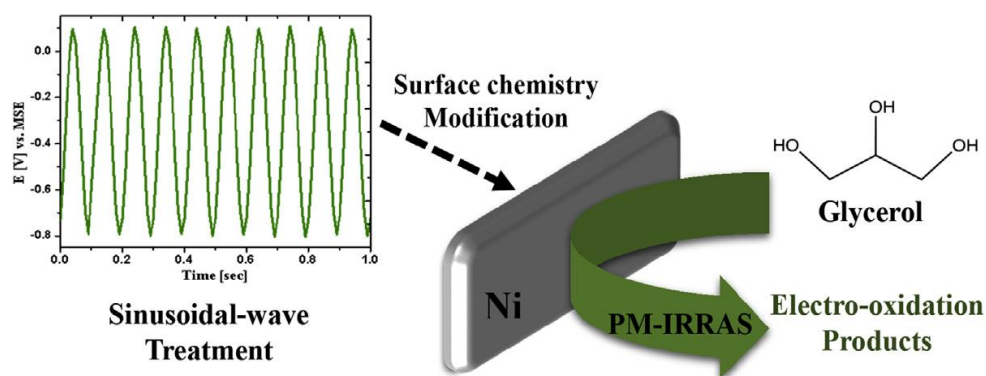
3 Electrochemical Modification of Nickel Surfaces for Efficient Glycerol Electrooxidation

Based on the paper:

Houache M.S.E., Cossar E., Ntais S., Baranova E.A., Journal of Power Sources, 2018, 375, 310-319.

Abstract

The glycerol electrooxidation reaction (GEOR) was investigated on nickel electrode in alkaline media following a sinusoidal-wave treatment in a solution of 0.1 M Na_2SO_4 + 30mM ascorbic acid. This treatment significantly increased the catalytic activity of Ni towards the GEOR. The electrochemical active surface area showed a six-fold increase, while the current density of glycerol oxidation was enhanced over four times with a concurrent onset potential decrease by 45 mV. SEM analysis before and after the treatment revealed some morphology changes through the formation of additional grooves and pits on the Ni surface. XPS confirmed that before the treatment, the surface consists of Ni metal in addition to NiO, $\text{Ni}(\text{OH})_2$ and NiOOH, whereas after the treatment, 97% of the surface is Ni hydroxide composed of Ni^{2+} and Ni^{3+} . Chronoamperometry coupled with in-situ polarization modulation infrared-reflection absorption spectroscopy (PM-IRRAS) for simultaneous analysis of products on the Ni surface and in the bulk solution showed that the main reaction products on both untreated and treated Ni surfaces are glyceraldehyde, carbonyl, carboxylate ions and some carbon dioxide.



3.1 Introduction

Depletion of fossil fuel resources and their consumption is progressively increasing due to the growing global energy demand. In this milieu, there is a noteworthy need in developing more sustainable alternatives to petroleum-derived fuels to satisfy the global energy requirements.^{1,2} Biodiesel, a clean-burning renewable biofuels is considered as an alternative fuel due to environmental, economic and technical

sustainability. Biodiesel is derived from vegetable oils or animal and/or waste fats through a trans-esterification reaction. This process generates 10 wt.% of glycerol as by-product.³ Although glycerol is utilized as raw material in the pharmaceutical, food, cosmetics and tobacco industries, the glycerol supply is still superior to the demand due to the expansion of biodiesel production. The surplus of glycerol has motivated the research that transforms glycerol into value-added products thus, making biodiesel environmentally benign with added financial benefits.⁴

Glycerol electrooxidation is an attractive approach for the synthesis of valuable chemicals. The electrochemical partial oxidation of glycerol in alkaline media consists of complex reaction pathways⁵ and produces a large number of useful intermediates, such as glycerate, tartrate, oxalate, hydroxypyruvate, glycolate, dihydroxyacetone, mesoxalate and formate ions. A mixture of these products during the glycerol electrooxidation reaction (GEOR) has been observed and reported in literature.⁶⁻¹¹ Some of these oxygenated species have industrial uses, from heavy metal complexing agents to polymer precursors or drug delivery agents. For instance, tartronic acid is valued at 1564 USD/g and is utilized in medicinal practice.⁵ Furthermore, glycerol electrooxidation in direct alcohol fuel cells (DAFCs) could potentially cogenerate electrical energy and produce a large number of high value-added chemicals.¹¹⁻¹⁵ This is in spite of its relatively low theoretical energy density of 5.0 kWh·kg⁻¹ if compared to ethanol and methanol, 8.1 and 6.1 kWh·kg⁻¹, respectively.¹⁶

A number of recent studies showed the GEOR on noble metals such as Pt, Pd and Au¹⁷⁻²³, which had satisfactory activity but low selectivity towards the desired products. To make the GEOR practically valuable, novel inexpensive and selective catalysts are necessary. Ni is one of the most commonly used non-noble metal catalyst and has been applied in numerous electrochemical systems such as fuel cells²⁴, alkaline batteries²⁵, sensors²⁶, supercapacitors²⁷ and as electrocatalysts for alcohol oxidation reactions in alkaline media.^{4,28-32} The complexity of the Ni surface chemistry in alkaline solutions and the Ni oxidation state does however strongly influence its efficiency, performance and catalytic activity.³³⁻³⁶ Nevertheless, the high activity of nickel, its anti-poison ability and long-term stability in alkaline solutions make it an attractive candidate for the GEOR. Several studies have reported a successful GEOR on Ni-based electrocatalysts^{4,28,29} and on different bimetallic Ni-M/C (M= Co, Fe, Pd, Pt) nanoparticles.^{4,28,29,37-41} In particular,

the bimetallic Pt₂Ni₁/C catalyst showed a marked reaction rate increase due to modification of the electronic and geometric structure in comparison to the Pt/C catalyst. This results in better catalytic performance for glycerol electro-oxidation as shown by a lower onset potential and higher current densities.³⁹ The Ni co-catalyst was therefore able to reduce considerably the Pt amount without reducing the activity.

Due to the complexity of glycerol oxidation mechanism and the variety of the produced compounds, it is necessary to monitor, control and link, if possible, the different products to reaction conditions, applied potential and the surface species of an electrocatalysts. Coupling electrochemical methods, e.g., chronoamperometry (CA) and/or linear sweep voltammetry (LSV) with *in-situ* vibrational spectroscopy to identify products for alcohol oxidation has been successfully applied for monitoring GEOR products.^{19,42-44} It was shown that Ni-based catalysts such as Ni/C, NiCo/C, NiCoFe/C and Pd_xNi_{1-x}/C in alkaline media produce various compounds, e.g., glycerate, glycolate, tartronate, oxalate and formate.^{14,15,28,29} A scheme of glycerol oxidation on PdNi and PdAg in alkaline media was proposed earlier¹⁴, in which the first step of the mechanism is glyceraldehyde formation, which is further oxidized to glycerate ion. The next step, depending on the nature of surface active sites and applied potential, could lead to formation of three intermediates: tartronate, formate and/or glycolate ions. The complexity of the reaction pathway implies that in order to design Ni-based electrocatalysts with bespoke activity and selectivity it is crucial to gain a better understanding of the nature of the Ni surface active sites and their role on GEOR and product distribution.

In the present study, we report the glycerol electrooxidation reaction on a polycrystalline Ni electrode. We investigate the reaction on untreated and electrochemically pre-treated Ni surfaces. The proposed treatment is based on the work of Baranova *et al.*⁴⁵, where an electrochemical sinusoidal-wave treatment was applied to Ni-based particles (Ni₉₉Pd₁) to improve their activity towards hydrogen evolution reaction (HER). The sinusoidal wave treatment in the presence of ascorbic acid resulted in a significant current density increase for HER due to the formation of a higher amount of Ni surface hydroxides. In the later study⁴⁶, the improved HER after square-wave treatment in the same electrolyte solution and potential window was associated with formation of surface Ni(OH)_x (x between 0 and 2) that promoted the reaction. Therefore,

in this work the Ni electrode before and after the sine-wave treatment was characterized by SEM and XPS to elucidate the role of treatment in the Ni morphology and surface chemistry. Furthermore, a detailed electrochemical study in combination with *in-situ* (PM-IRRAS) measurements was carried out to compare the activity of Ni before and after treatment and find the reaction products.

3.2 Experimental

3.2.1 Materials and electrochemistry

Electrochemical measurements were carried out using two conventional three-electrode electrochemical cells, namely, Teflon cell for the electrochemical oxidation of glycerol in alkaline solution and a cell made of Pyrex for electrochemical sinusoidal-wave treatment. BioLogic VSP Potentiostat/Galvanostat equipped with EC-Lab software (BioLogic Science Instruments SAS, Claix, France) was used to conduct all electrochemical measurements. The nickel wire (99.99% purity, Sigma Aldrich) of 0.5 mm in diameter served as a working electrode. Prior to each experiment, the “fresh” untreated Ni wire was polished using an aqueous suspension of 30 μm alumina (Al_2O_3 , Carveth metallurgical limited, Canada) and 3 μm Al_2O_3 (Buehler, USA) to obtain a mirror-like surface. The Ni wire was then rinsed with de-ionized water (Milli-Q® Millipore, 18.2 $\text{M}\Omega$ cm at 293 K) and sonicated in an ultrasonic bath for 20 minutes. Once polished, the Ni wire was placed in a Teflon casing, leaving a 1 cm portion of the wire exposed to the solution. This resulted in a geometric area of 0.161 cm^2 . Large surface area Pt mesh was used as a counter electrode. All electrolytic solutions were purged with N_2 for 15 min to remove any dissolved oxygen and a nitrogen stream was maintained during the experiment. All experiments were performed at room temperature.

3.2.2 Glycerol electrooxidation

The GEOR in alkaline solution was carried out using Hg/HgO (Koslow Scientific Company) reference electrode. The electrolyte solutions were prepared from KOH (EMD, ACS grade), Glycerol (Sigma-Aldrich $\geq 99\%$), and ultrapure de-ionized water (Milli-Q® Millipore, 18.2 $\text{M}\Omega$ cm at 293 K). Cyclic voltammetry (CV) and chronoamperometry (CA) measurements were carried out before and after the electrochemical treatment in 1M KOH and in 1M KOH + 0.1M glycerol. The scan rate was 50 mVs^{-1} .

3.2.3 Electrochemical treatment

The electrochemical treatment of the Ni electrode consisted of applying a sinusoidal-wave signal at a frequency of 10 Hz for 50 minutes. The upper and lower potential were 0.1V and -0.8V vs. Hg/Hg₂SO₄/K₂SO₄ (MSE) (Koslow Scientific) in a 0.1M Na₂SO₄ (Sigma-Aldrich 99 %) and 30mM ascorbic acid (Sigma-Aldrich reagent grade) solution.⁴⁵

3.2.4 Determination of the electrochemical active surface area (ECSA)

The method to determine the ECSA of Ni is based on the procedure proposed earlier by *Avaca et al.*⁴⁷ In this procedure, the freshly polished Ni electrode is cathodically polarized at E= -1.3 V for 5 min and then at E=-0.8 V for 10 min. This is done to reduce any traces of surface oxides/hydroxides and to remove any traces of H_{2(g)} generated in the respective polarization steps, which is in accordance with the earlier proposed method³³⁻³⁵ using the Equation (3.1):

$$\text{ECSA [cm}^2\text{]} = \frac{Q [\mu\text{C}]}{514 \left[\frac{\mu\text{C}}{\text{cm}^2} \right]} \quad (3.1)$$

where Q is the experimentally determined charge of α -Ni(OH)₂ formation. The theoretical charge value ($514 \frac{\mu\text{C}}{\text{cm}^2}$) is the charge required to form one monolayer of α -Ni(OH)₂. The value of ECSA was determined to be $0.35 \pm 8.3\%$ cm². The value of ECSA was used to determine the current density of glycerol oxidation and to compare the electrode performance before and after the treatment.

3.2.5 Characterization

Scanning electron microscopy (SEM) micrographs of Ni wire were taken using a Phenom ProX. Samples were prepared by placing a segment of Ni wire onto a specimen mount with an adhesive carbon conductive tab (TED PELLA, INC.). XPS measurements were carried out in a KRATOS Axos Ultra DLD with a Hybrid lens mode at 140W and pass energy 20eV using monochromatic Al K α radiation (h ν =1486.6eV). The pressure in the analysis chamber was lower than 10⁻⁹ mbar while the electron gun was deployed, eliminating the charging effects. The C1s XPS core level peak at 284.6 eV was used to calibrate the energy scale. The analysis of the Ni2p_{3/2} and O1s was performed using the CasaXPS software.

3.2.6 In situ photoelastic modulations infrared reflection absorption spectroscopy (PM-IRRAS) measurements coupled with electrochemical experiments.

In situ PM-IRRAS measurements were carried out using Bruker Tensor 37 spectrometer equipped with an external Polarization Modulation Accessory (PMA 50 XL) which was modified for beam reflection on electrode surface at a 63° incidence angle. The detector was a mercury cadmium telluride type (MCT), cooled in advance by liquid nitrogen. The signal was acquired by 256 interferograms with 8 cm⁻¹ resolution and the FTIR spectra were given in the 1000 cm⁻¹ and 4000 cm⁻¹ IR range. All the experiments were performed in a special tailored spectroelectrochemical cell with fitted CaF₂ prism.⁴⁸ The electrode potential was controlled by a PARSTAT 2263 potentiostat equipped with PowerSuite (Princeton Applied Research). The working electrode consisted of Ni foil surface (12.5 mm Diameter, 99.99% purity, Sigma Aldrich) before and after sine-wave treatment. In order to reduce the IR beam absorption, the WE was pressed against the prism and a thin layer of electrolytic solution was attained. The cell and PMA-50 XL chamber were thoroughly purged with N₂ and dry air to remove all interferences from atmospheric water and CO₂, respectively. For the chronoamperometry/PM-IRRAS experiments, the reference spectrum was acquired at the open circuit potential (OCP) typically, after 90 min of thoroughly purging with dry air, followed by sample spectra at various GEOR potentials chosen from the cyclic voltammetry profile. Sample spectra were acquired every 5 min for half an hour before stepping to another potential. Data processing and interpretation equations proposed earlier⁴⁹ yield equations (3.2) and (3.3), which correspond to the reflectance factor (R.F) of the surface and bulk solution species, respectively:

$$R.F_{\text{surface}} = \frac{\text{Sample } (R_{\text{dif}})}{\text{references } (R_{\text{dif}})} - 1 \quad (3.2)$$

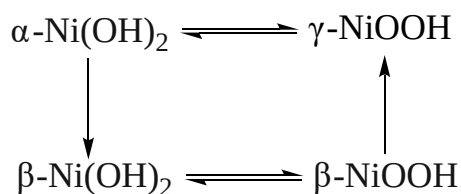
$$R.F_{\text{bulk}} = \frac{\text{Sample } (R_{\text{avg}})}{\text{references } (R_{\text{avg}})} - 1 \quad (3.3)$$

Where, the difference of absorption intensities [$R_{\text{dif}} = (R_p - R_s)$] and the bulk species as the average of the absorption intensities [$R_{\text{avg}} = (R_p + R_s)/2$].⁴⁸ Positive and negative going bands represent respectively the increase and decrease of species.

3.3 Results and discussion

3.3.1 Effect of the treatment on Ni electrochemical behavior in 1M KOH

The Nickel electrode was subjected to sinusoidal-wave treatment in 0.1M Na₂SO₄ + 30 mM ascorbic acid solution for 50 min at a frequency of 10 Hz with the impulse amplitude between 0.1V and -0.8V vs. MSE as described in details in ⁴⁵ and shown in Supplementary Information (SI), Figure A1. Figure 3.1 shows CVs of Ni before and after the sine-wave treatment in the cathodic Figure 3.1 (a) and anodic Figure 3.1 (b) regions in a N₂-saturated 1 M KOH solution. The observed peaks are typical for the nickel metal. The CVs in 1M KOH shows the formation of various phases over the lifetime of the Ni electrode, namely, α -Ni(OH)₂, β -Ni(OH)₂, β -NiOOH and γ -NiOOH. The Bode diagram below illustrates the phase change that is likely to take place during a normal cycle of Ni in an aqueous alkaline solution ⁵⁰:



The initial step is the oxidation of metallic nickel to nickel hydroxide, α -Ni(OH)₂ at potentials around $-0.8 \leq E \leq -0.4$ V vs. Hg/HgO. By increasing the potential to $-0.4 \leq E \leq 0.48$ V the transformation of the α -form into irreversible, less hydrated and more stable β -Ni(OH)₂ phase takes place, which then accumulates on the Ni surface.²⁰ It has been shown that β -Ni(OH)₂ is the predominant surface species in KOH solution, whereas some NiO could be sandwiched between metallic Ni and β -Ni(OH)₂.³⁴ At more positive applied potentials of $E > 0.48$ V vs. Hg/HgO, β -Ni(OH)₂ is oxidized to oxyhydroxide β -NiOOH with removal of a proton Figure 3.1b, anodic peak at around 0.5V (Figure 3.1 b). Under certain experimental conditions the β -NiOOH could be partially transformed to γ -NiOOH.⁵⁰ Finally, the γ -NiOOH is reduced into the unstable hydrated α -Ni(OH)₂ phase, which is then quickly converted to β -form.

The current associated with Ni hydroxide formation increases significantly after the electrochemical treatment (Figure 3.1). The electrochemical surface area (ECSA) before and after the treatment was determined using the α -Ni(OH)₂ peak and Equation 3.1 (Figure 3.1a). A marked increase in the α -Ni(OH)₂ peak indicates an enhancement of

ECSA as a result of treatment. The evaluated ECSA before and after treatment were 0.35 and 2.1 cm², respectively, corresponding to a $6 \pm 4.75\%$ time increase. Several methods for ECSA estimation of Ni electrodes have been reported earlier^{35,51-54}, for instance using the electrochemical double layer capacitance, C_{dl} found from electrochemical impedance spectroscopy (EIS) measurements^{52,53}, or based on adsorbed hydroxide species formed in the Ni(III) potential region⁵⁴ or recently proposed oxalate method.⁵¹ As stated in the literature^{35,51-54}, all these methods have limitations and involve some approximations. As α -Ni(OH)₂ peak was very well defined on the untreated and treated Ni electrodes and because all α -Ni(OH)₂ phase transforms fully and irreversibly to β -Ni(OH)₂ phase upon anodic polarization we assumed that ECSA found using this method could be a good estimation of the active surface area of bulk Ni.

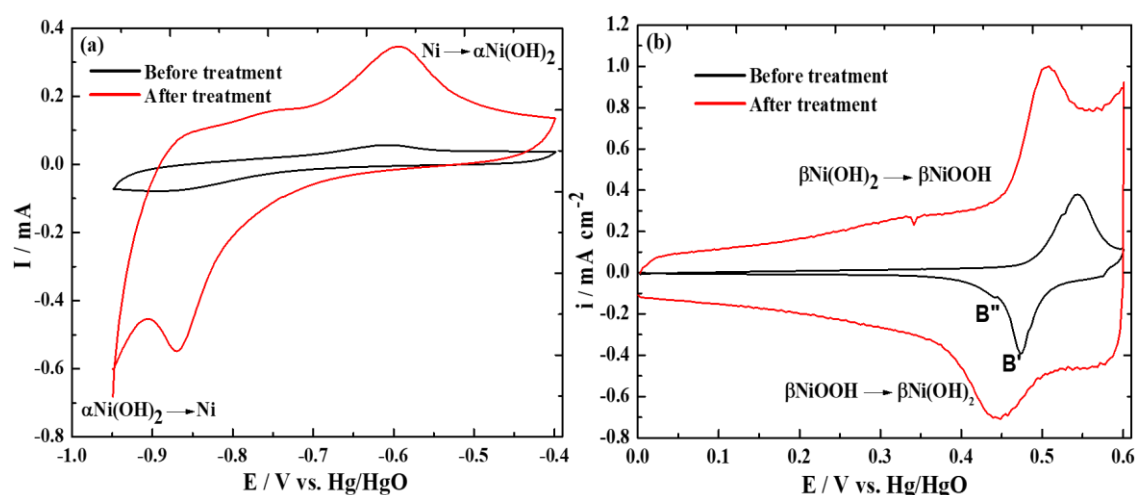


Figure 3.1. Cyclic voltammograms of Ni electrode in 1M KOH at $v = 50 \text{ mVs}^{-1}$ before and after electrochemical treatment in the cathodic (a) and anodic (b) region.

In Figure 3.1b, the current density is given per ECSA and despite much larger active surface area after the treatment the CVs show remarkable difference. After sine-wave treatment, current density for the pair of anodic peaks Ni(II)/Ni(III) centered at $\sim 0.54 \text{ V}$ increases by over three times and its maximum shifts by 45 mV to lower potentials, i.e., from 0.550V to 0.505V (Figure 3.1b). This indicates that higher amount of β -Ni(OH)₂ is initially present on the surface compared to the untreated Ni surface. Also, the CV curve for treated Ni electrode gives the quasi-reversible Ni(II)/Ni(III) transition with potential differences of 57 mV between anodic (0.505 V) and cathodic peaks (0.448 V), whereas, the untreated Ni exhibits much broader redox peak potential difference of 70 mV, indicating a poorer reversibility of the redox process. In addition,

as shown in Figure 3.1b, before treatment, the negative sweep of Ni electrode depicts two reduction peaks B' and B'', which could indicate the existence of two different oxyhydroxide phases, β and γ .⁵⁰ After the electrochemical treatment, the peak of β -NiOOH is still present but no reduction peak of γ -NiOOH is observed. It is difficult to say with the certainty if all γ -NiOOH phase is transformed to β or increase of both phases occurs and β -NiOOH peak overlaps with γ -NiOOH.

According to earlier work⁵⁵, the oxyhydroxide region is not sensitive to the surface orientation of single-crystal Ni electrodes. After several cycles, the peak potential for (100), (110) and (111) during the positive sweep are quite similar at 1.409, 1.407 and 1.413 V vs. RHE, respectively. In this work the untreated and treated Ni are 1.445 and 1.4V/RHE, respectively. Repeating the potential sweep for several cycles results in a slight increase of the current density values of the anodic and cathodic peaks as shown in Figure A2 in SI. This is attributed to the entry of OH⁻ groups into the Ni(OH)₂ surface layer, which prompts a progressive increase in the hydroxide layer thickness, corresponding to the Ni²⁺/Ni³⁺ transition.

To further investigate the surface restructuring of Ni before and after the treatment, we carried out CVs in 1 M KOH with increasing anodic potential limit up to 0.7 V (Figure 3.2). The CVs demonstrate that for both surfaces, the peaks for β -NiOOH formation and reduction increase with the anodic potential limit growth.

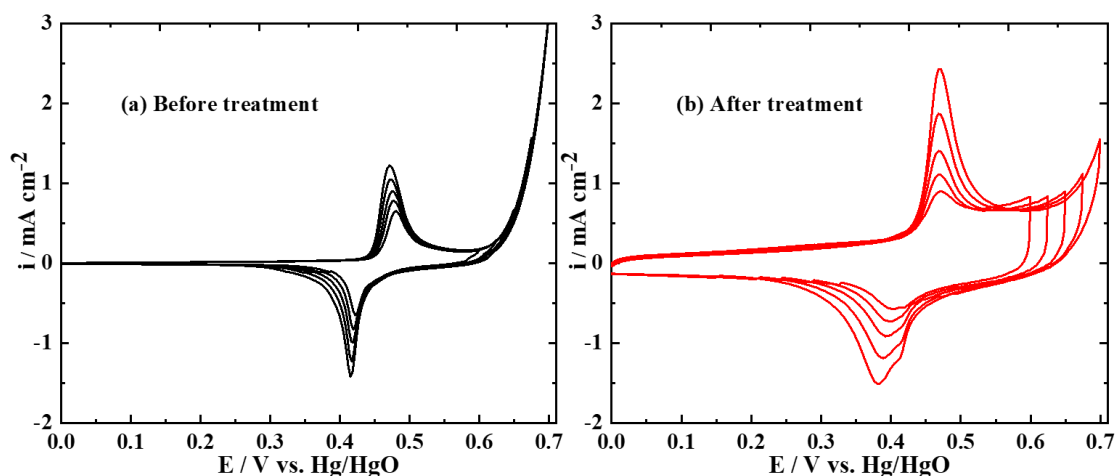


Figure 3.2. Cyclic voltammograms of Ni electrode in 1M KOH at $v = 50 \text{ mVs}^{-1}$ before (a) and after electrochemical treatment (b). 10th cycle is shown.

For Ni before treatment, anodic peak shifts to lower values while for the treated Ni the peak position is the same. The reduction peak shifts to lower value for both treated and untreated Ni electrodes. In addition, the electrode after the treatment shows an additional reduction peak/ shoulder at ~ 0.43 V, which increases with anodic potential. This peak might be assigned to a higher oxidation state of Ni^{4+} .⁵⁰ Besides, the sin-wave treatment has a negative effect on oxygen evolution reaction (OER). The current growth due to OER starts at ~ 0.62 and 0.65 V for untreated and treated sample, respectively and the current density at 0.7 V is much lower for the treated Ni electrode.

3.3.2 SEM and XPS of Ni electrode before and after the treatment

The effect of the electrochemical treatment on the morphology of the Ni electrode was explored using SEM. Figure 3.3a and b illustrate characteristic SEM micrographs of Ni electrode before and after the electrochemical treatment. The untreated Ni surface shows the presence of islands with relatively smooth surface at the micrometer scale and some pits. After the treatment, the surface morphology changes considerably showing deep parallel groves and many pits on the surface. This indicates that the geometric area has increased, which could contribute towards the higher currents and ECSA.

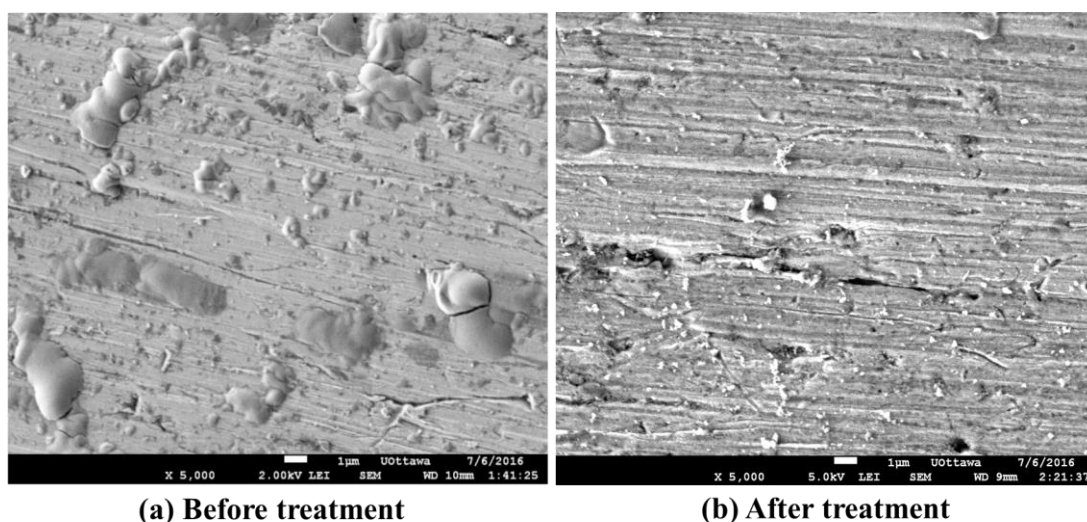


Figure 3.3. SEM of a Ni electrode before (a) and after (b) electrochemical sinusoidal-wave treatment in $0.1\text{M Na}_2\text{SO}_4 + 30\text{mM}$ ascorbic acid.

XPS measurements were carried out to obtain information about the chemical environment of Ni and surface species present on the surface before and after treatment. Figure 3.4 shows the $\text{Ni}2\text{p}_{3/2}$ and the $\text{O}1\text{s}$ XPS peak before and after the electrochemical

treatment, and Table 3.1 summarizes peak position, the FWHM and peak % relative intensity. As previously reported before^{46,56} the assignment of a single BE to a specific nickel oxidation state is challenging due to mixture of core level and satellites, as well as multiple splitting that complicate the interpretation of the corresponding oxygen peaks. Though, the safe assignment for each nickel oxidation state (Ni^0 , Ni^{2+} or Ni^{3+}) and for different nickel species e.g. NiO or Ni(OH)_2 based on the position of a predominant peak with high relative abundance is possible. The analysis of the $\text{Ni}2p_{3/2}$ peak of both fresh and used sample reveals the existence of four peaks beyond the satellite peak that is detected around 861.2 eV. The analysis of $\text{O}1s$ peak shows three different contributions (Figure 3.4 and Table 3.1). In addition, $\text{O}1s$ peak signal may contain a small contribution from the carbon tape used as a sample holder during XPS measurement, however it will not affect significant the relative intensity of the three components.

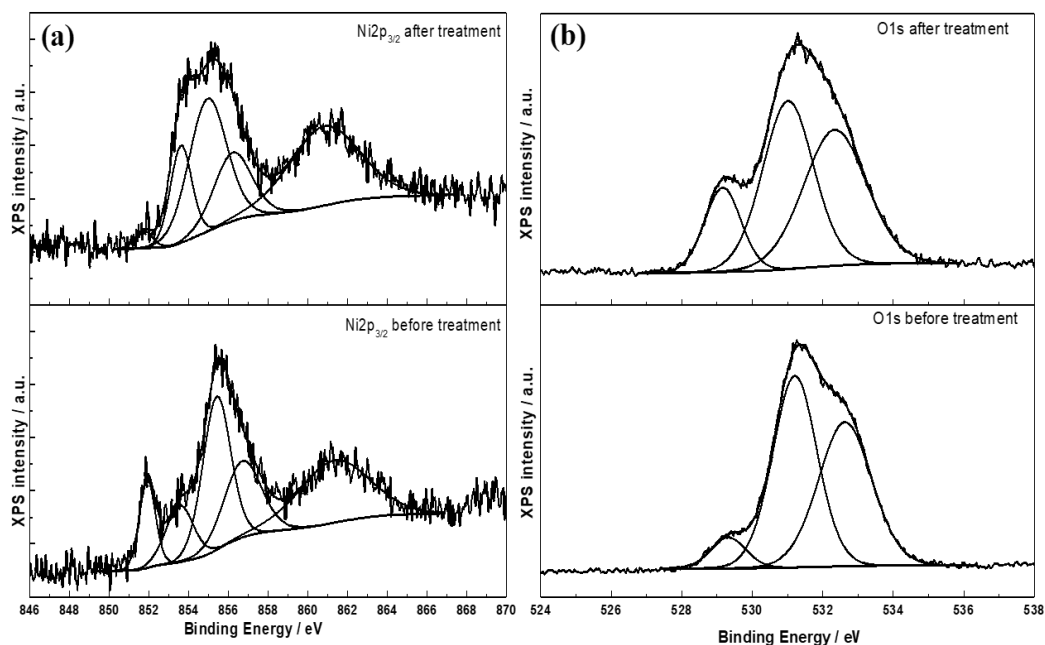


Figure 3.4. (a) $\text{Ni}2p_{3/2}$ and (b) $\text{O}1s$ XPS peak of the nickel electrode before (lower spectra) and after the electrochemical sinusoidal-wave treatment (upper spectra).

For the fresh sample, the peaks at 852, 853.6, 855.4 and 856.7 eV are attributed to metallic Ni, nickel oxide (NiO), nickel hydroxide and nickel atoms in nickel oxyhydroxide (NiOOH), respectively.^{45,56-59} The analysis of the $\text{O}1s$ peak shows the presence of peaks at 529.2 (O^{I}), 531 (O^{II}) and 532.6 eV (O^{III}). The one at lower BEs is characteristic of oxygen atoms in NiO , the O^{II} is attributed to oxygen atoms in hydroxyl groups due to the Ni(OH)_2 and NiOOH but also due to possible C-O contamination. The

O^{III} peak is characteristic of adsorbed water but also is related to atoms in C=O or O=C-O.^{56,57,59}

Table 3.1. XPS data and the chemical states of Ni in the untreated and treated Ni electrode.

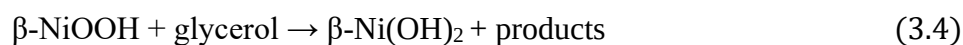
Samples	Ni2p _{3/2}			O1s		
	BE (eV)	FWHM (eV)	% relative intensity	BE (eV)	FWHM (eV)	% relative intensity
Ni before treatment	852	0.9	14	529.3	1.2	6
	853.6	1.6	16	531.2	1.5	49
	855.4	1.7	42	532.6	1.8	44
	856.7	2.2	28	-	-	-
Ni after treatment	851.9	0.9	3	529.2	1.2	16
	853.6	1.4	21	531	1.6	35
	855.1	2.1	50	532.6	2	50
	856.2	2.2	26	-	-	-

After the sinusoidal-wave treatment, the most significant change is the decrease of the signal of the component related to metallic Ni that now represents only 3% of the peak intensity. A small increase of the relative intensity of the component attributed to NiO was accompanied by increase of the corresponding O^I peak intensity thus confirming our assignment. XPS results show that after the treatment the surface has higher amount of Ni oxide and hydroxides that in combination with increased surface area could explain to the observed higher current densities in KOH electrolyte.

3.3.3 Effect of the electrochemical treatment on GEOR

Figures 3.5a and b show the cyclic voltammograms of the untreated and treated Ni electrode in 1M KOH (thin line) and 0.1M C₃H₈O₃ + 1M KOH (bold line) at 50 mV s⁻¹. The current growth due to glycerol electrooxidation starts at 0.48 and 0.44 V for untreated and treated Ni, respectively, these potentials also correspond to the beginning of β-NiOOH formation (Figure 3.1b and Figure A2 in SI). These overpotentials are somewhat higher if compared to the one reported for Ni nanoparticles supported on carbon. For Ni/C the GEOR starts at 1.2 V vs. RHE^{28,29}, while for the treated and untreated Ni the corresponding values vs. RHE are 1.33 V and 1.37 V respectively. The Ni electrode after the treatment shows up to 10 times higher current density for GEOR at 0.52 V and up to 4 times higher at 0.6 V than untreated Ni surface. During the negative potential scan the cathodic peak due to reduction of NiOOH to Ni(OH)₂ disappears completely. This is an indication of nickel oxyhydroxide consumption during the GEOR

with formation of $\text{Ni}(\text{OH})_2$, which is known as indirect electron transfer mechanism proposed by *Fleischmann et al.*³⁶ for alcohols oxidation on Ni electrode in alkaline medium. Furthermore, previous studies showed glycerol oxidation on the Ni electrode through the reaction with $\beta\text{-NiOOH}$ to form $\beta\text{-Ni}(\text{OH})_2$.^{4,26,28,29}



where the electrochemical step of NiOOH formation is followed by the chemical step of glycerol oxidation and NiOOH reduction to $\text{Ni}(\text{OH})_2$. Consequently, the oxidation of glycerol decreases or completely removes $\beta\text{-NiOOH}$ from the electrode surface. This explain the disappearance of the cathodic peak corresponding to $\beta\text{-NiOOH}$ to $\beta\text{-Ni}(\text{OH})_2$ reduction.

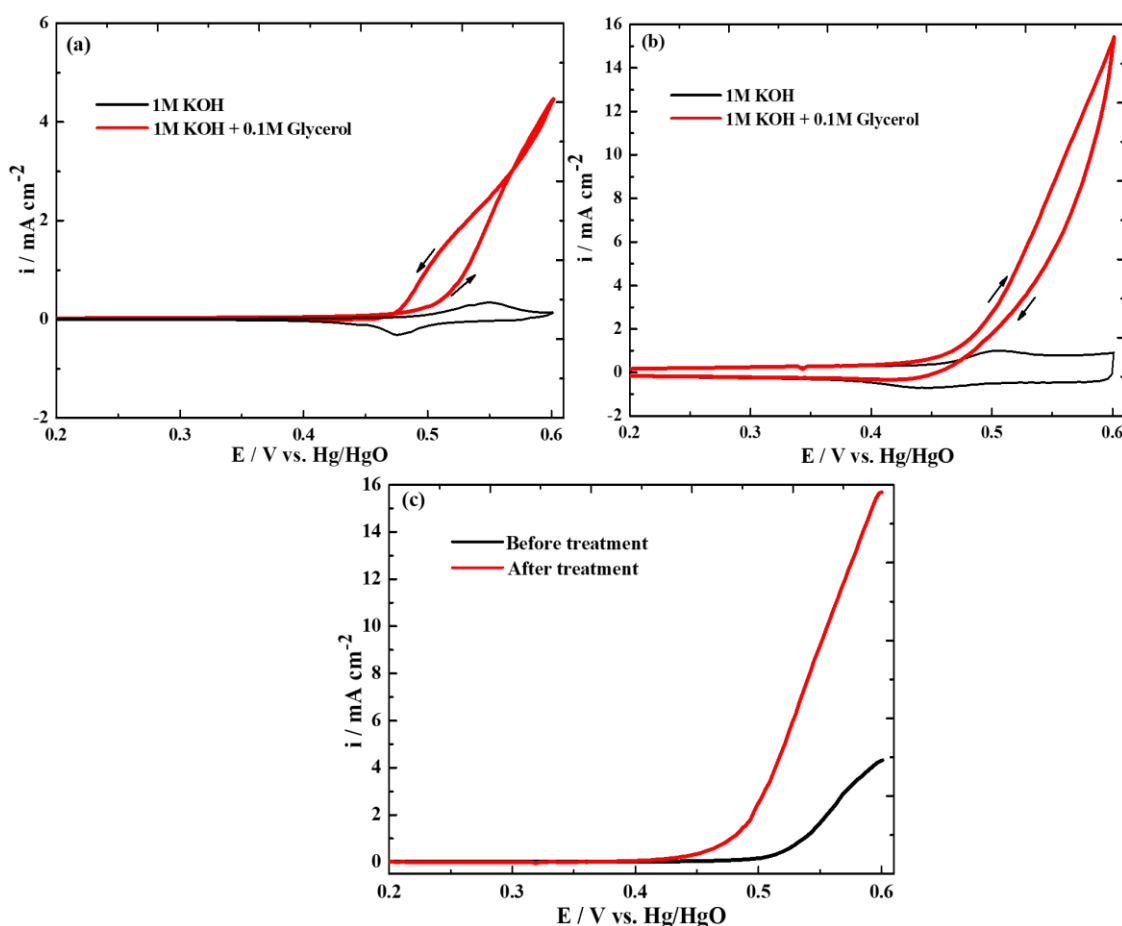


Figure 3.5. Cyclic voltammograms of glycerol electrooxidation on Ni electrode in 1M KOH (thin line) and in 1M KOH + 0.1M glycerol (bold line): (a) untreated Ni (b) after treatment Ni (c) Linear sweep voltammetry (LSV) for Ni before and after treatment in 1M KOH + 0.1M glycerol, 50 mVs⁻¹.

Other studies^{60,61} have suggested a direct electron transfer mechanism for GEOR, where alcohol molecules penetrate the Ni hydroxide surface and get oxidized by the OH^- ions trapped on the surface. In this case, the cathodic reduction peak will be present because NiOOH is not consumed in the reaction. Our results are in agreement with the indirect electron transfer mechanism, implying that nickel oxyhydroxide species, participate in glycerol oxidation according to reaction (3.4) and the absence of the reduction peak for $\text{Ni}(\text{OH})_2$ confirm this. Moreover, Figure A3 in SI show the effect of glycerol concentration. At low glycerol concentrations of 0.01M, the small reduction peak suggests that glycerol concentration is not enough to completely reduce the surface NiOOH . Therefore, for this low concentration, in addition to chemical process (3.4) an electrochemical reduction of NiOOH takes place. This is not the case for higher concentrations $\geq 0.05\text{M}$ for which the reduction peak is absent from CVs.

The hysteresis clearly seen on the CV of glycerol oxidation on Ni electrode before treatment (Figure 3.5 a, bold line) is due to the low amount of NiOOH phase present on the surface as its formation require more positive anodic potentials compare to the treated Ni. By comparing CVs with and without glycerol, we observe that reversal of current density occurs just after the peak maximum for NiOOH formation at 0.55V (Figure 3.5a, thin line). The higher current density on the reverse scan is due to the larger amount of nickel oxyhydroxide active phase. This is not a case for Ni after the treatment, as the surface contains more NiOOH , which is formed at lower potentials. Furthermore, there is no hysteresis on CVs of GEOR for higher concentrations of glycerol (0.2 and 0.5 M) in Figure A3 in SI. This indicates that higher amounts of NiOOH are required to oxidize glycerol and most of NiOOH is consumed during the forward scan in agreement with the reaction mechanism (3.4). The promotional effect of the sin-wave electrochemical treatment is further illustrated in Figure 3.5 c. LSV measurements clearly indicate that GEOR starts at much lower overpotentials on the treated surface $\sim 0.44\text{V}$ and result in higher current densities.

The chronoamperometry was used to study the steady-state performance of untreated and treated Ni electrode. CA measurements were carried out at 0.52V vs. Hg/HgO for 1h as shown in Figure 3.6. For both samples, after an initial drop in current density, a steady-state is achieved after 10 min. The anodic current densities obtained at

the treated Ni electrode (red line) are almost nine times higher than for the untreated electrode implying an improved electro-activity and its good retention.

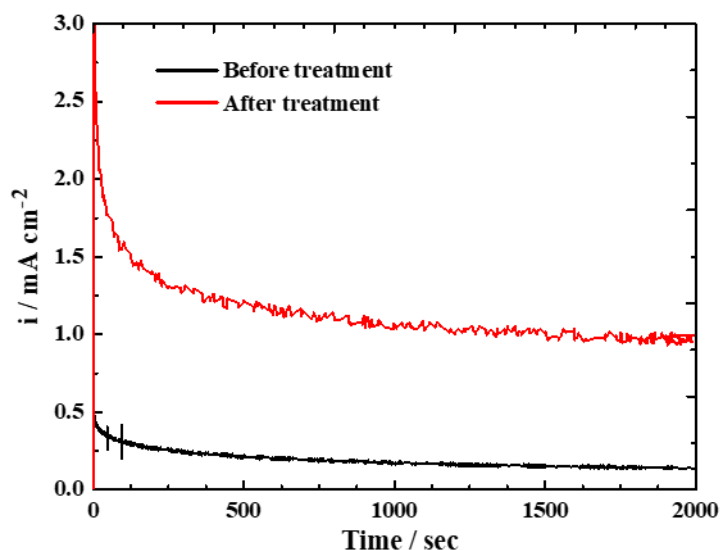


Figure 3.6. CA of a Ni electrode in 1M KOH + 0.1M glycerol before (black line) and after (red line) electrochemical sinusoidal-wave treatment at 0.52 V vs. Hg/HgO

3.3.4 In-situ PM-IRRAS of glycerol electro-oxidation on Ni before and after the treatment

In-situ PM-IRRAS was coupled with chronoamperometry to identify glycerol electro-oxidation products at various potentials on untreated and treated Ni surfaces. Unlike the regular IRRAS technique, PM-IRRAS with a single detector allows to differentiate between the oxidation species on the Ni electrode surface and bulk species within the cavity between the Ni and CaF_2 prism.^{48,49} The PM-IRRAS double modulation scheme allows the surface species to be referred to as the difference of absorption intensities [$R_{\text{dif}} = (R_p - R_s)$] and the bulk species as the average of the absorption intensities [$R_{\text{avg}} = (R_p + R_s)/2$].⁴⁸ Prior to the measurements, it was essential to ensure that there is no water vapor and atmospheric CO_2 in the optic path, which would interfere with the spectra features and additionally decrease the infrared (IR) intensity. For this reason, the IRRAS chamber was purged with dry air and the electrolyte with N_2 gas. Figure A4 in SI shows the tracking level of CO_2 background surface and bulk species spectra of an untreated Ni foil in 1M KOH + 0.1 M glycerol at open circuit potential, collected at different time intervals. After 1.5 hours, the recorded spectra confirm that there is no substantial influence of the CO_2 from air, which could contribute to spectral features during electro-oxidation (Figure A4).

Sets of PM-IRRAS spectra in the range of 1050 to 3800 cm^{-1} wavenumbers for treated Ni electrode at 0.34 V are shown in Figure 3.7. The figure shows evolution of spectra with time for species in thin cavity/bulk electrolyte. Negative and positive bands shown in the spectra are associated with products consumption and formation during GEOR, respectively.

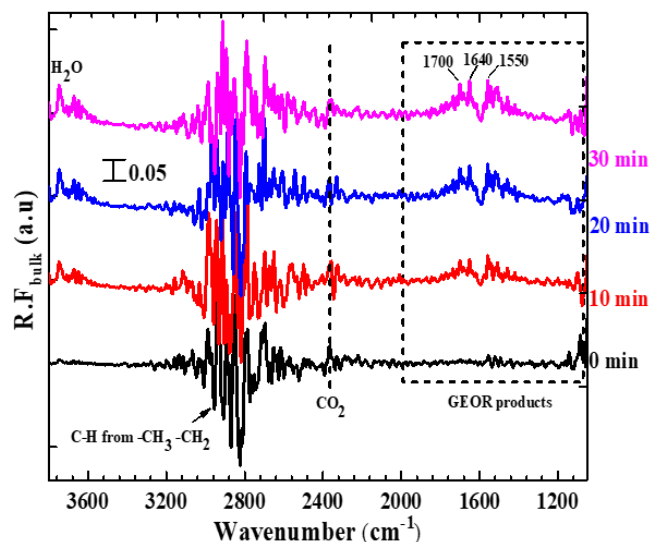


Figure 3.7. PM-IRRAS spectra of glycerol electrooxidation on Ni electrode after electrochemical treatment. Spectra represent species in the thin cavity/bulk solution and were recorded every 10 min while holding the electrode at 0.34V.

The region between 2700 – 3000 cm^{-1} shows several positive and negative features, which are due to the reorganization of the electrolyte molecules on the electrode surface and in the bulk solution. The negative direction band around 2908 cm^{-1} is attributed to C-H bond cleavage.⁴⁹ The peaks that appear with time around 3700 cm^{-1} are associated with water stretching vibrations. There is a clear growth of several peaks between 1100 and 1800 cm^{-1} as time increases from 0 to 30 min. The evolution of these peaks with time indicates that they correspond to the glycerol oxidation reaction products. More specifically, the peaks at 1640 and 1700 cm^{-1} correspond to glyceraldehyde and carbonyl species, respectively¹⁴ and the region with peaks around 1500 cm^{-1} may include the contribution of different carboxylates, e.g., tartronate, mesoxalate, oxalate ions and also could be influenced by H₂O bending vibration at 1580 cm^{-1} .⁴²⁻⁴⁴ These peaks are more clearly seen in Figure 3.8, which shows spectra obtained after holding electrode for 30 min at 0.34, 0.48, 0.5, 0.52 and 0.54V. Figure A5 depicts corresponding CAs obtained at each potential between 0.34V and 0.54 V. Figures 3.8 (a,c) and (b,d) show the bulk and

surface species at various applied potentials, respectively. The intensity of the bands between 1110 and 1800 cm^{-1} increases with applied potential indicating product accumulation. The IR spectra for the surface species are quite noisy due to the dynamic activities that take place on the electrode surface; therefore, they are difficult to evaluate with certitude. It is however seen that species produced at $\sim 1580 \text{ cm}^{-1}$ remain adsorbed on the surface. Carbon dioxide production (asymmetric stretching peak at 2353 cm^{-1}) could be distinguished on the spectra corresponding to the thin cavity/bulk solution. The CO_2 peak can be seen at 0.50V on Figure 3.8b and at 0.34V on Figure 3.8d in the bulk and on the surface of Ni.⁴⁹ Maximum CO_2 is produced at 0.48V but then its amount remains constant or decreases with increasing the potential.

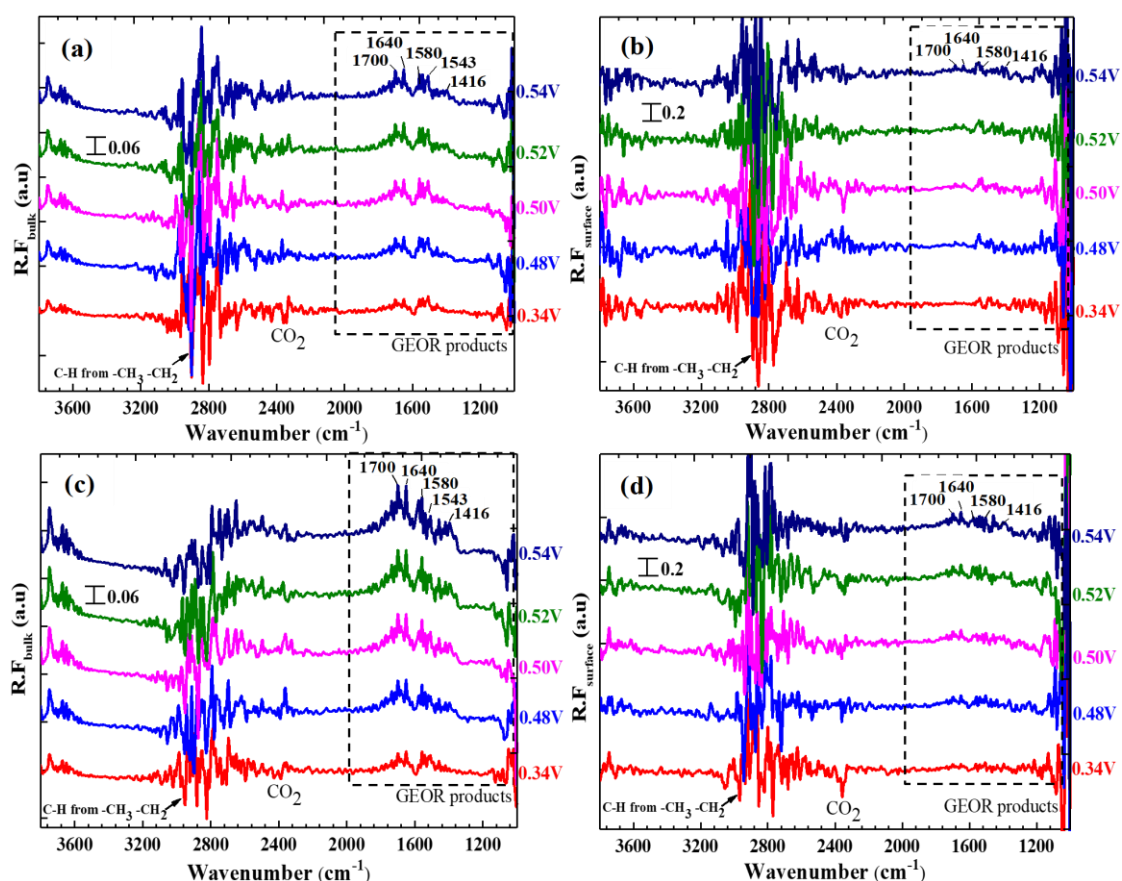


Figure 3.8. PM-IRRAS spectra of glycerol electrooxidation products on (a,b) untreated (c,d) treated Ni foil in 1M KOH+0.1 M glycerol at various potentials vs. Hg/HgO. The left-hand spectra illustrate oxidation species in the thin cavity/bulk solution and the right-hand spectra illustrate oxidation species on the surface.

At the same time an additional broad peak between 1340 and 1420 cm^{-1} starts to appear at 0.48 V, a (Figures. 3.8 a, c). This peak could correspond to carbonate formation with a corresponding peak in the range of 1390 -1420 cm^{-1} . Peak at around 1380 cm^{-1}

could also correspond to glycerate ion.⁶² For both treated and untreated Ni electrodes, we did not observe peak associated with linearly or bridged CO, contrary to previous studies on noble metal catalysts.^{4,28,29} Both untreated and treated Ni spectra have similar features, indicating no change in selectivity but only an increase of the reaction rate and product yield after sine-wave treatment as implied by the peak intensity increase. This is consistent with the fact that treated Ni exhibits a higher current density than the as-prepared Ni for GEOR.

In summary, the PM-IRRAS results show that glycerol is partially oxidized on Ni electrode and produces glyceraldehyde, carbonyl and some carboxylate ions in agreement with previous studies.^{14,31,32} Some CO₂ formation was observed that led to carbonate growth at higher potentials. Further HPLC analysis is required in order to confirm the product distribution. Furthermore, electrochemical treatment in ascorbic acid containing solution significantly increased the ECSA and glycerol electrooxidation current densities, however no significant difference in the product distribution was observed before and after the treatment.

3.4 Conclusion

Nickel electrode surface has been modified by applying sinusoidal-wave treatment in 0.1 M Na₂SO₄ and 30 mM ascorbic acid solution for 50 min. This treatment resulted in creating a highly active and stable GEOR catalyst. SEM images of the treated surface elucidated changes in morphology and surface roughening. The formation of deep grooves and pits on Ni surface was observed. XPS analysis confirmed modifications in the surface chemistry of Ni electrode and the most significant change is the decrease of metallic Ni and increase of Ni hydroxides. After the treatment the current density for GEOR grew substantially over 4 times in LSV and over 9 times in CA experiments. By combining chronoamperometry with *in-situ* PM-IRRAS measurements, we were able to simultaneously distinguish glycerol electro-oxidation products on/near the electrode surface and bulk species. The main products are glyceraldehyde, carbonyl and some carboxylate ions. Finally, both as-prepared and treated Ni surfaces have similar spectra features, indicating that the electrochemical treatment did not affect the selectivity. The proposed electrochemical treatment could be an efficient tool for activation of Ni based materials and nanoparticles for alcohols oxidation that proceed through NiOOH formation via the indirect charge transfer mechanism.

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Supplementary Information A: Chapter 3

Figure A1 demonstrates the sinusoidal-wave signal patterns in 0.1M Na₂SO₄ + 30 mM ascorbic acid electrolyte at -0.8 – 0.1V vs. MSE at 10 Hz for 50 minutes.

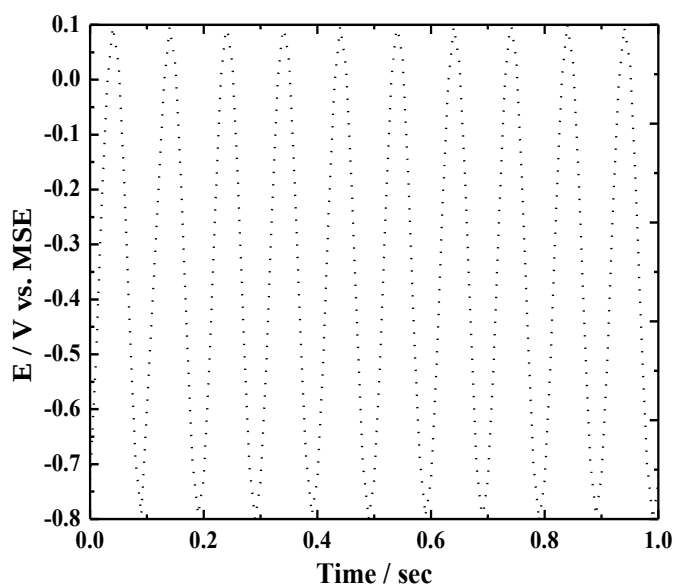


Figure A1. Form of Sine-wave signal applied on Ni electrode

Figure A2 shows the stability of the Ni electrode during cycling in 1M KOH.

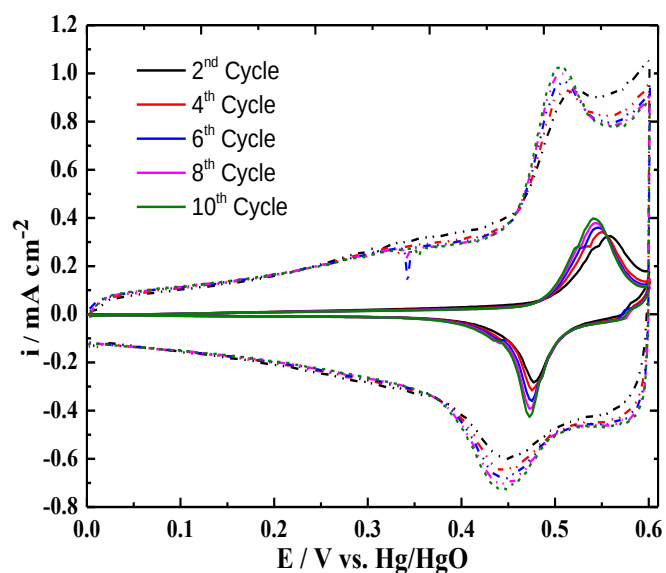


Figure A2. CVs of glycerol electro-oxidation on the Ni electrode in 1M KOH at 50 mVs⁻¹ scan rate; (solid line) before treatment and (dotted line) after treatment.

Figure A3 shows cyclic voltammetry of Ni electrode before treatment for various glycerol concentrations. The current density increases with increasing concentration.

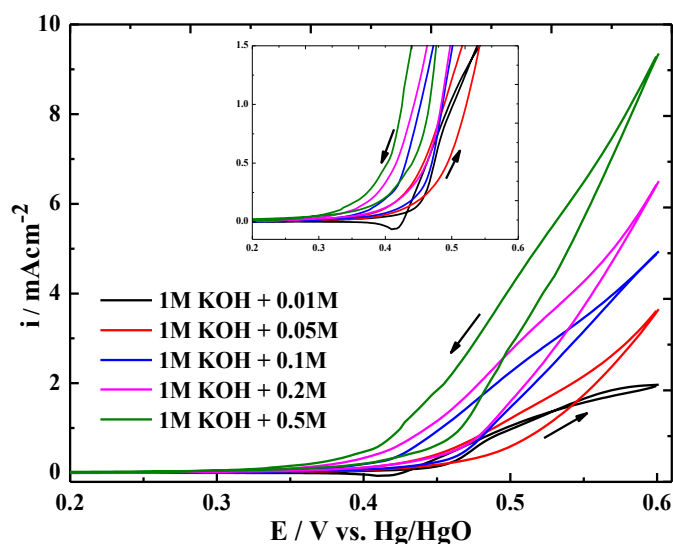


Figure A3. CVs of the untreated Ni electrode in 1M KOH containing various concentrations of glycerol.

Figure A4 illustrates the tracking level of CO₂ background at different time intervals before the actual measurements are initiated. The CO₂ level (negative peak at 2345 cm⁻¹) in surface and bulk species spectra is removed during purging dry air.

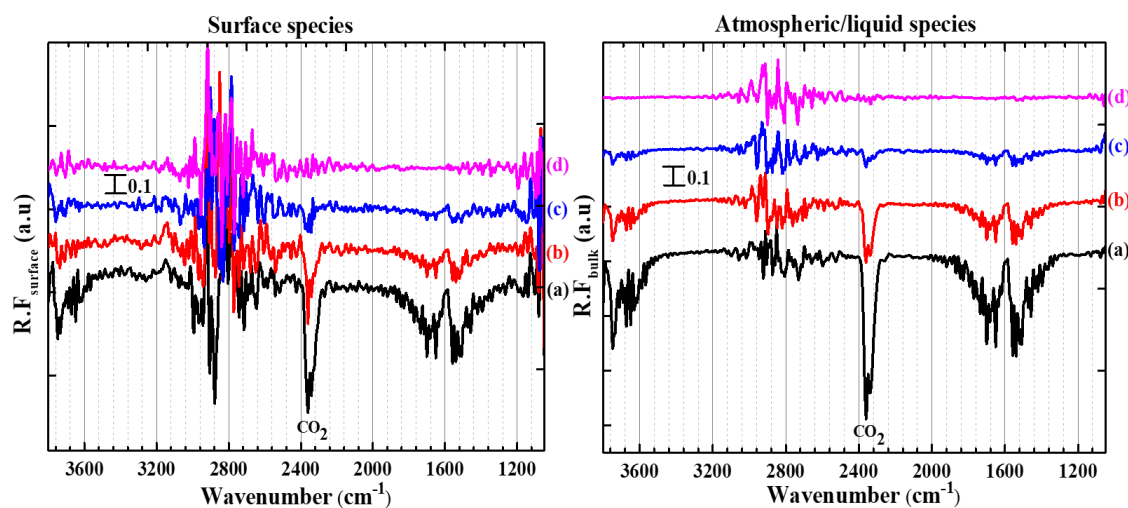


Figure A4. CO₂ tracking level background PM-IRRAS spectra of Ni foil in 1M KOH+0.1 M glycerol at open circuit potential (OCP); (a) 1.5 hrs., (b) 1 hr., (c) 30 min, and (d) 3min before measurements were initiated.

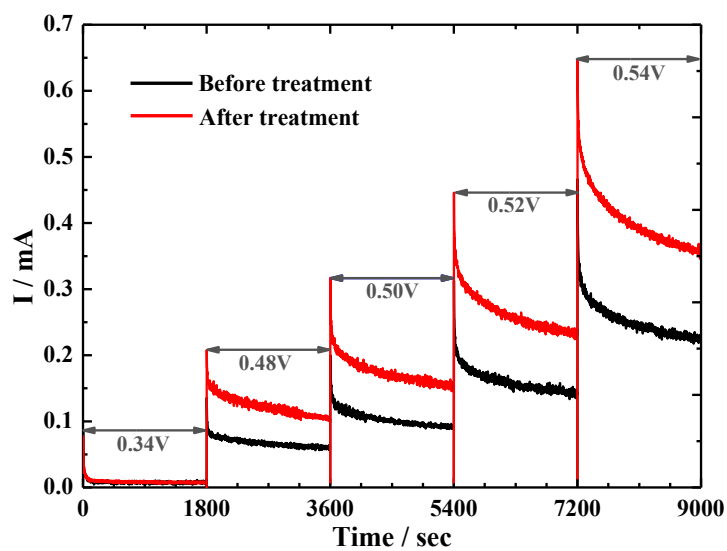


Figure A5. Chronoamperometry of the untreated (black line) and treated (red line) Ni electrodes in 1M KOH + 0.1M glycerol at different potentials, as indicated in the figure. PM-IRRAS spectra were recorded during each CA.

Chapter 4

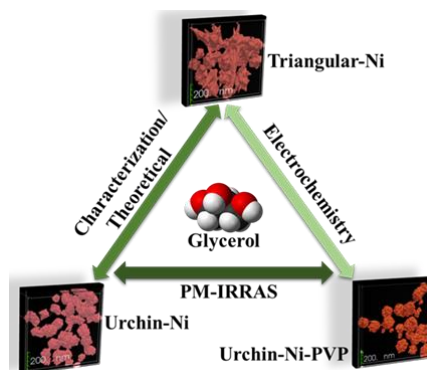
4 Morphology Alteration of Nickel Microstructures for Glycerol Electrooxidation

Based on the paper:

Houache M. S. E., Sandoval M. G., Safari R., Gaztañaga F., Escudero F., Hernández-Lagunad A., Sainz-Díazd C. I., Botton G. A., Jasen P. V., González E. A., Juan A., Baranova E. A., (In preparation for submission).

Abstract

Different shape-controlled microstructures of freestanding Ni were synthesised using modified polyol in the presence and absence of a capping agent (PVP). The direct visualization of crystal structure and morphology before and after electrochemical tests in KOH were characterized using a number of electron microscopy techniques. Detailed electrochemical characterizations illustrated that urchin-Ni-PVP has the highest catalytic activity among all investigated electrocatalysts for glycerol electrooxidation (GEOR). The improved activity was attributed to the surface area and the highly porous structure as identified by the tomography analysis. However, similar selectivity was observed on all three different shapes of Ni materials. Furthermore, density functional theory calculations of various low-index surface energies of both β -NiOOH and β -Ni(OH)₂ found that the (0 0 1) surface is the most thermodynamically stable. Based on the density of state study, we have detected metallic behaviour on the β -NiOOH (001) plane for O, Ni and mixed Ni-O atoms terminations. Among different terminations, the computed magnetization, electronic structure layer by layer and charge transfer on surface atoms indicted that Ni or Ni-O exposed β -NiOOH (001) surfaces as possible scenarios for glycerol adsorption on different charged sites on the surface.



4.1 Introduction

Glycerol has various industrial applications in pharmaceuticals solvents, cosmetics, food, plasticizers, beverage and food industries and direct glycerol fuel cells (DGFCs).

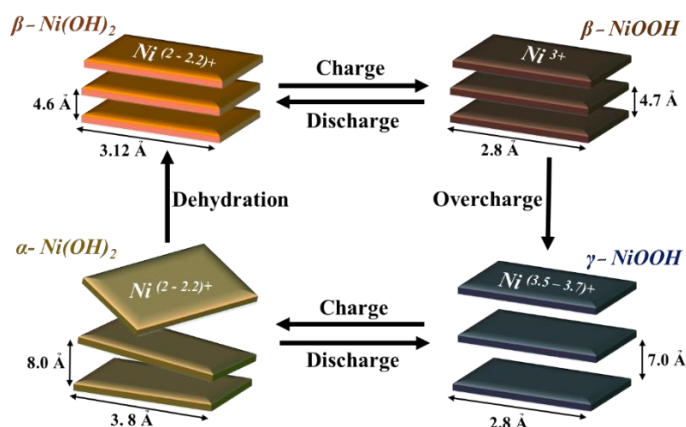
Biodiesel is generated through trans-esterification reaction of triglycerides present in vegetable oil and fats, with 10 wt% of low-grade glycerol as the by-product.¹⁻
⁴ Several issues are associated with the presence of glycerol in biodiesel at high concentrations, such as nozzles-clogging, poor engine performance and formation of carbon deposits.⁵ Furthermore, biodiesel combustion with glycerol leads to acrolein formation, unsaturated aldehyde, which is a toxic substance that associated with serious health problems related to digestive and respiratory systems.⁶ Thus, the glycerol concentration is viewed as vital parameter to determine the quality of biodiesel. In this context, fuel cells could afford a profitable answer to these issues. The application of glycerol electro-oxidation in DGFCs has gained renewed interests in the past 20 years⁷ due to its high charge density ($14 \text{ F}\cdot\text{mole}^{-1}$), low toxicity, high boiling point (290°C) and high theoretical energy density ($5 \text{ Wh}\cdot\text{kg}^{-1}$ vs. 8 and $6.1 \text{ Wh}\cdot\text{kg}^{-1}$ for ethanol and methanol, respectively).⁸ The electrochemical partial oxidation of glycerol can produce a numerous number of value-added products, such as oxalate, dihydroxyacetone, tartronate, glycolate and formate ions. All three-carbon electro-oxidation products are more valuable than low-grade glycerol e.g., tartronic acid costs ca. \$1564/g as a fine chemical against about \$0.2/g for glycerol.⁹

Ni-based catalysts are an attractive candidate due to high catalytic activity and long-term stability in alkaline media, anti-poisoning capability and availability at a low-priced. In addition, Ni-based materials have been applied over the last three decades in various electrochemical processes such as photocatalysis¹¹, alkaline batteries¹², supercapacitors¹³, sensors¹⁴, electrocatalysts for various organic oxidation and fuel cells.¹⁵⁻¹⁷ In all of these applications, the complexity of the nickel surface chemistry strongly impacts its catalytic activity, efficiency and performance.

Nickel behaviour is quite complex since it has several phases involved in the redox process as schematized by *Bode et al.* diagram (scheme 1) in 1969.^{18,19} All of the structures comprise of stack layers of edge-sharing NiO_6 octahedrons, differing only in their gap distance between the layers, the quantity of intercalated species (i.e. OH^- , SO_4^{2-} , H_2O and CO_3^{2-}) and the stacking sequence.²⁰⁻²³

Among them, $\alpha\text{-Ni(OH)}_2$ and $\gamma\text{-NiOOH}$ studies are relatively difficult as the intercalated species effected both phases by making them poorly crystallized and

turbostratic structure.²⁴ Furthermore, since α -Ni(OH)₂ and γ -NiOOH are related to β -Ni^{II} and β -Ni^{III}, it is essential to initially comprehend the features that characterize the fundamentals of β -phases. Thus, our work will be focused on the properties of β -hydroxides and oxyhydroxides.



Scheme 1. The Bode diagram demonstrating different variant of Ni hydroxides phases.

β -Ni(OH)₂ is highly crystalline compound, well characterized, isostructural with ABAB oxygen stacking sequence and H₂ in a tetrahedral environment (T1 structure) and space group of p-3m1 (brucite).^{25,26} The experimental lattice parameters are ($a = b = 3.13$ Å and $c = 4.66$ Å) which obtained at room temperature through Rietveld refinement of neutron diffraction. Thermogravimetric studies illustrate that α - and β - hydroxides dropped by $\sim 30\%$ and $\sim 1\%$ of their weight, respectively at 100 °C, indicating the vast amount of intercalated species extant in the α -Ni(OH)₂ structure.^{27,28} Further detailed information on β -Ni(OH)₂ can be attained from the infrared spectroscopy and extended X-ray absorption fine structure (EXAFS) techniques. The infrared method illustrated a sharp intense antisymmetric OH stretch at 3650 cm⁻¹, which reflects free hydroxyl group and a lack of H₂ bond.²⁹⁻³¹ Another experiment on EXAFS analysis exhibited coordination shells with 6 O₂ ions at 2.07 Å and 6.2 Ni ions at 3.13 Å.³² These data had similar results at different temperature of 77 K and 298 K. The EXAFS results could be elucidated in terms of the ionic radii of Ni²⁺ and O²⁻. The ionic radius of O²⁻ with six neighbours is 1.35-1.4 Å, whereas the ionic radius of Ni²⁺ is 0.69 ± 0.01 Å.³³ Taking the average of ionic radius of O²⁻ to be 1.38 Å and sum it with Ni²⁺ will give the Ni-O bond distance of 2.07 ± 0.01 Å. In addition, x-ray diffraction shows that β -Ni(OH)₂ (001) is the most intense and its strength and crystallinity enhances with pH increase.^{34,35} Hence the

electronic properties of β -hydroxide also have been stated to be *p*-type semiconductor with a ~ 4 eV band gap^{36,37}.

β -NiOOH structure is considered more complex than β -Ni(OH)₂. Based on *Olivia et al.* investigation, the oxygen stacking sequence in β -hydroxide (ABAB) alters upon oxidation to β -oxyhydroxides (ABCA), which is similar as γ -NiOOH in terms of oxygen stacking sequence.^{26,38} It has been reported there are two main possibility of β -NiOOH structure deviations from the brucite lattice structure which are either (i) overoxidation (forming γ -NiOOH) or (ii) uncompleted oxidation (β -Ni(OH)₂ residuals).³⁹ Whereas, other studies show no major structural alterations during redox oxidation between β -Ni^{II} and Ni^{III}.^{30,38,40} EXAFS analysis exhibited two possibilities of Ni-Ni distances in β -NiOOH, which are either 3.13 Å (assortment of Ni²⁺ and Ni⁴⁺)⁴¹ or 2.82 Å (Ni³⁺ in distorted octahedra).⁴² Tuning to electronic properties, β -NiOOH has been reported to be either *n*-type or *p*-type semiconductor.^{43,44} Thus, no final conclusion was drawn regarding the properties of β -oxyhydroxides since many questions are still unanswered.

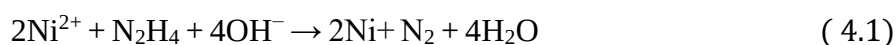
In this work, a combination of electron microscopy and electrochemistry is employed to observe the surface transformation of nickel to Ni hydroxide during cyclic voltammetry in KOH. Then, we report the GEOR on triangular Ni and urchin Ni in the presence and absence of a capping agent (PVP). *In-situ* (PM-IRRAS) analysis was carried out to identify the reaction products at various applied potentials. Then a theoretical DFT calculations were performed by first modeling the β -Ni(OH)₂ and β -NiOOH bulks (henceforth collectively termed NiOx). We analyze the low-index surfaces of these Ni-hydroxides compounds at an energetic level, considering the geometrical and electronic structure. The determination of the most likely exposed surfaces of NiOOH is crucial to identify the surface's key features that enable glycerol adsorption and reaction.

4.2 Experimental and computational methodology

4.2.1 Synthesis of different shape of Ni Nanoparticles

The synthesis was based on previous publications.^{45,46} Nickel (II) chloride hexahydrate was dissolved into 50 mM ethylene glycol in a refluxed three neck flask. The solution was under strong magnetic stirring and preserved at 100 °C on a hot plate. After 2 min, 1.7 mL of 0.1 M solution of hydrazine hydrate was added, and the color

altered to sky-blue indicating the formation of Ni-hydrazine complex. When injecting 1.5 mL of 0.1 M NaOH to the mixture, slowly the color of the reaction turned to black demonstrating the formation of nickel nanoparticles (Ni NPs) based on the following reaction 1:



The solution was kept under stirring at 100 °C for 30 min to ensure reaction completion, and then cooled down to room temperature. A permanent magnet was used to recover Ni NPs from the solution; NPs were then rinsed with ethanol three times. Finally, Triangular Ni NPs were separated by centrifugation at 6000 rpm for 10 min and stored in ethanol. Similar procedure was followed for Urchin NPs in the absence and the presence of capping agent polyvinylpyrrolidone (PVP-0.5g), where the concentration of NaOH was increased to 0.5 M NaOH.

4.2.2 Physiochemical characterization

Powder XRD patterns were collected with Rigaku Ultima IV multi-purpose diffractometer with Cu K α radiation ($\lambda = 1.5418\text{\AA}$) at 40 kV and 44 mA in the 2θ range of 20–80°. High-Resolution Scanning Electron Microscope (HRSEM) is FEI Magellan 400 operates at 1 to 30 KV. Transmission Electron Microscope is Philips CM12 TEM operates at 120 KV, as well as selected area electron diffractions (SAED) that have been done. Selected area aperture is 10 μm which selects an area that electron beam goes through particles and structures. This causes electron diffraction due to reflection of beam from specific planes from different compounds. For High-Resolution TEM and Tomography, FEI Titan 80-300 LB microscope in 200 KV which is suited for energy-filtered imaging, was used. In addition, all HRTEM data have been analyzed using GMS Digital Micrograph software for RGB contrast mapping and Fast Fourier Transform (FFT) for indexing. Furthermore, Tomography results have been processed using ImageJ and Inspect 3D software for image processing and TomViz software for 3D Visualisation. For electrochemical experiments, we have used Gamry Reference 600+ Potentiostat. Platinum electrode and Ag/AgCl were used as Counter and Reference electrodes, respectively. In order to operate electrochemical reactions, Ni nanoparticles have been settled on Stainless Steel Sheet using drop-cast method for working electrode of 0.1-0.6 V vs. Ag/AgCl with a scan rate of 20 mV/s in 1 M KOH.

4.2.3 Electrochemical spectrochemical characterization

The details of electrochemical and spectrochemical characterization techniques have been reported in our previous work.^{9,46,47} In summary the following methods were used:

- All GEOR electrochemical measurements were performed in a Teflon three-electrode electrochemical cell using (BioLogic Science Instruments SAS, Claix, France) at room temperature. All potentials were measured with respect to (Hg/HgO).
- In-situ PM-IRRAS measurements were equipped with PMA-50 XL chamber and a special designed spectro-electrochemical cell. Before initiating the experiment, our system was purged with dry air and N₂ for 1.5 hours to remove all atmospheric H₂O and CO₂ interferences.

4.2.4 Computational methods

For the bulk description, the systems β -Ni(OH)₂ and β -NiOOH were modeled as P $\bar{3}$ m1 spatial group (brucite structure). The staggered hydrogen arrangement was considered as the most likely β -NiOOH structure formed upon the complete oxidation of β -Ni(OH)₂, as Tkalych *et al.* suggested.²⁴ For the surface characterization a large system in the working crystallographic cell was needed to obtain a bulk with the right crystallographic and electronic properties of the Ni oxyhydroxide from the inner layers (Figure B1 in supporting information). Moreover, in order to study the surface stability in the both systems we simulate several low index surface finding that (001) surface is the most stable for both β -NiOOH and β -Ni(OH)₂ as illustrated in Table B1 in SI. This surface presents different terminations as illustrated in Figure B2 and B3. Depending on the way the OH groups surface is cut, the different pseudo-polymorphs can be studied. Thereby, all simulations were performed through the Vienna Ab-initio Simulation Package (VASP) with DFT, using the following electronic features between many others: 1) periodic system; 2) due to the particular electronic character of the Ni in Ni²⁺ and Ni³⁺, the spin-polarized and DFT+U approach of Dudarev *et al.*⁴⁸ was employed in order to ameliorate the previously known failures of over-delocalization of electrons; 3) a U–J correction of 5.5 eV was added via the Dudarev functional in combination with the Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional; and 4) the projector

augmented wave scheme was used to describe the inner cores (a more detailed description is provided in SI Figure B1-B5).

4.3 Results and discussion

4.3.1 Physiochemical characterization of different shape of Ni microstructures

Different shapes of Ni particles were synthesized using modified polyol method as shown in Figure 4.1a. Initially, the Ni^{2+} precursor $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ was reduced by hydrate hydrazine in the presence and the absence of PVP at pH 12, generating small Ni nanocrystals. Then, these particles were joined with other under the influence of the magnetic dipole interactions to obtain enlarged size Ni particles with selective spear-like branches, leading to lower magnetic anisotropic energy and surface energy. Finally, triangular and urchin electrocatalysts were fabricated.

The metallographic characteristics of the as-synthesized Ni samples were characterized by HRSEM (Figure 4.1b-d). The figures demonstrated that the Ni particles range in size between 100 and 130 nm. The crystallite particle size estimated by Debye–Scherrer’s formula using FWHM Ni (111) peak parameter and the shape factor 0.9 from X-ray diffraction (XRD) is 20.1, 13.7 and 18.9 nm for triangular-Ni, urchin-Ni with and without PVP, respectively (Figure B6 in SI). This testifies that Ni particles were composed of several nanometer-sized crystallites.

Moreover, the surface transformation of these three morphologies to Ni hydroxides were further investigated by HRSEM after applying 20 cycles of cyclic voltammetry (CV) in the range of 0.1-0.6 V vs. Ag/AgCl with a scan rate of 20 mV/s in 1 M KOH (Figure 4.1e-h). Before the conversion (Figure 4.1b), Ni microstructure resembles a very sharp triangular-shaped needle-like structure. After applying CV, the surface becomes much smoother with a layer covering the particles, which causes an apparent expansion (Figure 4.1f). While for urchin-Ni without surfactant, the particles appear as spheres with small extrusions, resembling a sea urchin with short spikes as illustrated in Figure 4.1g. After the cyclic reaction, no traces of extrusions were visible and the surface was rather rough. Furthermore, Figure 4.1d revealed that the addition of PVP (capping agent) on urchin-Ni allows for sharper spikes with no significant effect on

nanoparticle size. However, after conversion, these spikes are no longer sharp (Figure 4.1h).

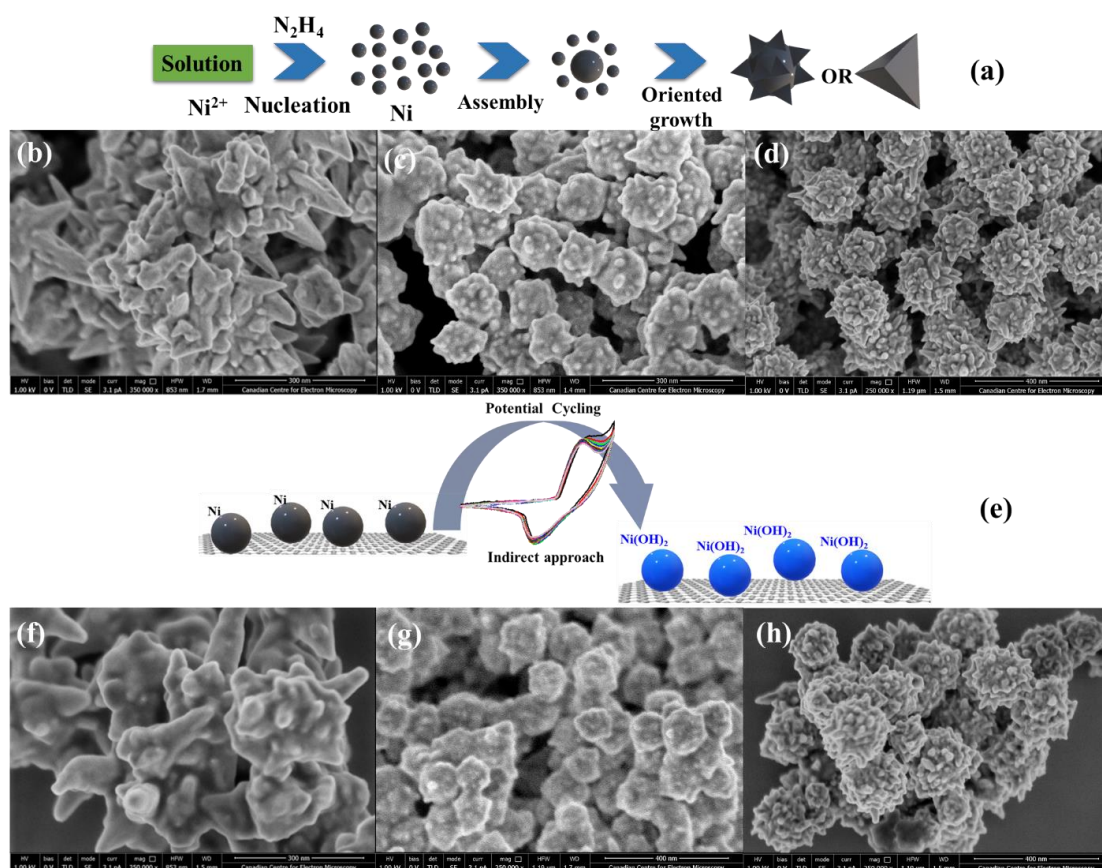


Figure 4.1. (a) Illustration of the fabrication process of different Ni morphologies. SEM micrographs before (top) and after (bottom) conversion of (b,f) triangular-Ni, (c,g) urchin-Ni and (d,h) urchin-Ni with PVP to β -Ni(OH)₂. (e) Schematic for one-step processing of Ni hydroxide in indirect approach.

Randomly chosen microparticles for TEM selected area electron diffraction point analyses show that each material has high polycrystallinity and a well-defined ring structure pattern (Figure 4.2). Specifically, the pattern of as-synthesized materials (Figure 4.2 a,e and i,) shows evidence of a typical face-centered cubic (*fcc*) structure of Ni (111), (200) and (220) (red rings), which in correlation with our XRD data (Figure B6 in SI). After conversion, an additional ring of Ni hydroxide crystalline planes appears (green ring) in Figure 4.2 c, g and k. While only, one plane seems to be strongly visible β -Ni(OH)₂(102), other planes may also exist for nickel hydroxide, however they are not detectable due to low nickel hydroxide content, as well as their close proximity to Ni diffraction rings.

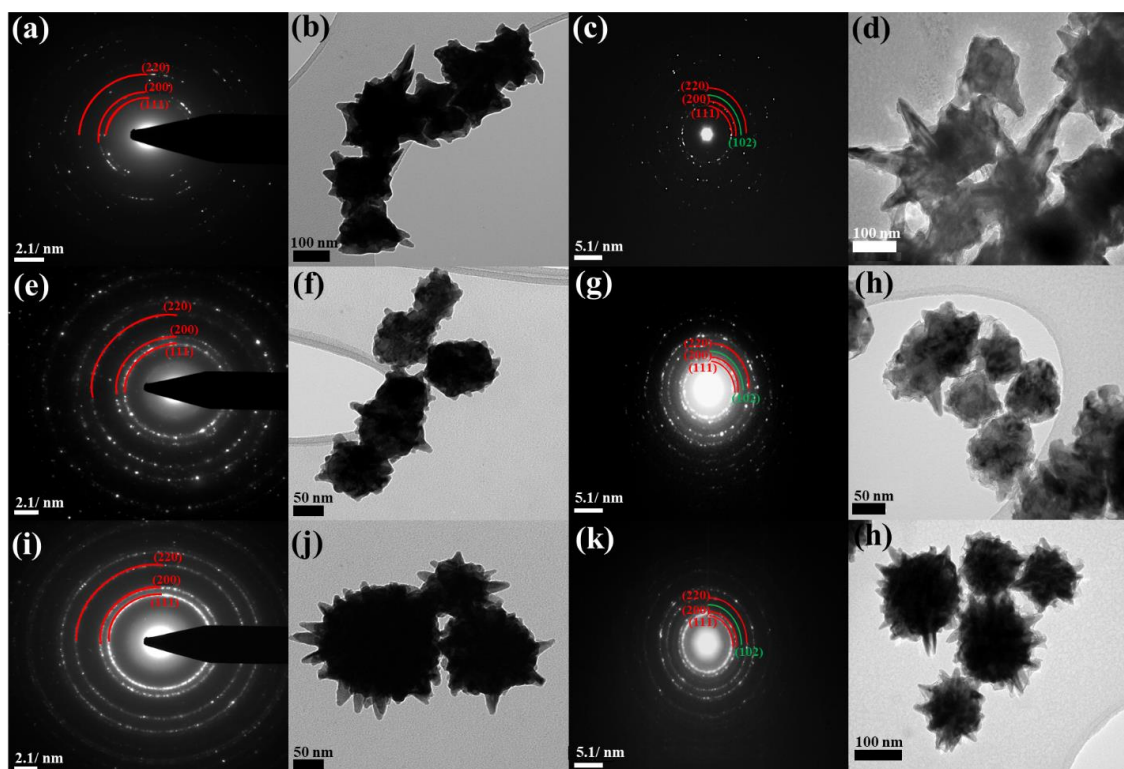


Figure 4.2. SAED patterns before (left-side) and after (right-side) conversion of (a,c) triangular-Ni, (e,g) urchin-Ni and (i,k) urchin-Ni with PVP to β -Ni(OH)₂. Low magnification TEM images of (b,d) triangular-Ni, (f,h) urchin-Ni and (j,h) urchin-Ni with PVP.

To visualize the co-existence of the two crystalline structures in real space, the microstructures of electrocatalyst were further investigated by RGB contrast and high-resolution TEM (HRTEM) images in Figure 4.3. For mapping of the spatial distribution of all phases, the RGB contrast helps to observe the locations of the β -Ni(OH)₂. As seen in Figure 4.3a, the whole structure of triangular Ni was identified with Ni planes (red) with no traces of Ni(OH)₂, which is in a good agreement with our XRD and SAED data. However, after CV, significant amounts of nickel hydroxide (green regions) were present (Figure 4.3b) and this confirms the conversion. Similar trend is shown in the RGB images (Figure B7 and B8 in SI) for Urchin-Ni in the absence and the presence of PVP.

It is worth noting that Ni planes are detected towards the core of the particles, while Ni hydroxide usually begins to grow on the edges, which is due to its contact with the electrolyte, making the surfaces easily converted. Figure 4.3c illustrates the HRTEM analyses of the exact location of triangular Ni after conversion (Figure 4.3b) and Fast Fourier transform (FFT) analysis used to separate the noise signal (usually high frequency) from the useful component. In order to decrease the error from the indexing

of the interplanar spacing in high-resolution real space images the crystalline planes of fcc Ni (220) and hexagonal β -Ni(OH)₂ (002) and (110) have been identified.

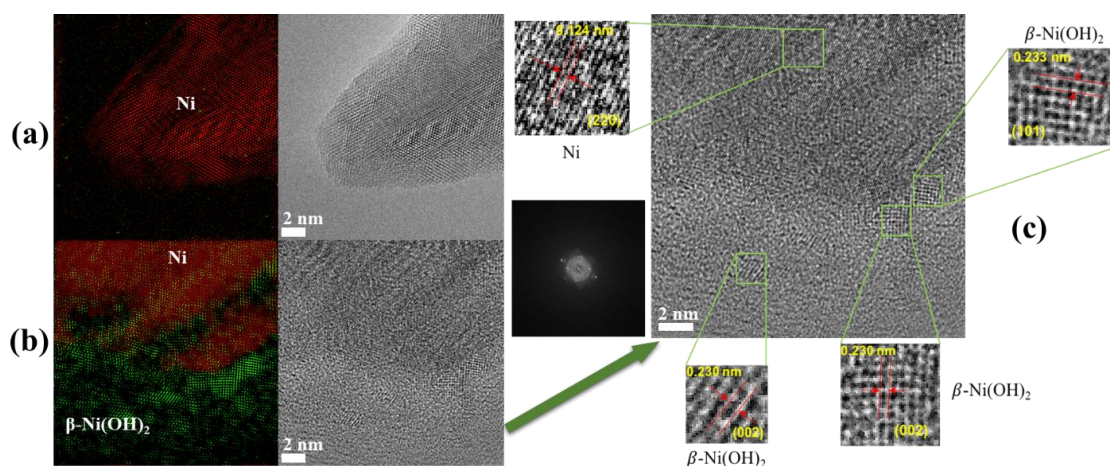


Figure 4.3. (a) HRTEM and RGB contrast micrographs of triangular-Ni (a) before and (b) after conversion. (c) Indexed HRTEM of triangular-Ni after conversion and FFT.

4.3.2 Electrochemical and spectrochemical of GEOR

Representative profiles of different shapes of Ni particles are illustrated in the cathodic region (Figure 4.4a) and anodic region (Figure 4.4b) in N₂-purged 1 M KOH electrolyte. The formation of various Ni phases is well established in our pervious work.^{9,46,47} The reversible oxidation of Ni to α -Ni(OH)₂ which takes place between -0.8 and -0.4 V vs. Hg/HgO was used to determine the electrochemical surface area (ECSA).^{9,49} Moreover, the evaluated ECSAs of the different shapes of Ni catalysts prepared with same loading are $1.36 \pm 3.2\%$, $1.61 \pm 7.2\%$ and $1.86 \pm 4.7\%$ cm² for triangular-Ni, urchin-Ni and urchin-Ni with PVP, respectively. This observation is in good correlation with the tomography analysis (Fig.B9 in SI) that examines and visualizes the internal structure of nanoparticles slice by slice. After reconstruction, the presence of internal porosity of different shapes of Ni follows the order: urchin-Ni with PVP > urchin-Ni > triangular-Ni. Based on the above analysis, the use of polymer ligands in the synthesis seems to increase the active surface area, which is due to its structure that consists of hydrophobic portion (i.e. alkane chain). This chain is adsorbed on the surface of Ni crystal nuclei, leading to higher active sites and uniform lower surface energy that leads to evenly forming catalyst.⁵⁰

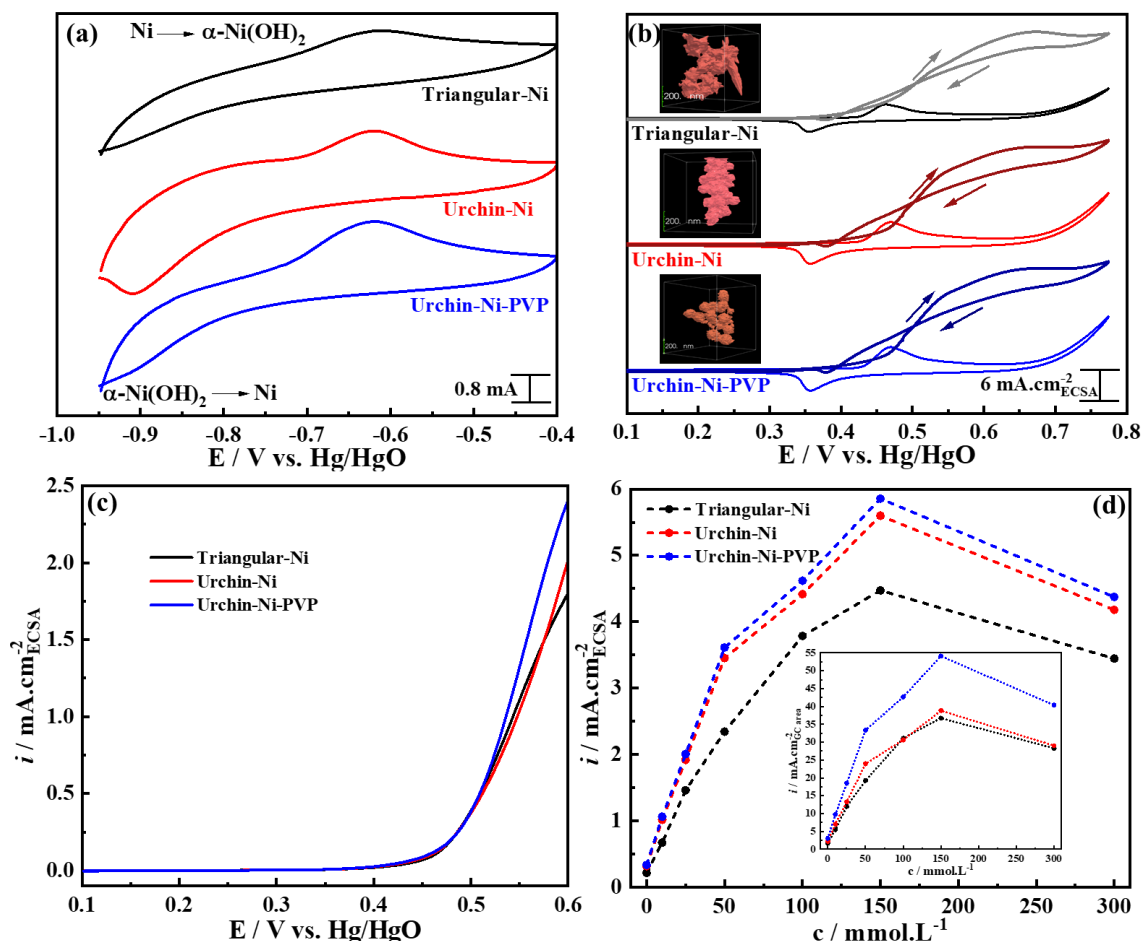


Figure 4.4. Cyclic voltammograms of Ni-triangular catalyst in 1M KOH (black line) and 1 M KOH + 0.1M glycerol (red line) in the cathodic (a) and anodic (b) region. (c) LSVs of GEOR at 1 mV.sec⁻¹ Comparison of the glycerol electro-oxidation on various glycerol concentration (d) in 1 M + x mM glycerol. Scan rate 50 mV.sec⁻¹ (10th Cycle).

Figure 4.4b shows the cyclic voltammetry of Ni in O₂-free solution of 1 M KOH (thin line) and 0.1 M glycerol + 1 M KOH (bold line) at 50 mV sec⁻¹. The CVs in the absence of glycerol exhibit a typical profile of Ni-based electrodes in alkaline solution⁵¹⁻⁵⁴: (i) the redox pair of Ni²⁺/Ni³⁺ in the region between ~0.3 and 0.6 V; and (ii) the oxygen evolution reaction (OER) in the region above 0.6 V vs. Hg/HgO. In the presence of 0.1 M of glycerol, the voltammetric profiles changes, leading to higher current density, whose values at 0.62 V are 3.8 mA.cm⁻²_{ECSA} (or 31.1 mA.cm⁻²_{GC area}), 4.4 mA.cm⁻²_{ECSA} (or 30.6 mA.cm⁻²_{GC area}) and 4.7 mA.cm⁻²_{ECSA} (or 42.6 mA.cm⁻²_{GC area}) for triangular-Ni, urchin-Ni and urchin-Ni with PVP, respectively. In all of these catalysts, the onset potential initiates at 0.41 V vs. Hg/HgO, indicating a similar GEOR kinetics. This potential also corresponds to the beginning of β-NiOOH formation, which is an electrochemical active species for glycerol oxidation and other organic molecules known

as the “indirect electron transfer mechanism”.⁵⁵ Figure 4.4c shows the linear sweep voltammetry (LSV) measurements at $1 \text{ mV}\cdot\text{sec}^{-1}$ indicating a similar trend in case of GEOR catalytic activity and the overpotential compared to Figure 4.4b.

Figure 4.4d illustrates the effect of different glycerol concentrations ranging from 10 to 300 mM as a function of current density of GEOR at 0.62 V. At this applied potential, the catalytic activity increases with concentration up to 150 mM of glycerol, followed by a sudden drop at 300 mM. Similar behaviour was detected for all three catalysts and the catalytic activity decreased in the following order: urchin-Ni with PVP > urchin-Ni > triangular-Ni. At the same time, OER shifts towards more positive potentials when increasing the glycerol concentration as shown in Figure B10 in the SI. This phenomenon was mainly attributed to the strong interaction of alcohol with high valence nickel species than with OH^- species.⁴⁶ Simultaneously, the cathodic peak reduces gradually until it disappears completely at 100 mM (Fig. B10 in SI). This is an indication that there is a change in the GEOR mechanism. At lower concentrations ($< 100 \text{ mM}$), the direct electron transfer pathway takes place, where the alcohol molecule incorporates the film of Ni hydroxide and become oxidized by the trapped hydroxyl ions as pointed out by Taraszewska *et al.*⁵⁶ Whereas at higher concentration ($> 100 \text{ mM}$), the glycerol is chemically consumed, leading to cathodic peak disappearance known as indirect mechanism.

The in-situ PM-IRRAS measurements were conducted to determine the product distributions formed along with GEOR as a function of applied potential. Figure 4.5 depicts the spectra obtained during CA measurements at different applied potentials from 0.34 to 5.4 V for 30 min. As mentioned in our previous publications^{9,46,47}, the spectra illustrate the oxidation species formed on the surface (Figure 4.5b) and in the bulk region i.e. distance between the CaF_2 prism and GC electrode in Figure 4.5b. It must be noted the presence of a negative band positioned at $\sim 1017 \text{ cm}^{-1}$ is clearly assigned to C-O stretching of glycerol in KOH solution, thus indicting the consumption of this reactant during electrooxidation.⁸ At all applied potentials, the spectra have mainly four peaks occur instantaneously at $\sim 1358, 1390, 1430$ and 1585 cm^{-1} , corresponding to symmetric and asymmetric COO^- stretching of formate, carbonate and carboxylate species.⁵⁴ These four absorption bands appear on all three different shapes of Ni NPs with different intensities, indicating that the main reaction products did not change in this study.

Moreover, a negligible amount of CO_2 was observed due to OH^- consumption, thus changing the interfacial pH to acid.⁵¹ A similar remark was detected in other investigation using Ni-based electrocatalysts towards GEOR.^{9,46,47,51-54}

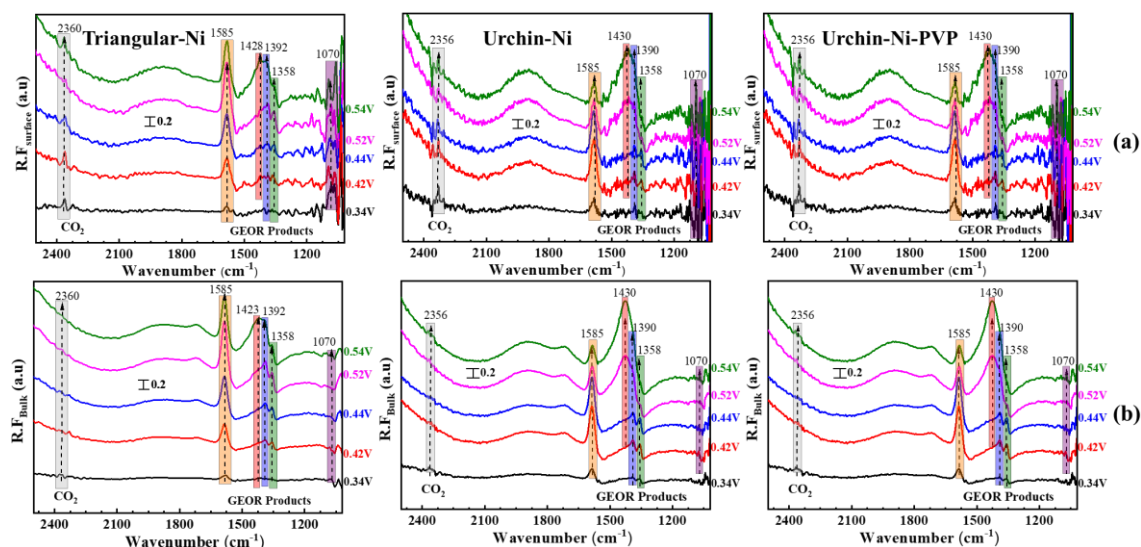


Figure 4.5. PM-IRRAS spectra during GEOR on different shapes of Ni NPs illustrate oxidation species (a) on the surface and (b) in the bulk/thin cavity solution in 1M KOH + 0.1 M glycerol at various potentials.

4.3.3 DFT result of $\beta\text{-Ni}(\text{OH})_2$ and $\beta\text{-NiOOH}$ different (001) surface termination

4.3.3.1 Geometric and energetic considerations

In order to determine which $\beta\text{-Ni}(\text{OH})_2$ and $\beta\text{-NiOOH}$ surfaces are most likely to be exposed, the energies were calculated for numerous low-index surfaces. The results are listed in Table B1, along with the equations used for the calculations (Equations B1-B5). All considered surfaces are stable, being the (001) surface the most stable in both cases. These results are in good agreement with previous work by *Tkalych et al.*²⁴ and experimental studies. So, our structural model was further validated in this regard.

The (001) surface has three possible terminations (facets) in both structures. The (001) plane can expose H atoms (pristine surface plane), O atoms (surface plane with superficial H atoms removed) or Ni atoms (surface with HO superficial atoms removed) denoted by (001)-H, (001)-O and (001)-Ni, respectively. Considering that in the reaction process a defective outmost layer is possible we also studied the O-Ni mixed termination

(surface with H superficial atoms removed, while only some of the O superficial atoms removed) denoted by (001)-O&Ni. The calculated surface energies are listed in Table 4.1.

Table 4.1. Surface energy (E_{surf2}), Fermi level (E_F) and work function (WF) for different terminations of the (001) cleavage plane for both β -Ni(OH)₂ and β -NiOOH systems.

	Cleavage plane completion	E_{surf2} (eV)	E_F (eV)	WF (eV)
β-Ni(OH)₂	(0 0 1) – H	0.16	-1.04	3.65
	(0 0 1) – O	0.16	-1.91	6.80
	(0 0 1) – Ni	0.16	-0.06	3.74
	(0 0 1) – O&Ni	0.14	-1.00	5.26
β-NiOOH	(0 0 1) – H	0.37	-1.41	4.88
	(0 0 1) – O	0.37	-1.97	7.11
	(0 0 1) – Ni	-0.17	-1.31	5.12
	(0 0 1) – O&Ni	0.35	-1.69	5.89

In the Ni hydroxide, the surface with mixed Ni and O atoms in the outmost layer is found to be the most stable, however the surface energies vary slightly from each other. For the Ni oxyhydroxide, the most stable termination is when all Ni is exposed in the outmost layer, with a noticeable reconstruction as shown in Figure B4g in SI.

4.3.3.2 Electronic structure and magnetic properties

From Figure B4 in the SI it is clear that the effect of different terminations in the outmost layer of the (001) surface is almost imperceptible in the DOS curves of the complete slab. For the sake of clarity, we also plotted the layer by layer DOS curves in Figure 4.6 and 4.7 for the (001) surface different terminations of β -Ni(OH)₂ and β -NiOOH, respectively. It can be noted in Figure 4.6 that the 2nd, 3rd and 4th layers that the main change in the DOS curves is a shift to lower energies for some of the terminations and that for the (001)-H surface the DOS curves are similar to that of the bulk as show in Figure 4.6a-c, h, i, k and l. Additionally, the most significant changes are in the first layer (Figure 4.6d, g and j). Regarding the local magnetic moment in the (001)-H surface the Ni atoms value of approximately $1.78\mu_B$ is consistent with a Ni⁺² oxidation state as is expected similar that on the bulk. When the superficial H are removed from the first layer, there is an important reduction on the magnetic moment, while the other layer has a similar value to that in the bulk. In the case of the (001)-Ni surface first layer the local magnetic moment slightly decrease these is a consequence the spin down contribution

have a small increase due to the DOS curves is shifted to lower energies (Figure 4.6g). In addition, it can be seen that the first layers of (001)-O, (001)-Ni and (001)-O&Ni surfaces show an increase of state across the Fermi level which could improve the conductivity of that systems.

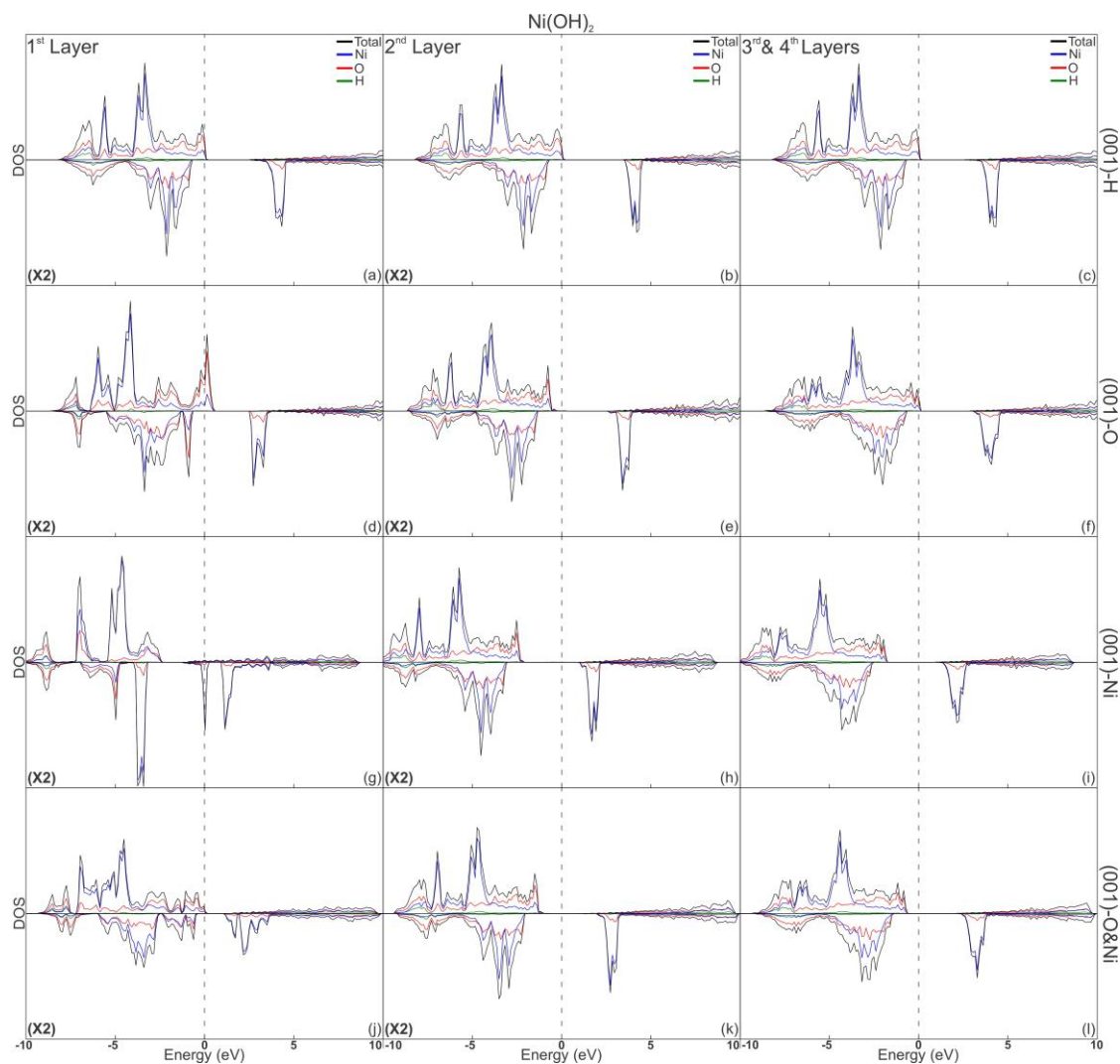


Figure 4.6. DOS Curves for the (001) surfaces terminations for β -Ni(OH)₂ phase. The Fermi level is located at 0 eV. For a better view the DOS for single layers are magnified.

In the case of the β -NiOOH phase the DOS curves are shown in Figure 4.7. It can be seen that only the first layer of each terminations presented changes, while the other layers are almost the same (Figure 4.7). For the first layer all system has states across the Fermi level, being the (001)-Ni and (001)-O&Ni surfaces those with more states around E_F this could indicate that in these systems there is an improvement in conductivity. Considering the magnetic behavior, the (001)-H first layer is similar to that in the bulk. For (001)-O an important reduction in the local magnetic moment appeared. This is a

consequence for the Ni atoms on the surface which have different oxidation states due to the removal of H. This surface some superficial Ni atoms, for $1.10\mu_B$ consistent with Ni^{+3} oxidation state and the other has $0.05\mu_B$ which has a Ni^{+4} oxidation state. These results are in good agreement to that reported by *Fildesky et al.*⁵⁷ In the case of (001)-Ni surface the first layer has an increase in the local magnetic moment of the superficial Ni with a value of $1.78\mu_B$ which is consistent with a Ni^{+2} oxidation state.

Regarding the center of the d-band energy in both systems the (001)-Ni and (001)-O&Ni surfaces are more reactive with an ε_d closer to the Fermi level, with the (001)-Ni surface for the Ni oxyhydroxide being the closest one.

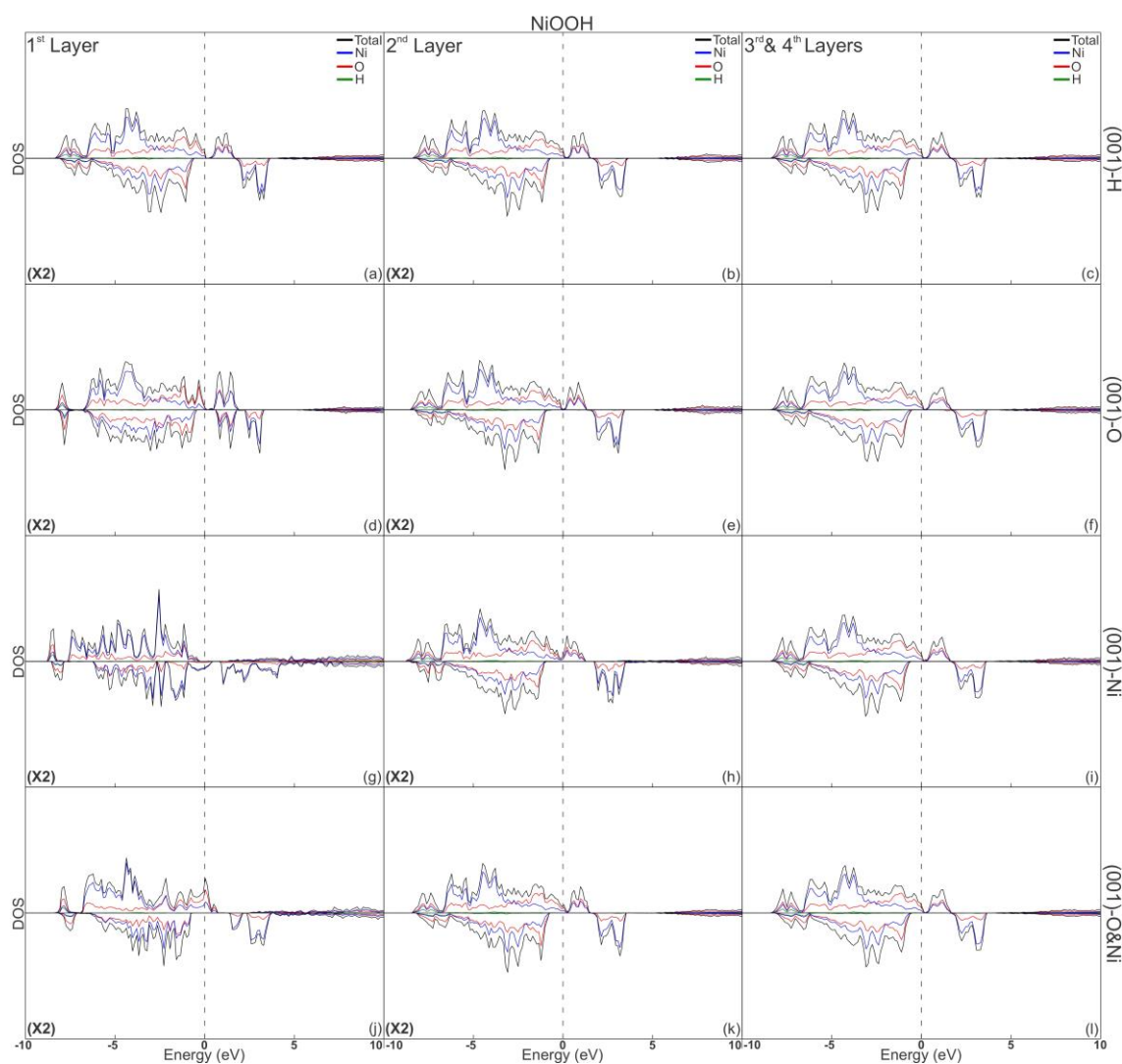


Figure 4.7. DOS Curves for the (001) surfaces terminations for β -NiOOH phase. The Fermi level is located at 0 eV. For a better view the DOS for single layers are magnified.

4.3.3.3 Charge transference

Figure 4.8 and 4.9 show the net charge transferred as layer-by-layer (into the smallest super-cell containing four Ni per layer) and onto the individual atoms in the cross section (upper and lower part of each one of the subfigures, respectively) in the last four layers of the (001) cleavage plane for both β -Ni(OH)₂ and β -NiOOH systems, respectively. In the bottom part of Figure 4.8 and 4.9, a darker blue color indicates more electron accumulation, while a darker red color indicates electron depletion (crossing through the white tone that indicates no electron transference). For each system, four different terminations of this cleavage plane are shown (from left to right side, named as the H-, O-, Ni- and O&Ni- exposed). From these figures it is clear that varying the cleavage plane composition, only the last layer is considerably affected in both systems. The charge is not equally distributed onto the atoms within the same layer, almost all of the charge transfer occurs between nickel and oxygen in all systems, where the oxygen atoms won electrons at the expense of hydrogen and nickel atoms losing electrons.

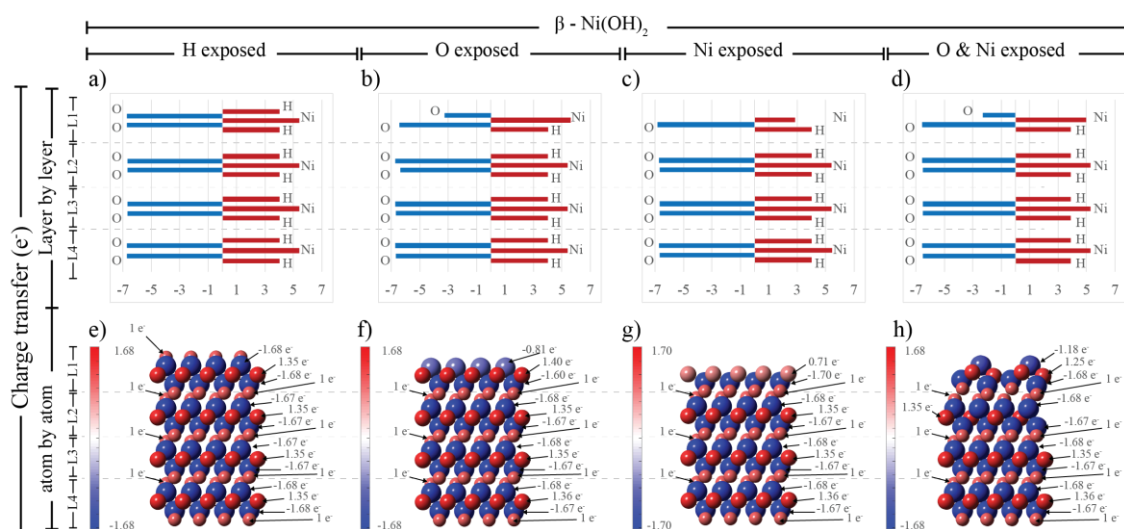


Figure 4.8. Electron charge transference of (001) cleavage plane to the β -Ni(OH)₂ system of the different surface termination are shown from the left to the right side, as H exposed (a and e), O exposed (b and f), O&Ni exposed (c and g) and Ni exposed (d and h). The upper part of the figure (a, b, c and d) shown the layer-by-layer charge transferred as sort in the lower part (e, f, g and h). The lateral view in the lower part shown the electron charge transferred atom by atom. L1, L2, L3 and L4 denote the 1st, 2nd, 3th and 4th layers, respectively.

In the β -Ni(OH)₂ system, the H-exposed surface has similar charge distribution for all layers, the H atoms lose 1 e⁻, the O atoms gains ~1.7 e⁻ and Ni atoms lose ~1.35 e⁻ (Figure 4.8a and e). In the last layer of the O-, O&Ni- and Ni-exposed surfaces, the Ni

lose around 1.40, 1.25 and 0.71 e⁻, respectively, while the lower O gain 1.6, 1.68 and 1.7 e⁻, respectively; besides the upper O gain 0.81 and 1.18 e⁻ in O- and O&Ni-exposed surfaces, in the same order, respectively.

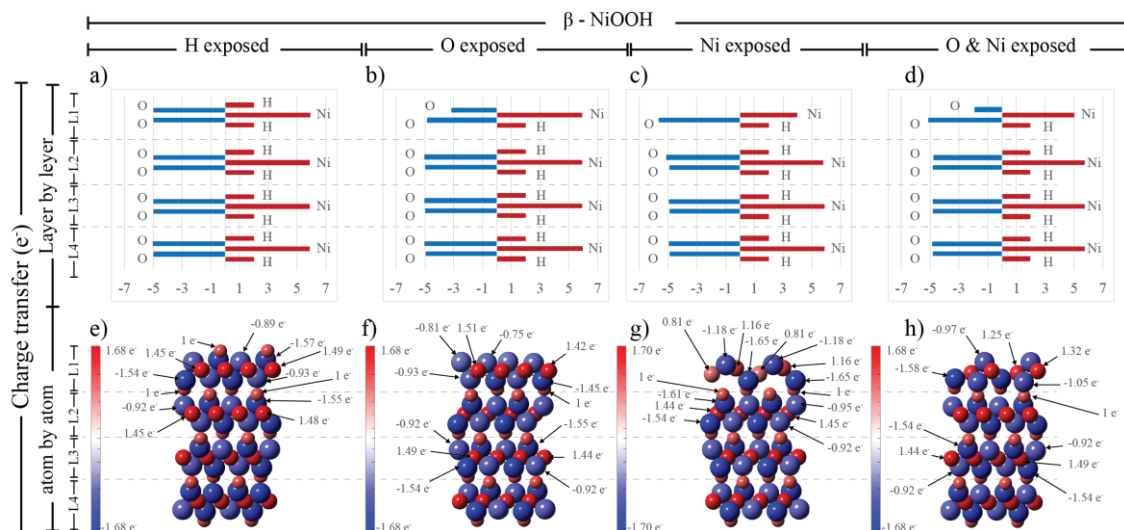


Figure 4.9. Electron charge transference of (001) cleavage plane to the β -NiOOH system of the different surface termination are shown from the left to the right side, as H exposed (a and e), O exposed (b and f), O&Ni exposed (c and g) and Ni exposed (d and h). The upper part of the figure (a, b, c and d) shown the layer-by-layer charge transferred as sort in the lower part (e, f, g and h). The lateral view in the lower part shown the electron charge transferred atom by atom. L1, L2, L3 and L4 denote the 1st, 2nd, 3th and 4th layers, respectively.

In the case of the β -NiOOH system (Figure 4.9), it can be seen that each hydrogen loses 1 e⁻ in all cases (Figure 4.9e, f, g and h). Particularly, for the H-exposed surface a similar charge distribution for all layers was observed, but the behavior of O and Ni atoms differed slightly with respect to β -Ni(OH)₂. Depending if they are bonded to a hydrogen or not: the upper O atoms bond gained around 1.57 and 0.89 e⁻ and the lower O gained 1.54 and 0.93 e⁻, respectively. Meanwhile, the Ni atoms lose around 1.49 and 1.45 e⁻ depending if they are bonded to an oxygen with hydrogen bonds or not, respectively (Figure 4.9a and e). For the O-exposed termination, the O atoms exposed won between 0.75 and 0.81 e⁻, and the lower won 1.45 and 0.93 e⁻, while the Ni atoms lose around 1.45 and 1.51 e⁻ depending if the lower oxygen is binding to an hydrogen or not, respectively (Figure 4.9b and f). In the O&Ni exposed case, the exposed O won 0.97 e⁻, and the exposed Ni lost 1.25 e⁻, while the nickel below the oxygen lost and the lower O won 1.58 and 1.05 e⁻ depending if they are bonded to a hydrogen or not (Figure 4.9d and h). The Ni exposed completion presents a surface reconstruction in the last layer as

illustrated in Figure S8-d and -h, the O bonded to an hydrogen that remain close to their position won around 1.65 e-, and others O atoms that had a significant shift position won about 1.18 e- while the Ni bonded to the O atoms with small shift position lost around 0.81 e- and the others nickels lost about 1.16 e- (Figure 4.9c and g).

In summary the electronic structure and charge transfer results show that the layer interactions in both systems are weak. Also, in the case of β -NiOOH different terminations affect the local magnetic moment of superficial Ni atoms, which show important changes in their values and the Ni atoms oxidation states. This fact could explain experimental results without considering a multiphase composition of the sample. The increase in the density of state around the Fermi level, which improves the conductivity, and the fact that the center of d-band calculation suggests that this is the most reactive surface could indicate that this is a suitable surface for the electrooxidation of glycerol to occur. We have performed further calculations (to be reported in more detail in future work) on glycerol adsorption on these Ni-hydroxides compounds but preliminary results are also supported by the charge result of this surface and of glycerol (see SI), which shown that the surface presented superficial Ni atoms with positive charge that could interact with the negative charged O atoms of the molecule. Also, according to the distorted configuration that the molecule could have after the interaction with the surface the positive charged H and C atoms in the molecule could interact with the positive charged O atoms on the surface.

4.4 Conclusion

Different electron microscopies characterizations showed the conversion of mono-metallic Ni to Ni hydroxides during cyclic voltammetry causing an expansion of particles. Effectively, nickel hydroxide is formed on the shell while nickel remains in the core. The presence of both phases is demonstrated with electron diffraction. The electrochemical oxidation of glycerol in alkaline media showed the catalytic activity of mono-metallic Ni catalyst depends on the morphology and decreases as Ni-urchin-PVP > Ni-urchin > Ni-triangular in a potential range higher than 0.4V vs. Hg/HgO. All different shape-controlled microstructures either follow indirect electron transfer mechanism at higher glycerol concentration ≥ 100 mM or the direct electron transfer pathway at low concentration. *In situ* infrared spectroscopy measurements illustrated that main products are mainly symmetric and asymmetric COO⁻ stretching of formate,

carbonate and carboxylate species with no significant effect for GEOR reaction pathway. Furthermore, DFT calculation indicated that the most stable plane in β -NiOOH is (001)-Ni as a metallic state. This is a suitable characteristic for its participation during electrooxidation reactions. In addition, the surface termination exposes a mix of Ni^{+3} and Ni^{+4} oxidation states representing interesting couples for electrochemical reactivity. The computed map of charges on the surfaces offered suitable places for glycerol interactions under electrooxidation that are subject of the future work.

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Supplementary Information B: Chapter 4

1. Computational method and surface model

All calculations were performed using spin-polarized DFT-based within the all-electron, frozen-core projector-augmented-wave (PAW) formalism^{1,2} with periodic boundary conditions as implemented in VASP code.^{3,4} The PBE functional in generalized gradient approximation (GGA) for the exchange-correlation term⁵ was used. Plane-wave basis set, with a cutoff energy of 750 eV was considered. All the structures have been optimized until the forces acting in each atom are less than 10^{-4} eV/Å and the energy convergence is less than 1 meV. It well known that standard DFT fails on the description of transition metals oxides as a result of spurious self-repulsion and the missing derivative discontinuity in the exchange-correlation functional that lead to over delocalization of electrons. Then, the Hubbard correction as implemented by Dudarev et al was used to partially correct these problems.⁶ A effective U of 5.5 eV was used for the Ni(III) 3d orbitals, derived from linear response theory, which was taken from ref.^{7,8} A Γ -point-centered Monkhorst-Pack k-point meshes of $6\times 6\times 4$ and $5\times 5\times 3$ for β -Ni(OH)₂ and β -NiOOH, respectively⁹ was considered.

For the bulk model of the β -Ni(OH)₂ phase we use its usual brucite-type structure made of hexagonal OH-Ni-OH tri-layer sheets superimposed in simple stacking of 1H-type (T1), with a ABAB oxygen stacking sequence and hydrogen in a tetrahedral environment.^{10,11} In the case of β -NiOOH phase, usually obtained in an ill-crystallized state, its structure is not well characterized in the literature. Considering that numerous previous studies suggest that the oxidation of nickel hydroxide proceeds without major structural modifications,¹²⁻¹⁴ we chose a representative P-3m1 (brucite) structure to model β -NiOOH. Besides this, one must choose where to locate the H atoms forming the OH groups. In this work we considered the most likely β -NiOOH structure formed upon the complete oxidation of β -Ni(OH)₂ with the staggered hydrogen arrangement in which 50% are present at each side in all sheets, being arranged in such way that all Ni atoms have a NiO₃(OH)₃ coordination sphere, as suggested by Tkalych *et al.*¹⁵ To calculate the most stable surfaces of these two phases, numerous low-index surfaces were considered. Therefore, initial structures were cleaved along (100), (010), (001), (101), (111) and (102) planes in order to generate slabs. A vacuum layer of 15 Å was introduced between the

slabs, which were sufficient to prevent interactions between periodic images of the slabs. These surfaces were modeled using a 6-layers super-cell. The thickness of the slab should be such that it approaches the electronic structure of 3D bulk in their inner most layers. Only the first three layers are allowed to relax, while the three remaining layers (bulk like) were kept fixed. The relaxation of the 4th layer changes the energy less than 4 meV. The surface energy (E_{surf}) for each considered cleavage plane for both systems is computed as:

$$E_{\text{surf}}(\xi) = \frac{1}{2 S(\xi)} \{E_{\text{slab}}^{\text{rel}}(\xi) - N_{\xi} E_{\text{Bulk/Atom}}(\Phi)\} \quad (\text{B1})$$

Where $S(\xi)$ is the surface area of the slab, N_{ξ} is the number of atoms in the slab ξ , $E_{\text{Bulk/Atom}}(\Phi)$ is the bulk energy per atom of the Φ system, with $\Phi = \beta\text{-Ni(OH)}_2$ or $\beta\text{-NiOOH}$.

Regarding the electronic structure and reactivity, the d-band center (ε_d) was calculate used the Hammer-Nørskov method¹⁶⁻¹⁹:

$$\varepsilon_d = \frac{\int_{-\infty}^{\infty} E \rho(E - E_F) dE}{\int_{-\infty}^{\infty} \rho(E - E_F) dE} \quad (\text{B2})$$

with $\rho(E - E_F)$ is the DOS projected on the d-states of the metal and E_F is the Fermi energy.

2. Theoretical calculations

2.1 Bulk structures

For testing our theoretical methodology, we calculate some bulk properties like DOS of the bulk system and magnetism and compare with previous theoretical studies. The lattice parameters are $a = b = 3.16 \text{ \AA}$ and $c = 4.65 \text{ \AA}$ and $a = b = 2.93 \text{ \AA}$ and $c = 4.86 \text{ \AA}$ for $\beta\text{-Ni(OH)}_2$ and $\beta\text{-NiOOH}$ respectively. These values are in good agreement with that reported in the literature.^{15,20} As expected, octahedrally coordinated with low-spin d^7 Ni(III) is characterized by a Jahn–Teller distortion according to ligand field theory: two Ni–O bond lengths exist in the optimized $\beta\text{-NiOOH}$ staggered structure (1.89 and 2.00 $\text{\AA}$, which compare well with experimentally measured bond lengths of 1.88 and 2.07 $\text{\AA}$).²¹

Regarding the electronic structure Figure B1 shown the DOS curves for β -Ni(OH)₂ and β -NiOOH. It can be seen that for β -Ni(OH)₂ there is a band-gap of about 3 eV these results are similar to other theoretical values reported in the literature^{15,20} (see Fig B1a). Also, this is consistent with experiments reporting this phase as wide-gap insulator with a band-gap of approximately 4.0 eV.²² In the oxyhydroxide case the DOS shown a semi metallic behavior with a minority spin band-gap of approximately 1.45 eV (see Figure B1b), which is consistent with reported DFT+U calculations.²³ This result does not agree with experimental result that reported a value of 1.7-1.8 eV.²² This is a usual consequence because the Hubbard correction is not enough to solve all DFT problems with the transition metal oxides, hybrid potentials are also needed.^{23,24} Also, it can be noted that in both cases the spin up and spin down contribution to the DOS are asymmetric, which is consistent with the appearing of an induced magnetic moment. The oxidation states of Ni atoms at each structure were consistent with the atomic magnetizations. For β -Ni(OH)₂ the magnetic moment per Ni atom is 1.78 μ_B , this magnetization value corresponds to a Ni²⁺ oxidation state. In β -NiOOH structure the local magnetic moment per Ni atom of 1.15 μ_B reveals that the oxidation state is Ni³⁺, which corresponds to an electronic configuration of $t_{2g}^6 e_g^1$. Similar results were reported by *Fidelsky et al.*²³

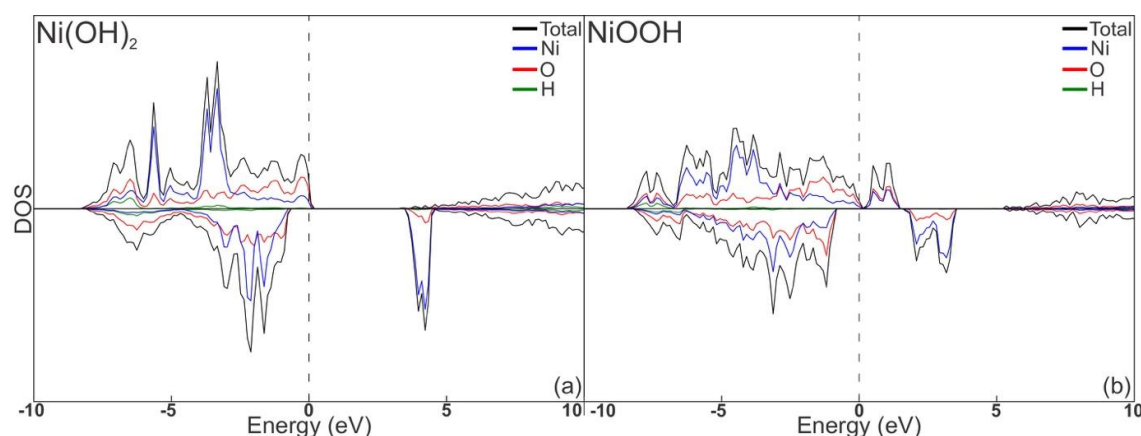


Fig. B1. DOS curves for the bulk systems: β -Ni(OH)₂ (a) and β -NiOOH (b).

2.2 Surface calculations

The (001), (010), (100), (011), (101), (102), (110) and (111) surfaces were studied in suitable slabs. Table B1 summarizes the surface energy values for the different surfaces in both phases. Our results show that the (001) surface is the most stable in both cases.

Table B1. The slab energies of different low index planes for the β -Ni(OH)₂ (a) and β -NiOOH phases

Cleavage planes	E_{surf1} (J/m ²)	
	NiOOH	Ni(OH) ₂
(1 0 0)	0.190	0.735
(0 1 0)	0.224	0.675
(0 0 1)	0.032	0.019
(0 1 1)	0.192	0.126
(1 0 1)	0.209	0.583
(1 0 2)	0.182	0.112
(1 1 0)	0.300	0.221
(1 1 1)	1.216	0.202

This finding is in good agreement with that reported by *Tkalych et al.*¹⁵ and *Martirez et al.*²⁴ The (001) plane in both structures has three possible termination surfaces (χ) with H, O, and Ni atoms exposed on the outmost layer as illustrated in Figure B2a-c, e-g and B3a-c, e-g). For comparison, we also considered the O&Ni surface termination, which consist in an outmost layer compose by a mix of Ni and O atoms as shown in Figure B2d, h and B3d, h). We selected these structures because under reaction condition is highly possible that the systems present a defective layer.

In these surfaces the usual form of surface energy definition is not suitable. Then, the surface energy for the different surface termination χ (E_{surf2}) was calculated using the following equation:

$$E_{\text{surf2}}(\chi) = E_{\text{cl}}(\chi) - E_{\text{rel}}(\Phi) \quad (\text{B3})$$

The cleavage energy, $E_{\text{cl}}(\chi)$, was computed by:

$$E_{\text{cl}}(\chi) = \frac{1}{N_{\chi} S} \left\{ \sum_{\chi=1}^{N_{\chi}} E_{\text{slab}}^{\text{unrel}}(\chi) - N_{\text{T.A.}} E_{\text{Bulk/Atom}}(\Phi) \right\} \quad (\text{B4})$$

Where N_{χ} is the number of considered surface terminations, S is the surface area of the slab, and $E_{\text{slab}}^{\text{unrel}}(\chi)$ is the unrelaxed energy of the χ slab, $N_{\text{T.A.}}$ is the total number of atoms contended in all χ slabs.

The relaxed energy of the χ surface, $E_{\text{rel}}(\chi)$, was computed as:

$$E_{\text{rel}}(\chi) = \frac{1}{2S} \{E_{\text{slab}}^{\text{rel}}(\chi) - E_{\text{slab}}^{\text{unrel}}(\chi)\} \quad (\text{B5})$$

Where $E_{\text{slab}}^{\text{rel}}(\chi)$ is the relaxed energy of the χ slab. For more detailed description see refs. ²⁵⁻³⁰ These results are reported in the main text.

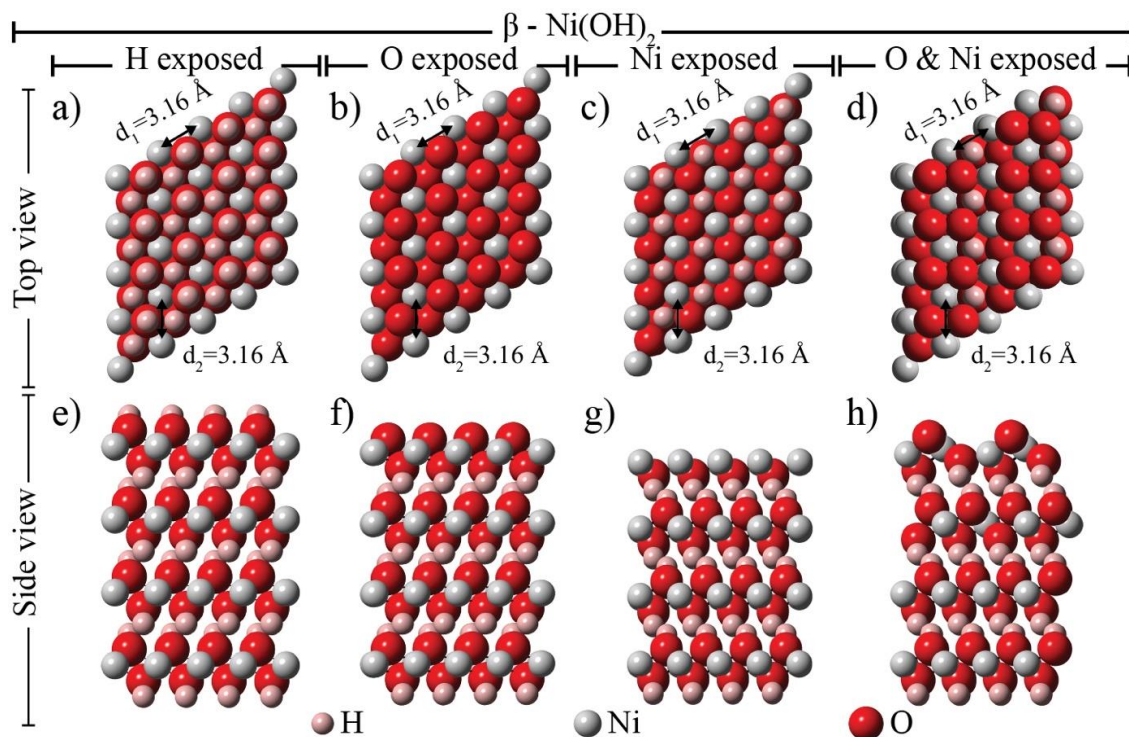


Fig. B2. Top views (top: a, b, c and d) and lateral view (bottom: e, f, g and h) of (001) cleavage plane to the β -Ni(OH)₂ system. From the left to the right-side different surface terminations are shown as H exposed (a and e), O exposed (b and f), O&Ni exposed (c and g) and Ni exposed (d and h).

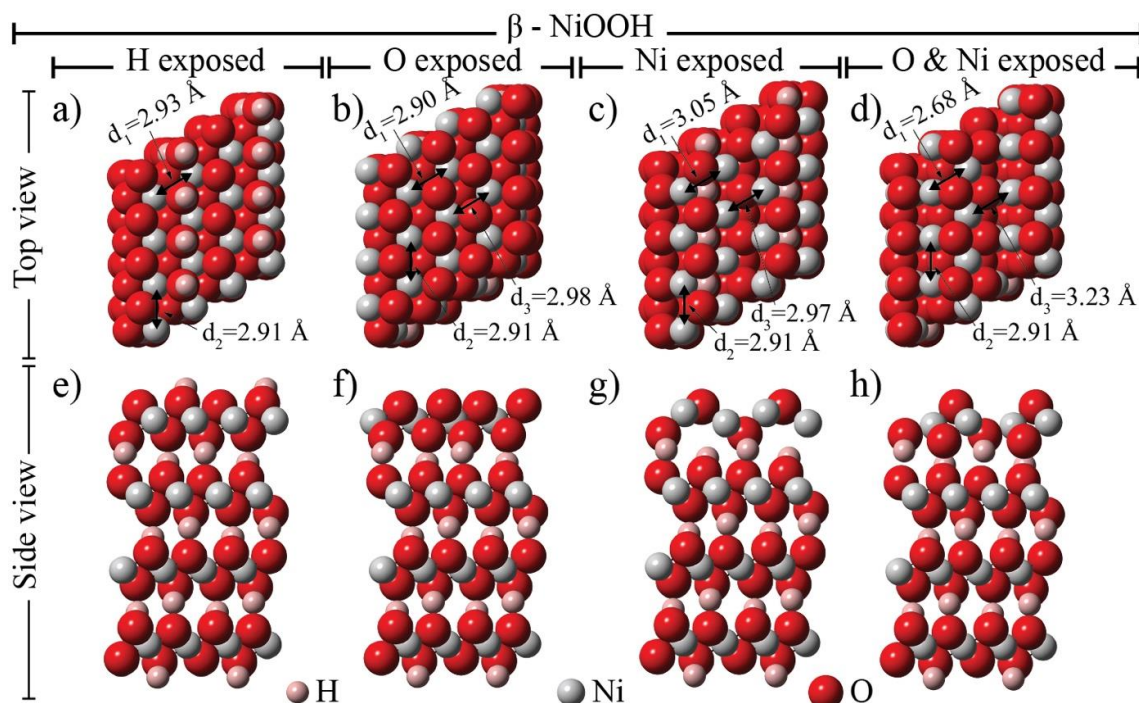


Fig. B3. Top views (top: a, b, c and d) and lateral view (bottom: e, f, g and h) of (001) cleavage plane to the β -NiOOH system. From the left to the right-side different surface terminations are shown as H exposed (a and e), O exposed (b and f), O&Ni exposed (c and g) and Ni exposed (d and h).

Regarding the electronic structure for different terminations of (001) on both structures, the DOS plots are shown in Figure B4. The oxyhydroxide DOS plots have a magnification of 2 to a better comparison. It can be noted that for the (001) terminated in H atoms -i.e. the complete surface- in both cases has the same behavior as bulk cases (compare Figure B1 with Figure B4a-b). In the β -Ni(OH)₂ structure, the different termination shown small changes around the Fermi level and in the O and Ni terminated surfaces it can be see a small increase in conductivity (Figure B4c, e and g). For the oxyhydroxide surfaces terminations, the DOS curves are similar, being the more important change a shift to higher energy in the Ni terminated case as illustrated in Figure B4b, d and h. Also, like in the bulk cases the spin up and spin down termination are asymmetric. In this figure it is very challenging to observe the effect of the different termination because it only affects the first layer. A more detailed discussion is presented in the main text.

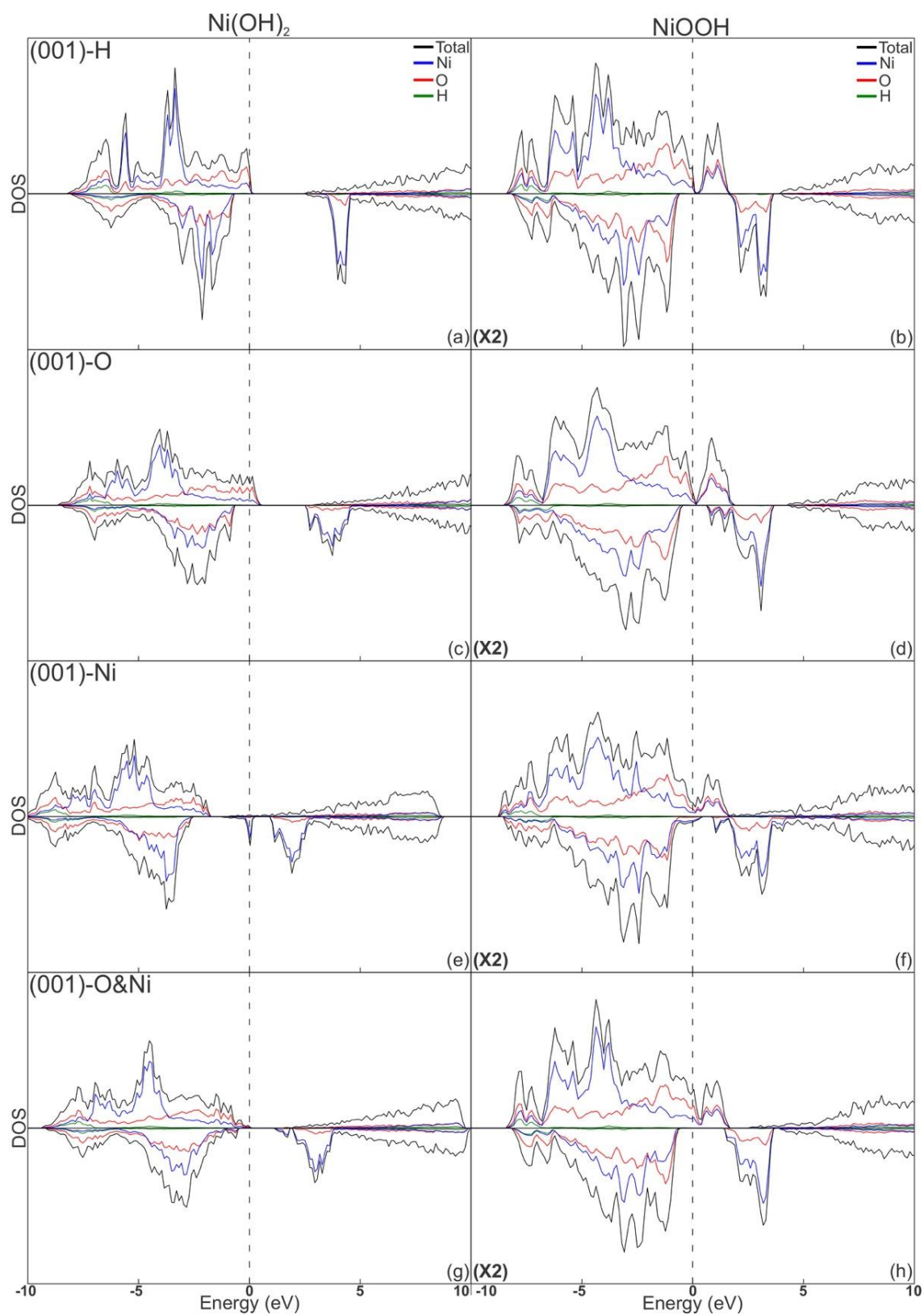


Fig. B4. DOS curves for the (001) surfaces terminations for: β -Ni(OH)₂ (a, c, e and g) and β -NiOOH (b, d, f and h) phases.

2.3 Glycerol molecule

As an indication, to be taken into account for possible adsorption configuration, we studied the charge transference on glycerol molecule in vacuum. We used the methodology to calculate electronic charges on atoms Bader analysis as implemented by Tang *et al.*^{31,32}

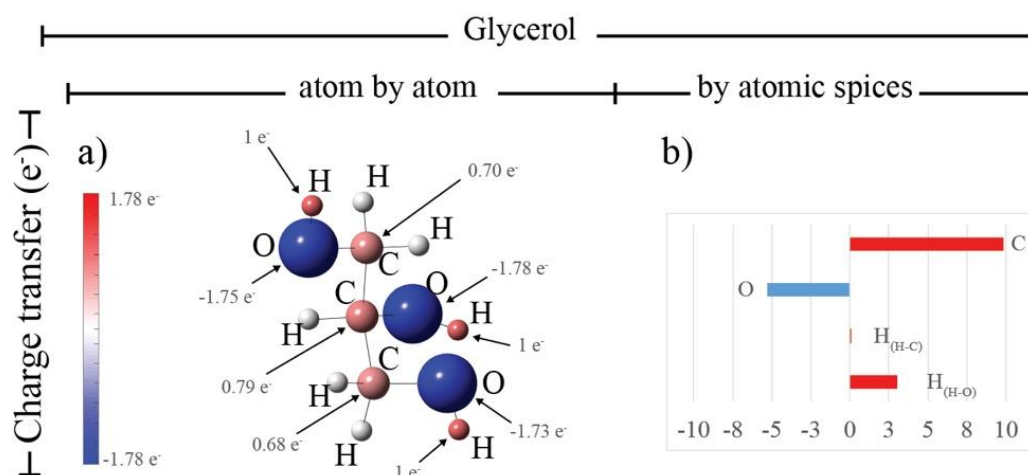


Fig. B5. Glycerol molecule electron charge transference. Atom-by-atom charge transferred (a). Electron charge transferred by atomic species (b).

It can be seen in Figure B5 that the O atoms are negatively charged, while the C atom and the H atom bonded to O atom are positive charged. This could indicate that the O atom prefer to be bonded to a Ni positively charged atom and depending how the molecule is distorted during the adsorption process the positive charged C and H could be bonded to O negatively charged on the surface.

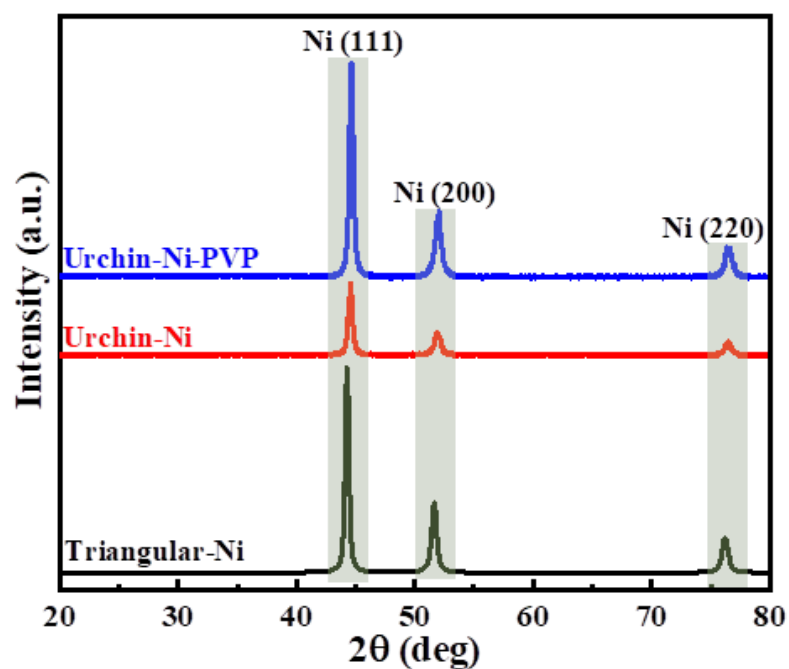


Fig. B6. XRD patterns of different shape of Ni Nanoparticles.

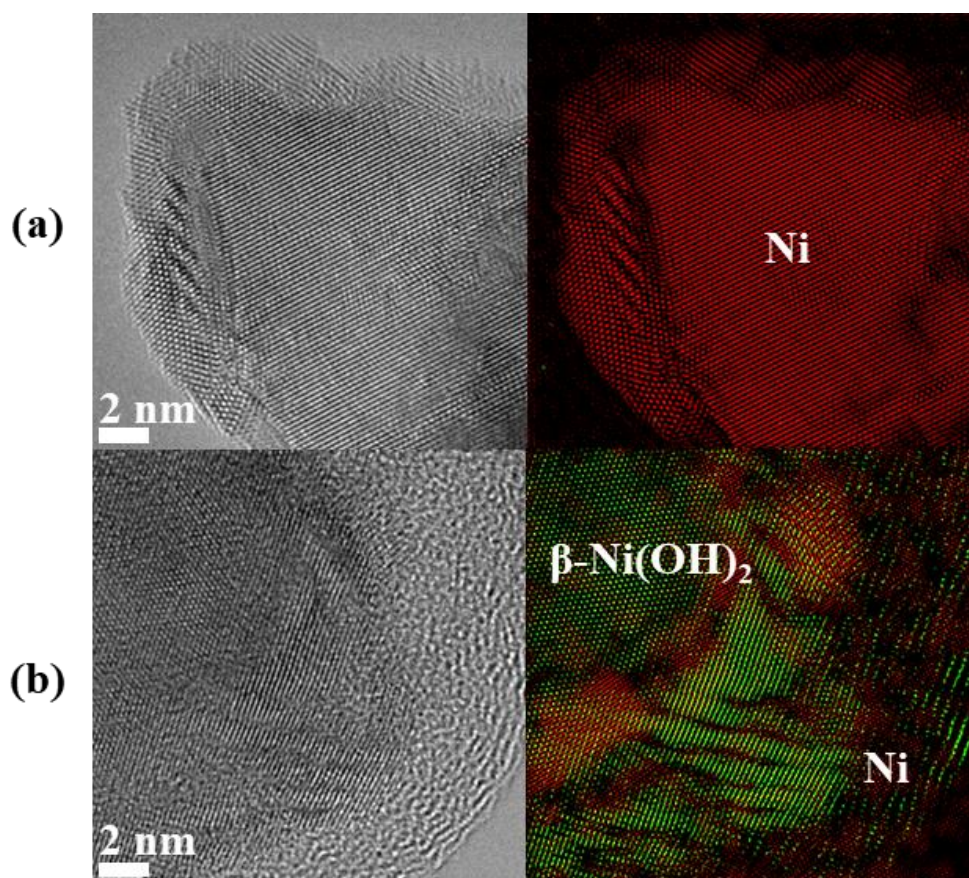


Fig. B7. (a) HRTEM and RGB contrast micrographs of urchin-Ni (a) before and (b) after conversion.

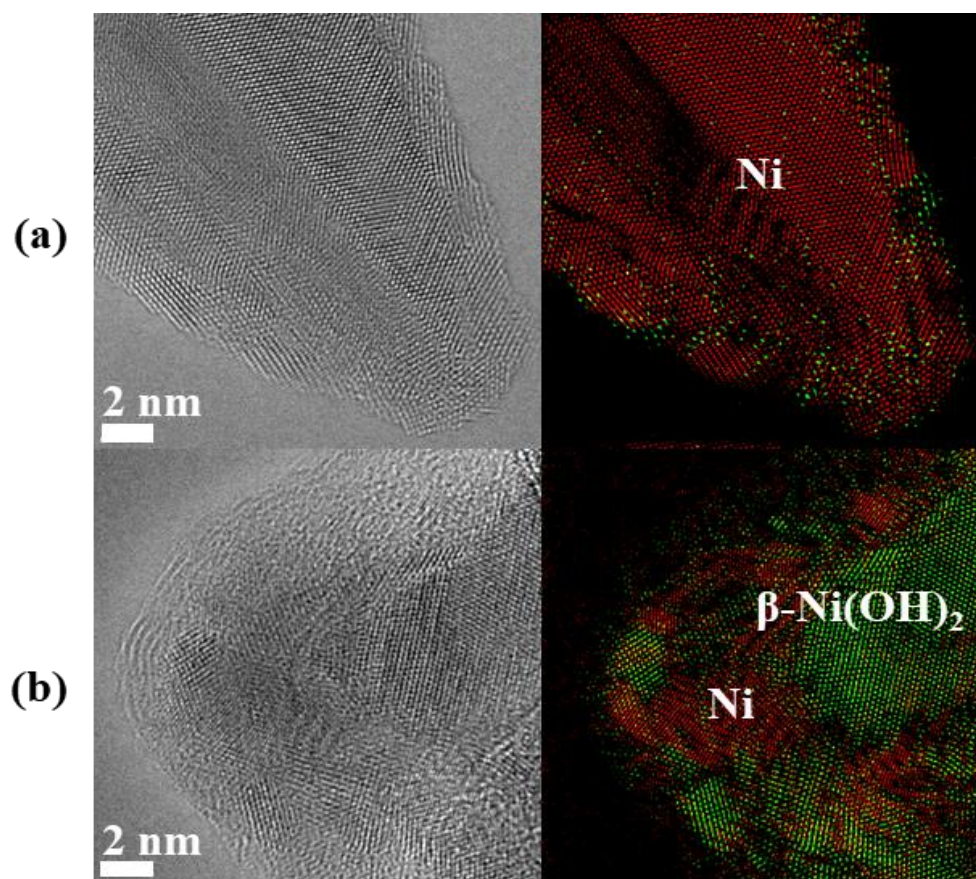


Fig. B8. (a) HRTEM and RGB contrast micrographs of urchin-Ni in the presence of PVP (a) before and (b) after conversion.

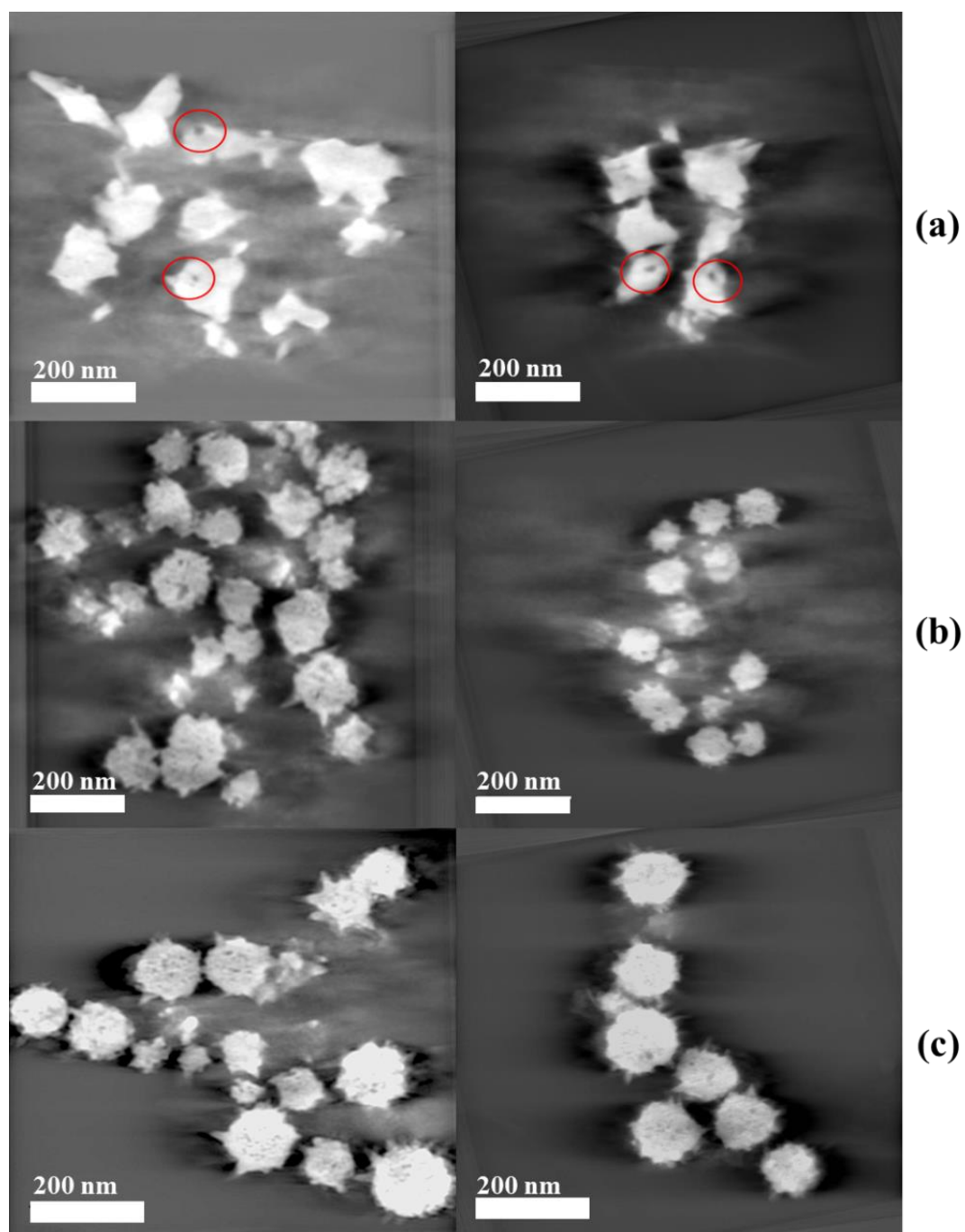


Fig. B9. Tomogram slice No. 400 out of 836 of controlled shaped nickel nanocrystallites before (Left) and after (Right) Conversion in 0.1 M KOH. (a) Triangular-Ni, (b) urchin-Ni and (c) urchin-Ni with PVP.

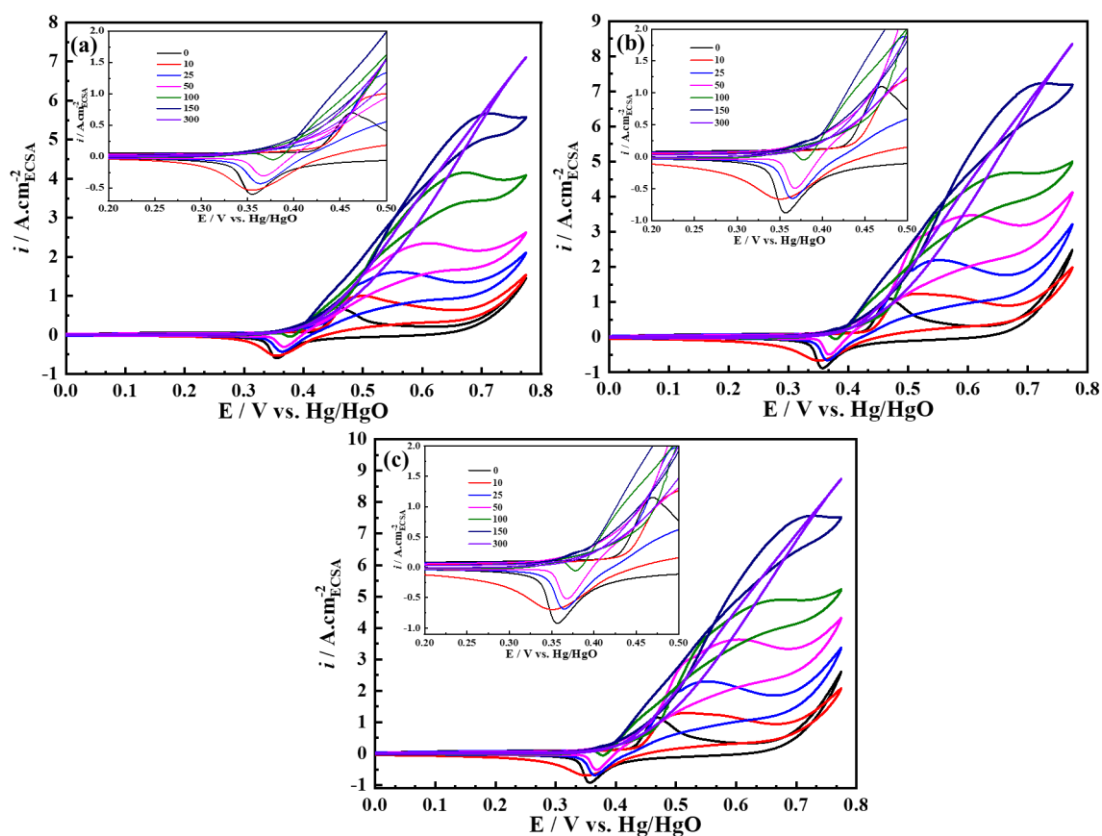


Fig. B10. Cyclic voltammograms of (a) triangular-Ni, (b) urchin-Ni and (c) urchin-Ni with PVP in 1M KOH + x mM glycerol (x = 10, 25,..., 300) at 50 mVs⁻¹(10th cycle).

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Chapter 5

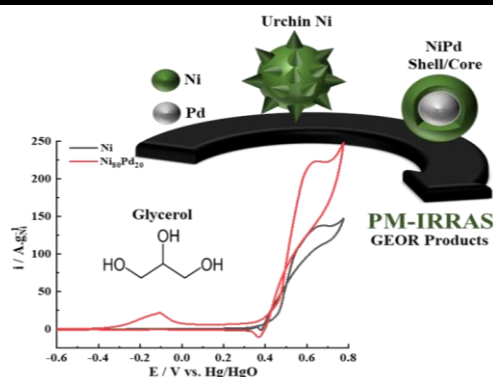
5 Electrochemical Valorization of Glycerol on Ni-rich Bimetallic NiPd Nanoparticles: Insight into Product Selectivity Using in-situ PM-IRRAS

Based on the paper:

Houache M. S. E., Hughes K., Ahmed A., Safari R., Liu H., Botton G. A., Baranova E. A., ACS Sustain. Chem. Eng., 2019, 7(17), 14425-14434.

Abstract

Glycerol partial electrooxidation was studied on $\text{Ni}_x\text{Pd}_{1-x}$ ($x = 100, 95, 90$ and 80 at.%) nanoparticles synthesized using a polyol method. The shape-controlled urchin-like monometallic Ni and spherical $\text{Ni}_x\text{Pd}_{1-x}$ catalysts were synthesized. The morphology, crystal structure and the composition of Ni-rich catalysts were characterized using a number of physicochemical techniques. Detailed electrochemical characterizations showed that Ni and $\text{Ni}_x\text{Pd}_{1-x}$ NPs are active for GEOR and that the reaction either follows the direct electron transfer mechanism at low glycerol concentrations or the indirect electron transfer mechanism at high concentration. Among all investigated electrocatalysts, $\text{Ni}_{80}\text{Pd}_{20}$ exhibited the highest current density at lower overpotentials due to both a synergetic effect of Ni and Pd and smaller particle size of $\text{Ni}_{80}\text{Pd}_{20}$. In-situ polarization modulation infrared-reflection absorption spectroscopy (PM-IRRAS) at various anodic potentials allowed discriminating the reaction products and intermediates directly on the electrode surface and in the electrolyte solution. PM-IRRAS showed that the main reaction products on $\text{Ni}_x\text{Pd}_{1-x}$ are glyceraldehyde, carbonyl groups for mesoxalate and tartronate ions, carboxylate ions and traces of carbon dioxide. $\text{Ni}_x\text{Pd}_{1-x}$ catalysts are promising anode materials for glycerol oxidation to value added products and could be potentially combined with cathodic hydrogen production or CO_2 electro-reduction processes in alkaline media.



5.1 Introduction

Renewable fuels such as biodiesel have attracted a growing interest in the last decade with a goal to reduce our dependence on fossil fuels and reduce global greenhouse gas emissions.¹ Biodiesel is derived from vegetable oils and/or waste fats through a trans-

esterification reaction. Although it is a green fuel, its production generates 10 wt.% of glycerol as a by-product.² The biodiesel industry produces millions of kilograms of low-value glycerol, which must be either stored or disposed of, creating environmental concerns. Glycerol thermal combustion for energy production is not a solution, as the process generates toxic substances, such as acrolein.³

Although glycerol is employed as a raw material within various industries such as food, pharmaceuticals, cosmetics and tobacco products, its supply is still superior to the demand, thus making the overproduction of glycerol a global challenge that should be effectively addressed in a timely manner. Upgrading this biodiesel by-product into value-added products using electrochemical technologies is a promising approach in making biodiesel production more environmentally friendly with added financial benefits.¹

Electrochemical oxidation of glycerol to value-added products without three-carbon (C-C-C) cleavage with concurrent cathodic production of hydrogen or CO₂ electro-reduction in an electrolytic cell has attracted significant attention in the recent years.⁴ The electrochemical partial oxidation of glycerol shows several possible pathways in alkaline media⁵ and generates a number of useful chemicals such as tartronate, glycerate, hydroxypyruvate, oxalate, dihydroxyacetone, glycolate, formate and mesoxalate ions. Usually, a mixture of these oxygenated species is obtained during glycerol electrooxidation reaction (GEOR).⁶ Some of these chemicals are useful industrial precursors for instance in polymer and pharmaceutical manufacturing.⁷ Several studies have reported the development of efficient and selective electrocatalysts for glycerol electrooxidation. Among noble metal catalysts, palladium and platinum led to formation of glycerate ions, mesoxalate and/or tartronate.⁸⁻¹¹ For gold catalyst, similar products were detected, however hydroxypyruvate ion formation was also reported, indicating that Au may have a different pathway for glycerol electrooxidation.¹²⁻¹⁴ For these three electro-catalysts, if the applied potential is increased over 0.8 V vs. RHE, the formation of carbon dioxide occurs, indicating the cleavage of the C chain bond for glycerol.¹⁵ Thus, this C-C-C cleavage is not suitable for the recovery of high value-added products. Since 2000, over 160 reports on glycerol electrooxidation were published. The majority of studies have been focused on noble metals such as Pt, Pd and Au.¹⁶ Nickel was reported to be an effective electro-catalyst for various organic and inorganic

compounds in alkaline media such as methanol¹⁷, ethanol¹⁸, urea¹⁹ and ammonia.²⁰ Nickel is an interesting candidate for GEOR in alkaline media^{2,16}, because it is stable and cheap. The preparation of nano-structured Ni catalysts with well-defined size and shape as well as bimetallic Ni materials could improve the catalytic activity of nickel and in some instances its selectivity.⁴ It has been proposed, for bulk Ni¹⁶ and Ni nanoparticles²¹ that electrooxidation of glycerol proceeds in the region of nickel oxyhydroxide formation ($\text{Ni}(\text{OH})_2/\text{NiOOH}$ couple), where NiOOH is an active surface species for GEOR. HPLC analysis illustrated that the main reaction product is formate, while tartronate, glycolate, oxalate and glycerate were also observed. Additionally, Ni/C and FeCoNi/C demonstrated the best conversion ratio of glycerol to glycolate and formate, and CoNi/C exhibited the highest glycerol conversion ratio (17.9%). A bimetallic $\text{Pt}_2\text{Ni}_1/\text{C}$ ²² $\text{Pd}_{60}\text{Ni}_{40}/\text{C}$ ²² and Au/Ni core/shell support on polystyrene (PS) spheres²³ catalysts exhibited a noticeable reaction rate enhancement due to modifications in the geometric and electronic structure of the material in comparison to the Pt/C, Pd/C and Au/PS catalysts, respectively. The Ni co-catalyst was therefore able to significantly decrease the Pt, Pd and Au amount without affecting their activities.^{22,23} A glycerol oxidation scheme on PdAg and PdNi in alkaline solution was proposed earlier²², in which the initial step of the mechanism is glyceraldehyde formation, which is further oxidized to the glycerate ion. Afterwards, depending on the applied potential and the nature of the surface-active sites, three intermediates could be formed: tartronate, glycolate and/or formate ions. To design Ni-based electrocatalysts with high selectivity and activity, it is therefore vital to gain a better comprehension of the nature of the nickel surface active sites and their role on glycerol electrooxidation reaction and its product distribution.^{2,6,16} Recently, we demonstrated that bulk Ni could be efficient for glycerol electrooxidation after an activation procedure consisting of applying a sin-wave treatment.¹⁶ In-situ polarization modulation infrared-reflection absorption spectroscopy (PM-IRRAS) measurements on Ni bulk electrode²⁴ showed that formation of a number of products: carbonyl, some carboxylate ions and glyceraldehyde. Both treated and as-prepared Ni surfaces had similar spectra features, indicating that the sinusoidal treatment did not affect the selectivity. The obtained product distributions demonstrated a rapid formation of glycerate ions, acting as both products and reaction intermediates for the formation of smaller molecules after C-C-C bond cleavage.

In the present work, we report glycerol electrooxidation on $\text{Ni}_x\text{Pd}_{1-x}$ ($x = 100, 95, 90$ and 80 at.%) nanoparticles in 1M KOH . First, Ni-based NPs were characterized using various physicochemical techniques: X-Ray Diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), Energy Dispersive X-ray Spectroscopy (EDS) mapping, high-angle annular dark-field (HAADF) imaging and electron energy loss spectroscopy (EELS). Then electrochemical measurements were carried out on the Ni-based NPs using cyclic voltammetry (CV) and chronoamperometry (CA) in combination with in-situ (PM-IRRAS) measurements for reaction product analysis.

5.2 Experimental section

5.2.1 Materials

Nickel (II) chloride hexahydrate (99.999%) and hydrazine hydrate (50-60 % purity; degree of hydration, ~ 1.5) were both purchased from Sigma-Aldrich. Sodium hydroxide (97%) and ethylene glycol (99.96%) was supplied by Fisher Scientific, and PdCl_2 (99%, Alfa Aesar). Ethanol (Fisher Scientific) was used for the preparation of powders. Ultrapure de-ionized water (Milli-Q® Millipore, $18.2\text{ M}\Omega\text{ cm}$ at 293 K) was used to prepare all electrolytes.

5.2.2 Preparation of $\text{Ni}_x\text{Pd}_{1-x}$ nanoparticles

All catalysts were synthesised using polyol method in the presence of hydrozine.²⁵ For preparation of monometallic Ni NPs, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.357 g) was directly dissolved in ethylene glycol (50 mM) in a three-necked round bottom flask. The solution was heated to $100\text{ }^\circ\text{C}$ under magnetic stirring using a hot plate. After 2 min, 0.1M of $\text{N}_2\text{H}_4 \cdot \frac{3}{2}\text{H}_2\text{O}$ (1.7 ml) was added to the mixture. After addition of hydrazine, the color of the solution changed rapidly from green to light blue indicating the formation of Ni-hydrazine complexes $[\text{Ni}(\text{N}_2\text{H}_4)_2]^{+2}$. 4.5 ml of 0.5M NaOH was then injected, which slowly turned the color of the reaction mixture to black, indicating the formation of Ni nanoparticles. The solution was then maintained at $100\text{ }^\circ\text{C}$ under strong magnetic stirring until it changed into a clear solution and was then cooled down to room temperature. Ni NPs were recovered from the solution using a ferrite ring permanent magnet, then washed with ethanol three times. The resulted product was separated by centrifugation at 6000 rpm for 10 min and stored in ethanol. $\text{Ni}_x\text{Pd}_{1-x}$ nanocatalysts with ($x = 95, 90$ and 80 at.%)

were prepared through a similar procedure, using an appropriate amount of PdCl_2 precursor salt in ethylene glycol. All other parameters were kept constant.

5.2.3 Physicochemical characterization

The X-ray diffraction (XRD) patterns of Ni-based catalysts were recorded with Rigaku Ultima IV multi-purpose diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) at 40 kV and 44 mA in the range of $20\text{--}80^\circ 2\theta$ with $0.5^\circ 2\theta \text{ min}^{-1}$ scanning rate. The particle crystallite size is estimated using Debye-Scherrer equation:

$$D = \frac{0.9\lambda_{\text{Cu}}}{\beta_{1/2} \cos \theta} \quad (5.1)$$

Where λ_{Cu} is the X-ray wavelength, $\beta_{1/2}$ is the line broadening over the Full Width at Half Maximum (FWHM) in radians, and θ is the Bragg angle. The TEM micrographs were obtained using JEOL JEM 2100F Field Emission (FE) TEM operating at 200 kV. Scanning electron microscopy (SEM) analysis of Ni particles was carried out using on both a JEOL JSM-7500F FE-SEM and a FEI Magellan ultrahigh-resolution SEM for low voltage imaging conditions to optimize surface sensitivity. EDS mapping was done with a FEI Osiris TEM operated at 200 KeV. The FEI Tecnai Osiris Scanning Transmission Electron Microscope was equipped with a field-emission electron source and four silicon drift detectors for optimal Energy Dispersive X-ray spectrometry. High Angle Annular Dark Field in STEM (HAADF-STEM) imaging and some EDS analysis was carried out by FEI Titan 80-300 in 300 KeV. For the latter instrument, EDS spectra were analyzed with INCA software on the same system. All spectra and images were extracted from INCA. Electron energy loss spectroscopy (EELS) was measurements for these samples were carried out on a FEI Titan 80-300 microscope operated at 300 KeV with Quantum EELS spectrometer fitted with a K2 direct electron detector camera from Gatan.

5.2.4 Electrochemical and in-situ photoelastic modulations infrared reflection absorption spectroscopy (PM-IRRAS) measurements

All experiments were performed at room temperature in a conventional three-electrode electrochemical cell made of Teflon. BioLogic VSP Potentiostat/Galvanostat equipped with EC-Lab software (BioLogic Science Instruments SAS, Claix, France) was used to conduct all electrochemical measurements. A glassy carbon (GC) electrode with

a geometric surface area of 19.62 mm^2 was used as the current collector for unsupported nano-catalysts (Pine Research Instrumentation). All potentials were measured with respect to mercury/mercury oxide (Hg/HgO) (Koslow Scientific). Platinum wire served as a counter electrode. All solutions were prepared using deionized water $18.2 \text{ M}\Omega$. The background solution of all electrochemical experiments was a 1 M KOH (85.6% purity; EMD, ACS grade) with varying concentrations of glycerol (99.9% purity; Fisher Scientific). All electrolytic solutions were purged with N_2 gas for 15 min to remove any dissolved oxygen and a nitrogen stream was maintained during the experiment. The ink was made of 6 mg of NPs, 1 mL of water, $200 \mu\text{L}$ isopropanol and finally $100 \mu\text{L}$ Nafion solution.²⁴ The mixture was then sonicated for 5 min to form a homogeneous mixture. The ink solution ($10 \mu\text{L}$) was deposited onto the pre-polished GC-electrode surface and air-dried at 60°C for 10 min and used as the working electrode. Currents obtained in CV (5th cycle) and CA experiments are normalized per unit mass of Ni content in the catalyst, unless otherwise stated.

The detail procedure of in-situ PM-IRRAS measurements, data processing and interpretation equations have been reported earlier.^{16,24} In short: the working electrode (WE) consisted of a glassy carbon (GC) electrode covered by Ni-based NPs ink, as shown above. The WE was pressed against the CaF_2 prism to reduce the IR beam absorption by electrolyte ($1\text{M KOH} + 0.1\text{M glycerol}$). The spectro-electrochemical cell and PMA-50 XL chamber were purged with N_2 and then dry air for at least 90 min to remove all interferences from atmospheric water and CO_2 , respectively. Then the reference spectrum was acquired at the open circuit potential following by sample spectra at various GEOR potentials between -0.25 and 0.54V vs Hg/HgO. Each spectrum was acquired every 10 min during 30 min CA before stepping to the next potential.

5.3 Results and discussion

5.3.1 Physicochemical characterization of $\text{Ni}_x\text{Pd}_{1-x}$ NPs

Figure 5.1 illustrates the XRD pattern of as prepared Ni and NiPd catalysts of different Ni:Pd atomic ratios. Ni-based catalysts consist of three characteristic peaks at approximately 44.56 , 51.76 and $76.38^\circ 2\theta$. This indicates that the resultant particles were

pure face-centered cubic nickel (fcc) (JCPDS Card No. 04-0850). No characteristic peaks of Ni oxides or hydroxides were detected, which suggested that metallic particles were formed.

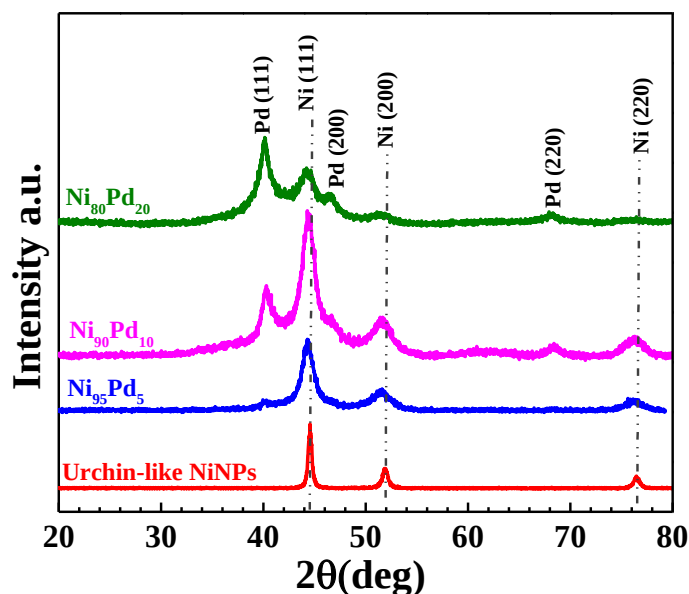


Figure 5.1. XRD patterns of $\text{Ni}_x\text{Pd}_{x-1}$ Nanoparticles

The Ni (111) peaks were slightly shifted to lower 2θ values in the NiPd catalysts with increasing Pd content. This shift may indicate some partial alloying between Ni and Pd through incorporation of Pd atoms into the fcc structure of Ni. However, the presence of fcc Pd peaks confirms some partial alloying and formation of bi-phase particles. Using Debye-Scherrer (Eq. 5.1), the crystallite particle size for the prepared catalysts was estimated using the FWHM of Ni (111) peak and the background at $\sim 55^\circ 2\theta$. The crystallite size decreased in the following order: Ni > $\text{Ni}_{95}\text{Pd}_5$ > $\text{Ni}_{90}\text{Pd}_{10}$ > $\text{Ni}_{80}\text{Pd}_{20}$ as summarized in Table 5.1. This indicates that addition of Pd decreased the crystallite size of Ni.

Table 5.1. The peak position and crystallite size of Ni and $\text{Ni}_x\text{Pd}_{x-1}$ catalysts.

Catalysts	2θ position (deg)		Crystallite size (nm)
	Ni (111)	Pd (111)	Ni (111)
Ni	44.56	N/A	18.9
$\text{Ni}_{95}\text{Pd}_5$	44.38	40.38	6.4
$\text{Ni}_{90}\text{Pd}_{10}$	44.38	40.30	5.5
$\text{Ni}_{80}\text{Pd}_{20}$	44.26	40.14	5.3

HR-SEM and TEM of the as-prepared Ni particle is illustrated in Figure 5.2. The resulting particles size is in the range of 100 to 130 nm. This could be due to strong attractive magnetic force between colloids that precipitate, which tend to agglomerate easily into larger particles.²⁶ Compared to the crystallite sizes calculated from the XRD data, the nickel particles were composed of several nanometer-sized crystallites.

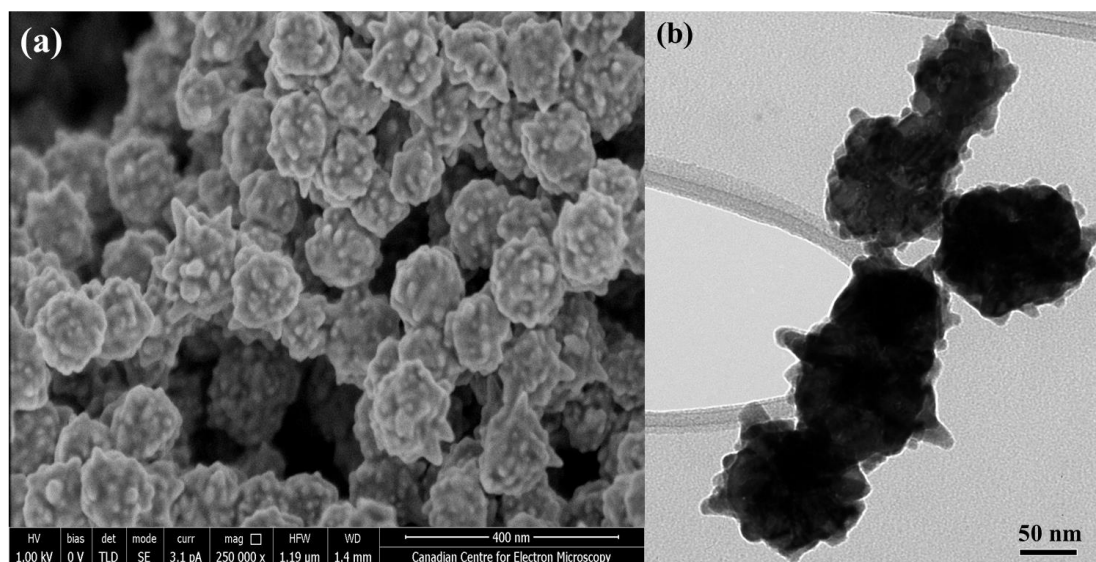


Figure 5.2. HR-SEM (a) and TEM (b) images of Ni-urchin NPs, prepared with a modified polyol technique.

The as-prepared $\text{Ni}_x\text{Pd}_{1-x}$ nanoparticles were 10-15 nm in size (Figure 5.3 and 5.4). The bimetallic NPs were characterized using STEM-EDS elemental mapping for the respective elements (Figure 5.3). The HAADF-STEM images of the Ni-Pd nanoparticles were performed to provide elemental analyses of the material. Figure 5.3(a,e,i) and Figure 5.3(b-d), (f-h) and (j-l) show the chemical maps of the Ni-Pd in $\text{Ni}_{95}\text{Pd}_5$, $\text{Ni}_{90}\text{Pd}_{10}$ and $\text{Ni}_{80}\text{Pd}_{20}$ NPs, respectively. In this figure, separate mapping of Ni and Pd are illustrated successively, and the last images (Figure 5.3 (d,h and l)) depict the composition mapping with Ni and Pd overlaid. It can be seen from the figures that Pd is agglomerated in specific areas of the sample, suggesting the presence of large clusters in the material, likely due to the synthesis method.

Furthermore, $\text{Ni}_{90}\text{Pd}_{10}$ has been further characterized using high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM). Figure 5.4a illustrates the HAADF-STEM image at low magnification with the distribution and morphology of the nanoparticles with the size between 10-15 nm. In addition, the figure

shows the EDS spectrum of the elemental composition of Ni₉₀Pd₁₀. The spectrum indicates the presence of both Ni and Pd. The distribution of the chemical elements of the Ni shell-/Pd core nanoparticle was also investigated by scanning transmission electron microscopy combined with electron energy-loss spectroscopy (STEM–EELS).

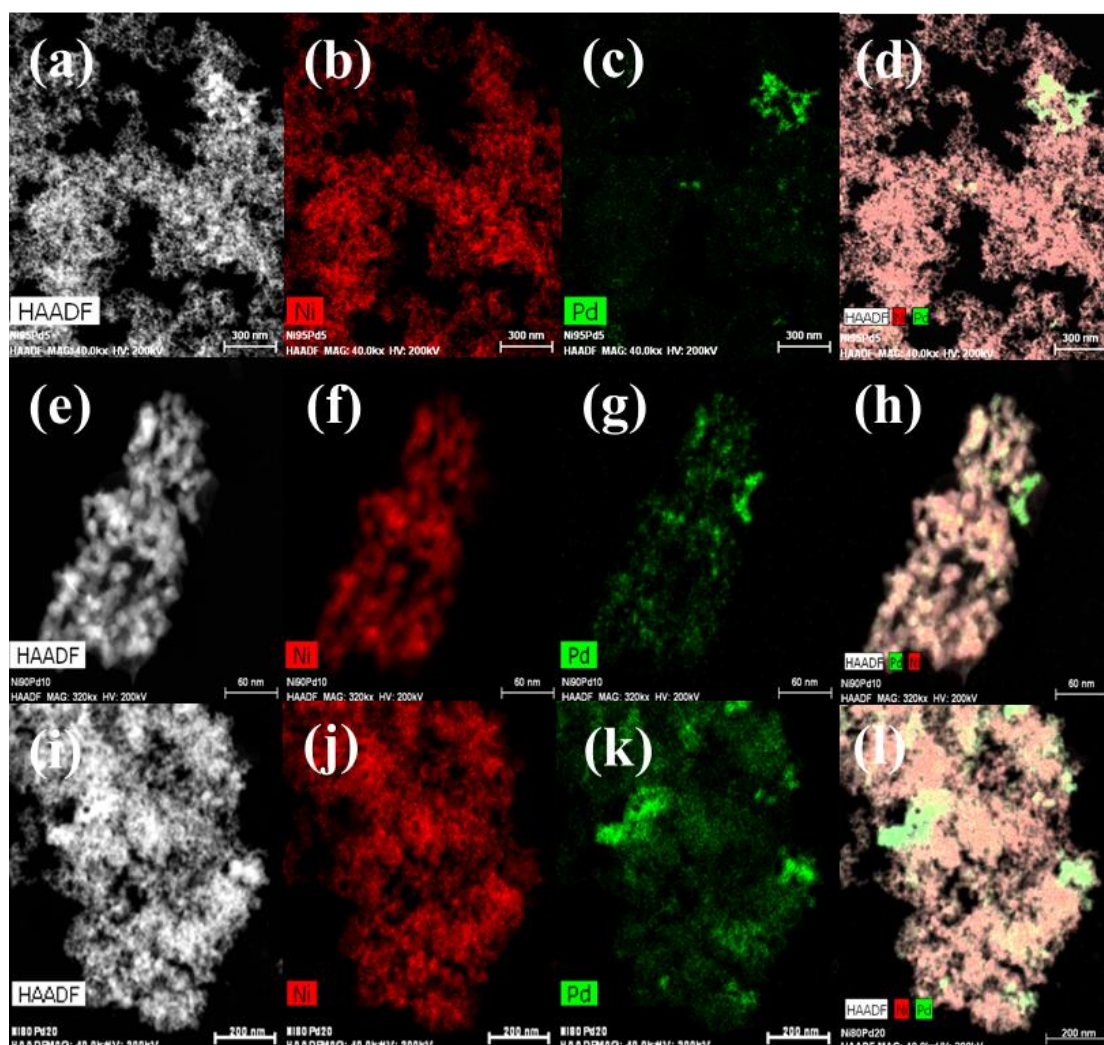


Figure 5.3. STEM-EDS mapping of Ni and Pd (a-d) Ni₉₅Pd₅, (e-h) Ni₉₀Pd₁₀ and (i-l) Ni₈₀Pd₂₀

Figure 5.4(b-c) illustrates the result for the STEM–EELS mapping of the Ni/Pd shell/core nanoparticles. The corresponding STEM–EELS map of Ni-Pd clearly reveals that Pd is present in the core and Ni is segregated on the surface forming the shell, which in turn is covered with some Pd. This corresponds to Pd-core NiPd double-shell structure, present as a result of the synthesis procedure. Pd tends to be in the core, because its precursor salt is easily reduced by ethylene glycol and reduced Pd clusters serve as seeds for Ni reduction and growth. In Figure 5.4b, the STEM–EELS spectrum depicts the

presence of the peaks' C–K signal at 280 eV (associated with the carbon film of the grid), Ni L_{2,3} signal at ~850 eV and the Pd-M_{4,5} signal at ~400 eV. Based on above physicochemical characterization of Ni_xPd_{1-x} NPs, Pd acted as heterogeneous nucleation agent preventing Ni from growing, resulting in a smaller crystallite size compared to monometallic Ni.

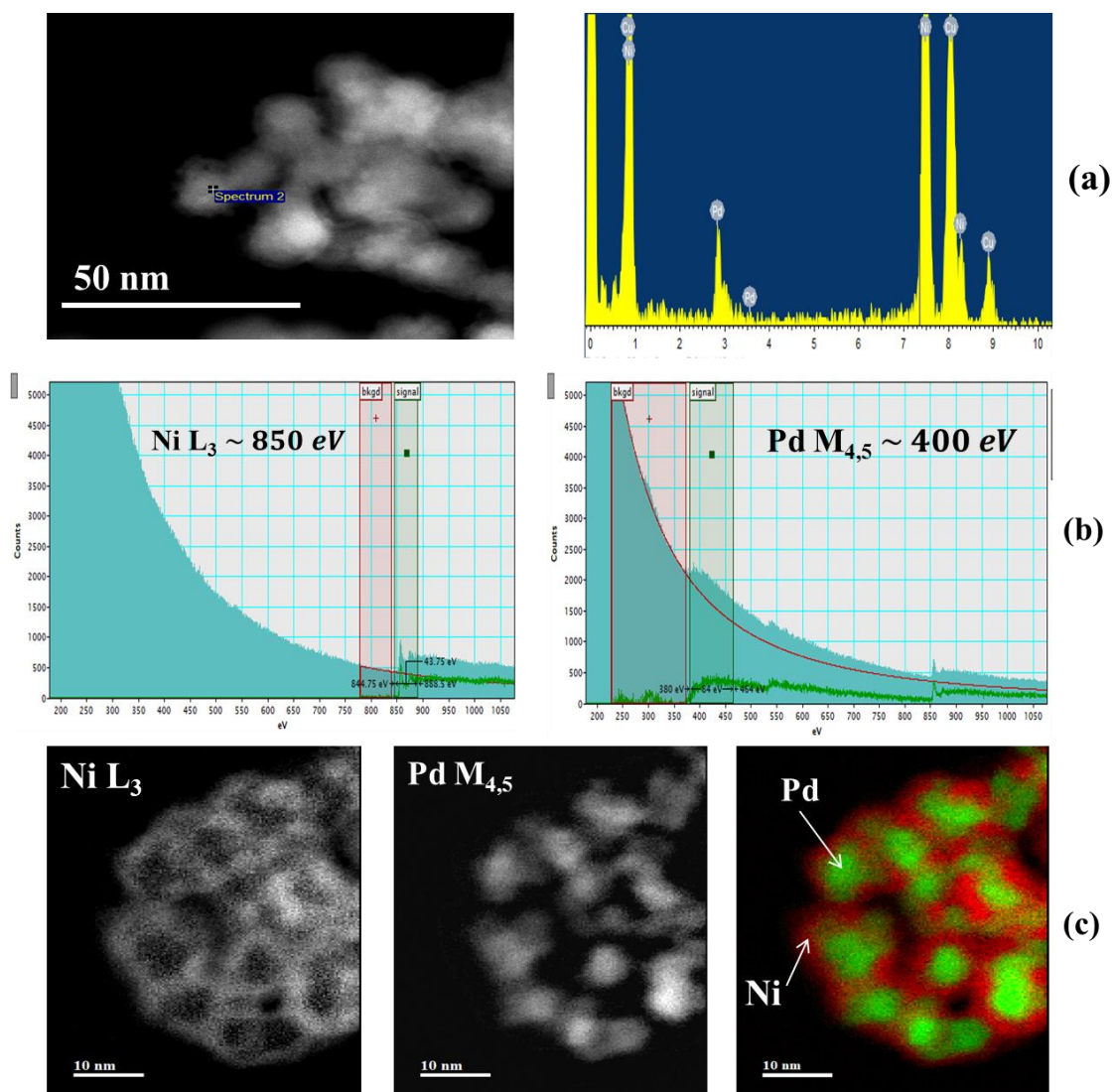


Figure 5.4. (a) HAADF-STEM images and EDS Spectrum of Ni₉₀Pd₁₀, (b) EELS Spectrum Obtained at High Spatial Resolution, (c) EELS Map of Ni-L₃ and Pd-M_{4, 5}.

5.3.2 Glycerol electrooxidation

5.3.2.1 Electrochemical tests with and without glycerol in 1M KOH

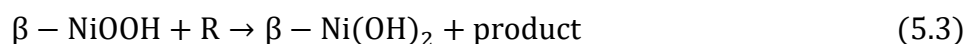
Figure 5.5 (a-d) shows stable cyclic voltammograms (CVs) of Ni_xPd_{1-x}, in 1M KOH (black line) at 50 mV sec⁻¹. The surface oxidation of nickel in alkaline solution is well established.²⁷ At anodic potentials β-Ni(OH)₂ is oxidized reversibly to β-NiOOH,

with a peak maximum at ~ 0.44 V vs. Hg/HgO. At more positive potential values, $> \sim 0.5$ V a γ -NiOOH phase could be formed. These species adopt a crystallographic structure similar to that of α -Ni(OH)₂ and can be electrochemically reduced back to α -Ni(OH)₂.²⁸⁻
³⁰ At higher potentials than 0.67 V, the oxygen evolution reaction (OER) takes place, occurring concurrently with the growth of NiOOH.³⁰ In the cathodic scan, a peak at ~ 0.35 V corresponds to the reduction of β,γ -NiOOH back to β -Ni(OH)₂. The addition of Pd results in increase in Ni³⁺/Ni²⁺ redox peak for all bimetallic catalysts if compared to monometallic Ni. This increase could be explained by the lower particle size of NiPd materials compared to Ni urchins, resulting in the higher active surface area of bimetallic catalysts. For Ni₈₀Pd₂₀, the cathodic peak at ~ -0.36 V (Figure 5.5d inset, black line) corresponds to the PdO reduction, which is formed at positive potentials in the anodic scan according to:^{31,32}



This peak was almost negligible for Ni₉₅Pd₅ and Ni₉₀Pd₁₀ indicating better Pd distribution inside Ni. Adding Pd enhanced the current density of Ni(II)/ Ni(III) peak. For Ni₉₅Pd₅, the current density of Ni²⁺/Ni³⁺ peak centered at 0.527 V increased by five times compared to Ni particle whereas for Ni₈₀Pd₂₀, the peak current density increased by over four times and its maximum shifted by 20 mV to lower potentials, i.e., from ~ 0.44 V to 0.42 V. Furthermore, addition of Pd also had a positive effect on OER. The current growth due to OER started at ~ 0.64 V on Ni₈₀Pd₂₀ compared to that of Ni at 0.67 V with the current density being almost five times higher for Ni₈₀Pd₂₀ compared to Ni. Such behavior can be explained by the larger active surface area of bimetallic NiPd catalysts that show smaller particle size than Ni and due to an electronic interaction between Ni and Pd atoms that affects the formation of NiOOH phase.

Glycerol electrooxidation on Ni_xPd_{1-x} catalysts occurs in the potential region where the oxidation of Ni²⁺ to Ni³⁺ takes place (Figure 5.5, red line). As earlier proposed^{2,16,21,33,34}, the active surface species for glycerol electrooxidation is β -NiOOH and its formation is needed before glycerol oxidation can occur. The “indirect” electron transfer mechanism, initially proposed by *Fleischmann et al.*³⁴ for oxidation of organic compounds, combines electrochemical formation of NiOOH following by chemical oxidation of organics by Ni oxyhydroxide with its concomitant reduction to Ni(OH)₂:³⁴



where R = glycerol.

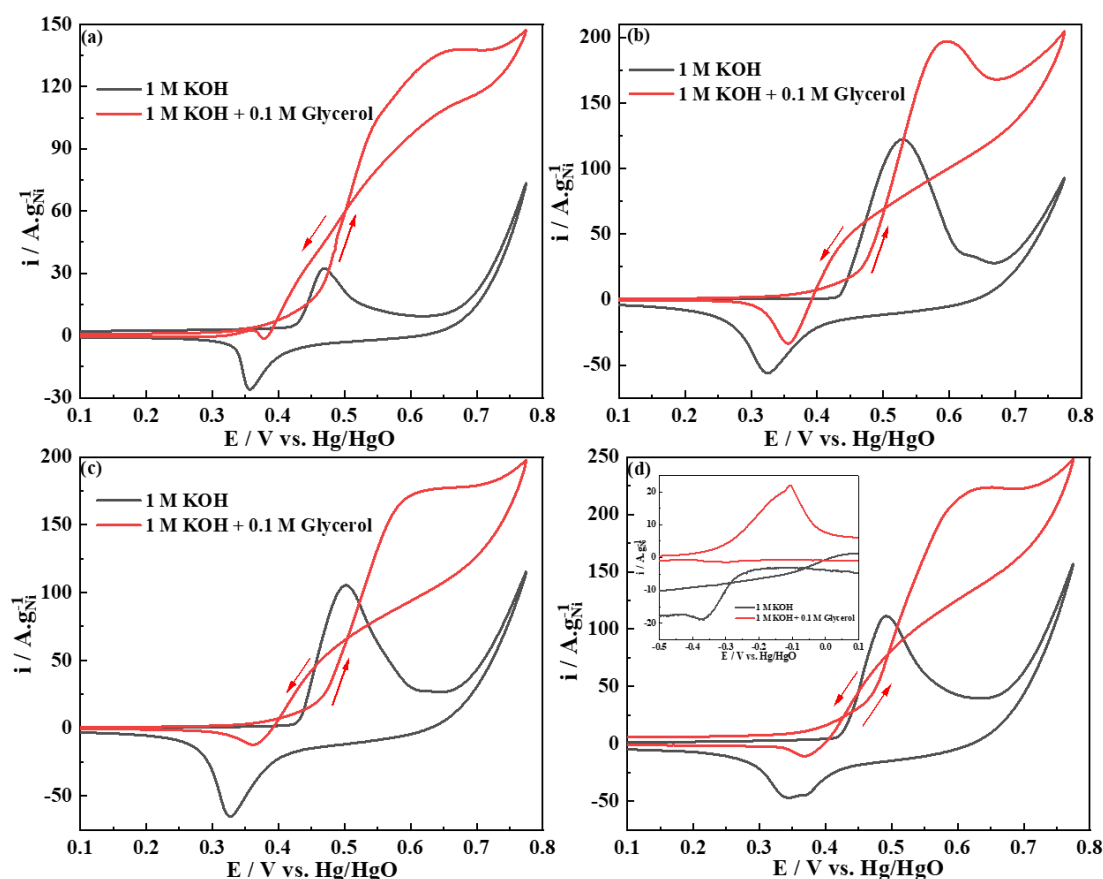


Figure 5.5. Cyclic voltammograms of $\text{Ni}_x\text{Pd}_{1-x}$ catalysts in 1 M KOH (black line) and in 1 M KOH + 0.1 M glycerol (red line): (a) Urchin-Ni, (b) $\text{Ni}_{95}\text{Pd}_5$, (c) $\text{Ni}_{90}\text{Pd}_{10}$ and (d) $\text{Ni}_{80}\text{Pd}_{20}$. Scan rate 50 mVs^{-1}

As seen from Figure 5.5 there is small cathodic peak for all catalysts in the glycerol containing solution suggesting that some NiOOH is chemically consumed by glycerol according to (5.3). This will be further discussed in the following section. The three bimetallic compositions showed higher mass activity towards GEOR if compare to urchin-Ni NPs. Among the different compositions, the $\text{Ni}_{80}\text{Pd}_{20}$ electrocatalyst showed the highest peak current density, reaching $220.5 \text{ mA mg}^{-1}_{\text{Ni}}$, if compared to $130 \text{ mA mg}^{-1}_{\text{Ni}}$ on Ni. For $\text{Ni}_{80}\text{Pd}_{20}$ catalyst an oxidation peak at -0.1V (Figure 5.5d inset, red line) corresponds to glycerol electrooxidation on Pd sites indicating that Pd alone has much lower oxidation potentials compare to Ni.^{35,36} This peak was only observed for larger Pd content of 20 at. % indicating some surface segregation of Pd phase.

The onset potential decreased with increase in Pd content as follows: 0.41, 0.36, 0.34 and 0.32V for Ni, Ni₉₅Pd₅, Ni₉₀Pd₁₀ and Ni₈₀Pd₂₀, respectively. Moreover, these overpotentials are lower than the ones reported for Ni nanoparticles supported on carbon (Ni/C).^{2,21,33} For Ni/C the GEOR started at 1.3 V vs. RHE in 0.1M KOH + 0.1M glycerol, while for Ni₈₀Pd₂₀ the corresponding value vs. RHE is 1.21 V. The earlier reported¹⁶ GEOR overpotentials on bulk Ni electrode in 1 M KOH + 0.1M glycerol before and after the treatment in ascorbic acid showed higher overpotentials of 1.33 V and 1.37 V vs. RHE, respectively, than the data obtained in this report.

5.3.3 Effects of glycerol concentration

The effect of glycerol concentration was investigated on the four catalysts. Figure 5.6 (a-d) shows the CVs recorded on the Ni and NiPd NPs in 1M KOH containing different concentrations of glycerol, ranging from 10 to 300 mM. Figure C1 in supplementary information (SI) illustrates a zoomed portion of the CVs in Figure 5.6. The current density of glycerol electrooxidation at ~0.62 V for four catalysts as a function of concentration are plotted in Figure 5.6e. At this potential only glycerol electrooxidation takes place and oxygen evolution reaction could be neglected, in particular, at lower glycerol concentrations.

The overall behavior of the four catalysts are similar: there is an increase of the current density with concentration up to 150 mM of glycerol (Figure 5.6e), following by a decrease of activity at 300mM. The current density decreased in the following order: Ni₈₀Pd₂₀ > Ni₉₅Pd₅ > Ni₉₀Pd₁₀ > Urchin-Ni. Moreover, when increasing the glycerol concentration, the OER shifts toward more positive potentials. This could be due to the stronger interaction of glycerol with high valence Ni species than with hydroxyl species (OH⁻).^{2,15,33} Such electrochemical behavior was already observed in the oxidation of glycerol²¹, isopropanol³⁷, acetyl salicylic acid³⁸ on a nickel electrode surface.

At the same time, the cathodic peak decreases with concentration increase for all the catalysts. The peak almost disappears at 100 mM for Ni Figure 5.6a. and at 150 mM for NiPd catalysts. This indicates the change in the oxidation mechanism. At higher concentrations (>100 mM), the indirect oxidation mechanism takes place, whereas at lower glycerol concentration this mechanism is direct, where glycerol molecules incorporate into Ni hydroxide surface and become oxidized by the surface OH⁻ ions.

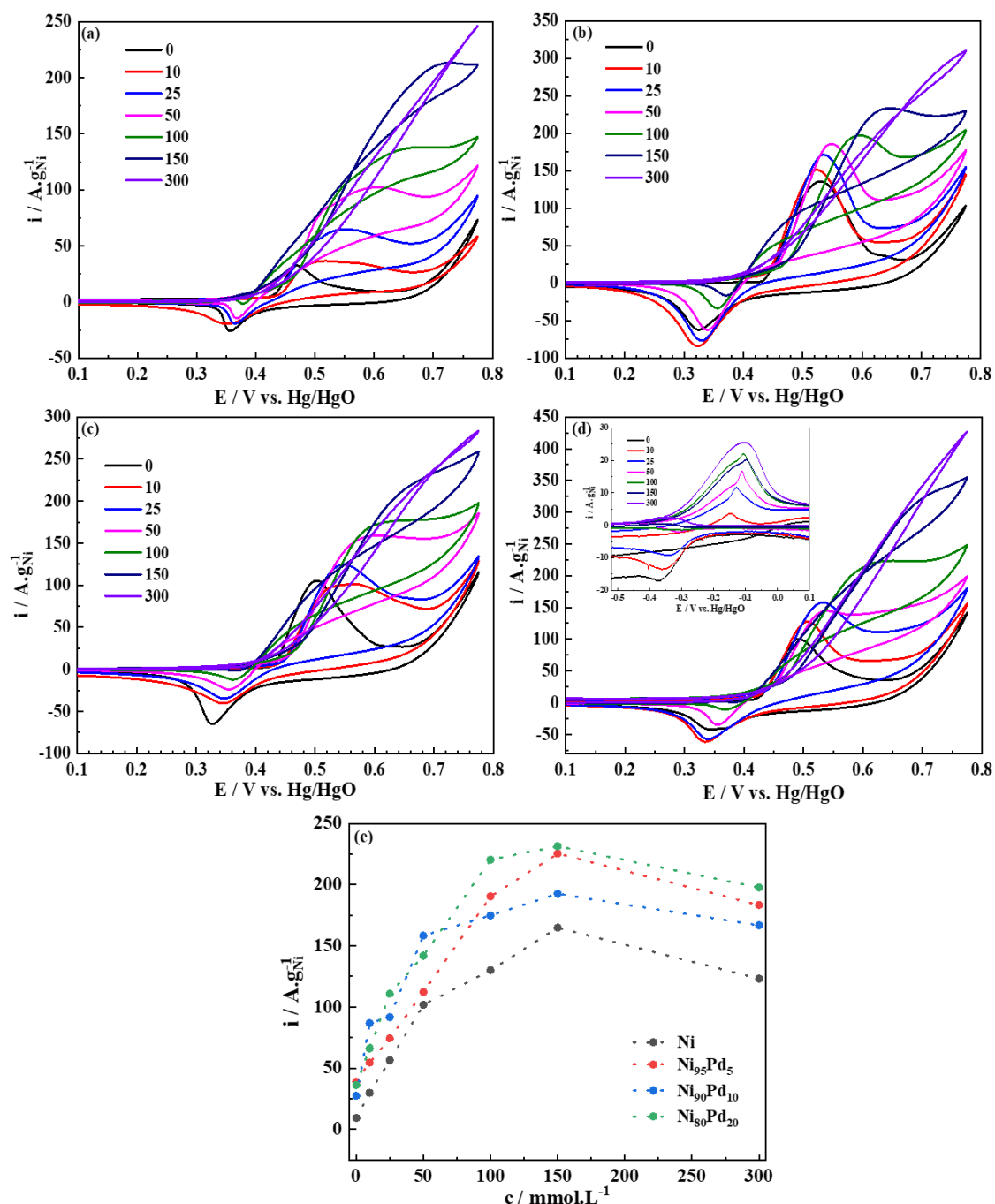
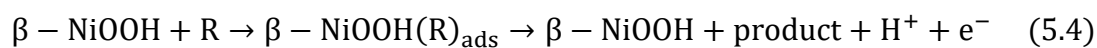


Figure 5.6. Cyclic voltammograms of (a) Ni, (b) Ni₉₅Pd₅ (c) Ni₉₀Pd₁₀ (d) Ni₈₀Pd₂₀ and (e) comparison of the glycerol electrooxidation current density on four catalysts in 1M KOH + x mM glycerol as indicated in the figure at 0.62V.

In this case, NiOOH is not consumed in the reaction and the cathodic reduction peak will be present on the CV ^{32,39}:



It is clear that the reaction rate of the direct electron transfer (5.4) vs indirect electron transfer (5.3) pathways depends on the glycerol electrooxidation concentration in the electrolyte. At high glycerol concentration ranging from 100 to 300 mM for (Ni-urchin) and from 150 to 300 mM for ($\text{Ni}_x\text{Pd}_{1-x}$ catalysts), when all active sites are saturated by glycerol, direct mechanism takes place as illustrated in Figure 5.6 and SI 5.1.

5.3.4 Identification of glycerol electrooxidation products using in-situ PM-IRRAS

In-situ PM-IRRAS measurements were carried out simultaneously with CAs at various anodic potentials. Figure C2 shows the chronoamperograms on $\text{Ni}_x\text{Pd}_{1-x}$ catalysts in between 0.34 and 0.54 V vs. Hg/HgO for 30 min. Figure 5.7 (a-h) summarizes PM-IRRAS spectra collected during CA measurements at 0.34, 0.42, 0.44, 0.52 and 0.54 V vs. Hg/HgO. PM-IRRAS measurements simultaneously record spectra in the bulk solution (measured by the average absorption intensities of s- and p- polarized light, left-hand side of Figure 5.7) and spectra corresponding to the electrode surface (measured by the difference absorption intensities of s- and p- polarized light, right-hand side of Figure 5.7).^{16,24} A typical spectra confirming the absence of water vapor and atmospheric CO_2 in the optical path are shown in Figure C3.

Figure 5.7 (a,c,e,g) and (b,d,f,h) show the bulk and surface species at various applied potentials, respectively. The potentials were chosen from the different regions of the CV profile (Figure 5.5) and are meant to shed more insights of the reaction dynamics and/or intermediates/products at those regions. The surface species spectra look quite noisy, compared with the bulk solution spectra due to the dynamic activities that occur on the electrode surface during glycerol oxidation. Positive and negative bands shown in the spectra are associated with species formation and consumption during GEOR, respectively. For Ni, $\text{Ni}_{95}\text{Pd}_5$ and $\text{Ni}_{90}\text{Pd}_{10}$, glycerol oxidation products appear at 0.34V and the bands increase with potential. For $\text{Ni}_{80}\text{Pd}_{20}$, oxidation products were already detected at -0.25V, corresponding to glycerol oxidation on Pd phase in agreement with CVs (Figure 5.5 and 6 insets). Several bands corresponding to different products could be identified: formate ion ($1355, 1390$ and 1585 cm^{-1}) and glycolate ion (1355 and 1070 cm^{-1}).^{21,40-42} The band at 1585 cm^{-1} was attributed to the stretching of COO^- associated with the formation of glycerate, oxalate, tartronate, mesoxalate ions.³¹ Furthermore, this band could be influenced by H_2O bending vibration that cannot be excluded.⁴³⁻⁴⁵

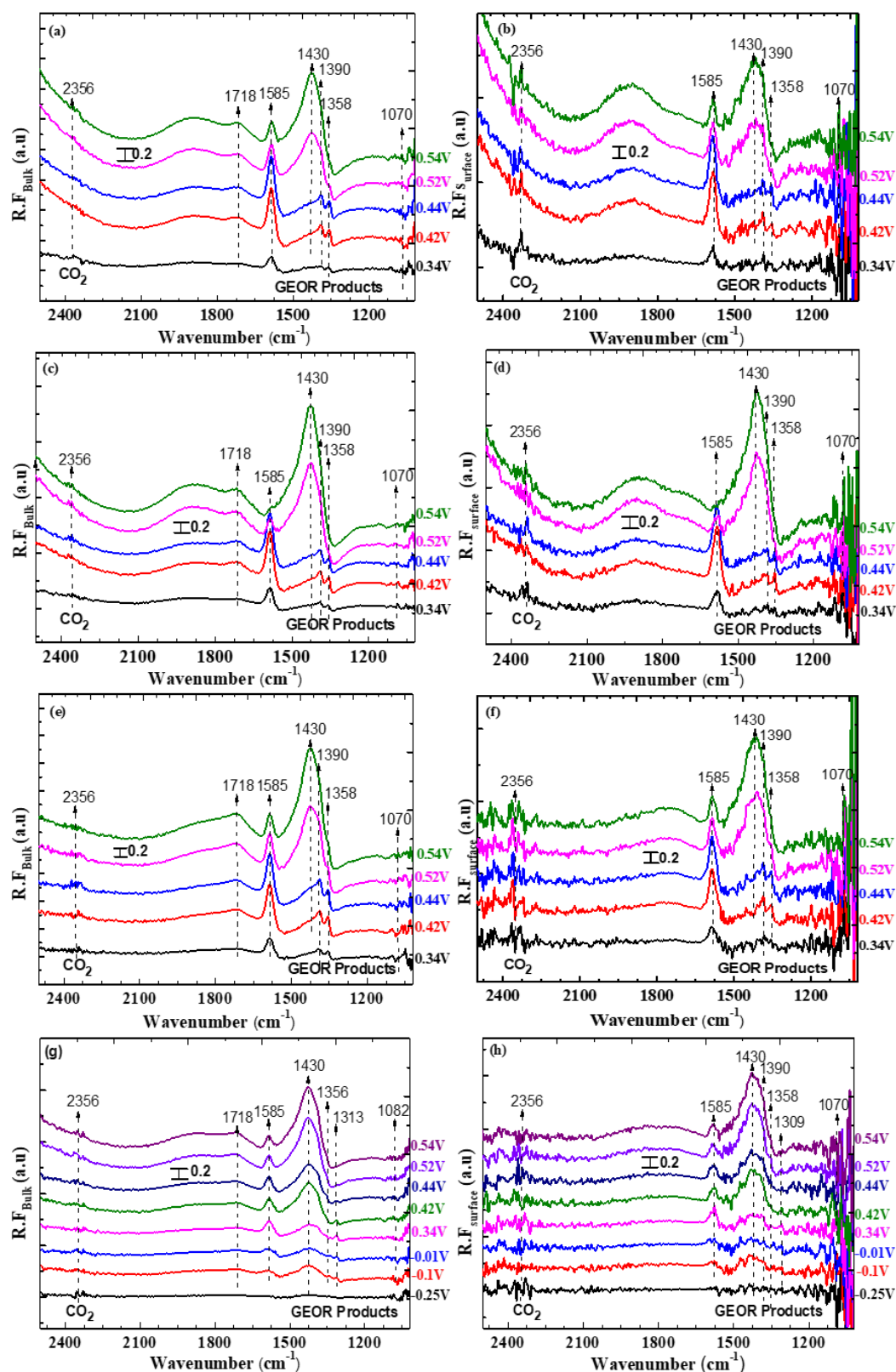
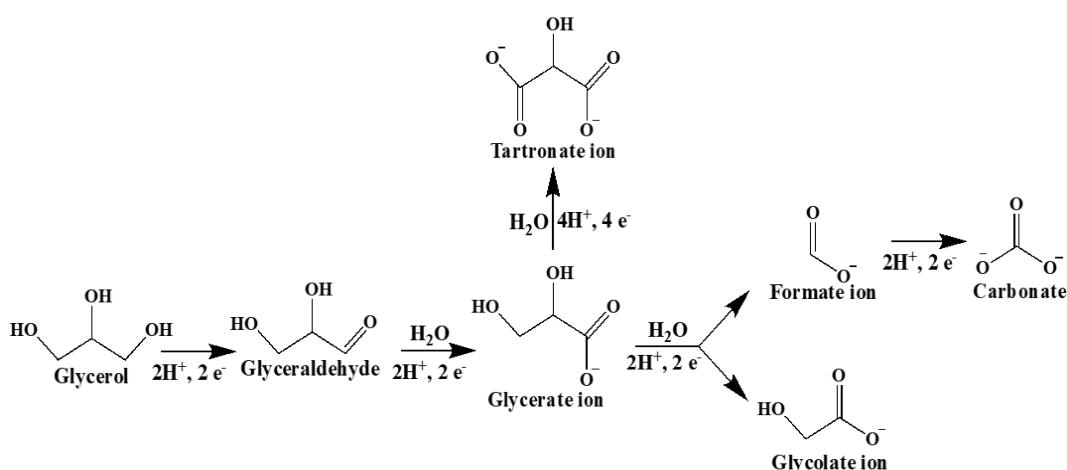


Figure 5.7. PM-IRRAS spectra during glycerol electrooxidation on (a,b) Ni (c,d) Ni₉₅Pd₅, (e,f) Ni₉₀Pd₁₀ and (g,h) Ni₈₀Pd₂₀ in 1M KOH+0.1 M glycerol at various Potentials as indicated in the figure. The left-hand spectra illustrate oxidation species in the thin cavity/bulk solution, while the right-hand spectra illustrate oxidation species on the surface.

The stretch mode at 1585 cm^{-1} also could be attributed to acyl intermediate species, which binds to the metal coordination through the carbon of the $\nu(\text{C}=\text{O})$ as reported earlier for Pt (111) in alkaline media.⁴⁶ Similar behavior was also detected by McManus et al. when glyceraldehyde was thermally decomposed on Pt (111) surface with a $\nu(\text{C}=\text{O})$ acyl stretch mode centered at 1595 cm^{-1} .⁴⁷ The broad band at 1720 cm^{-1} is characteristic of the $\text{C}\equiv\text{O}$ stretching vibration of a $\text{C}-\text{COO}^-$.^{2,33,44} CO_2 production (at 2353 cm^{-1} - asymmetric stretching peak) could be distinguished on the spectra corresponding to the thin cavity/bulk solution and on the surface. Maximum CO_2 is produced at 0.34 V; however, this amount remains constant with increasing potential. The CO_2 appearance in alkaline medium is an indication of the depletion of OH^- in the thin layer configuration due to change in the interference pH since CO_3^{2-} cannot be further produced.^{21,46} An additional broad peak 1430 cm^{-1} starts to appear at 0.52 V. This peak could correspond to the carboxylate group and carbonate. The band at 1720 cm^{-1} is mostly present in the solution indicating that the formed (tartronate and mesoxalate) desorbs from the surface. It should be noted that addition of Pd do not influence Ni selectivity and the same peaks are seen for all catalysts.

The proposed reaction mechanism of GEOR is summarized up on Scheme 5.1. Clearly, Ni-urchin and $\text{Ni}_x\text{Pd}_{1-x}$ NPs present a complex reaction pathway and generate various intermediate species with the exchange of electrons.



Scheme 5.1. Proposed reaction mechanism for glycerol electrooxidation on $\text{Ni}_x\text{Pd}_{1-x}$ catalysts in alkaline media based on the literature.

Initially, glycerol is oxidized to glyceraldehyde which is further oxidized to glycerate. Afterwards, glycerate is oxidized to tartronate or C-C bond cleavage forming

formate and glycolate. Finally, the formate leads to the formation of carbonate. These mechanistic hypotheses are in agreement with previous studies.^{2,16,33} However, based on our HPLC analysis for carbon supported Ni-based catalysts, glycerol is only highly selective towards formate, these data will be published separately in near future.

5.4 Conclusion

Mono- and bi-metallic $\text{Ni}_x\text{Pd}_{1-x}$ ($x = 100, 95, 90$ and 80 at.%) nanoparticles were synthesized using a polyol method. Based on EELS mapping for $\text{Ni}_{90}\text{Pd}_{10}$ at very high spatial resolution, the palladium is mostly present in the core of the NPs, although some particles do not have Pd signals, suggesting heterogeneous distribution at the finer scale. Addition of Pd enhanced the mass activity of glycerol electrooxidation. Among $\text{Ni}_x\text{Pd}_{1-x}$ catalysts with different ratios, the $\text{Ni}_{80}\text{Pd}_{20}$ had the highest current density and lowest onset potential for GEOR. At low concentration of glycerol ≤ 100 mM for Ni, and ≤ 150 mM for $\text{Ni}_x\text{Pd}_{1-x}$ catalysts, the GEOR followed the direct electron pathway. At higher glycerol concentrations, the opposite trend is observed and the indirect electron pathway took place. In-situ PM-IRRAS measurements showed that main products are glyceraldehyde, carbonyl and carboxylate ions. No significant changes in the product selectivity were found for NiPd compared to monometallic Ni. Overall, this work demonstrates that Ni and low-Pd content NiPd nanoparticles are attractive electrocatalysts for electrochemical valorization of glycerol in alkaline media.

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Supplementary Information C: Chapter 5

Figure C1 demonstrates a zoomed portion of the CVs in Figure 5.6.

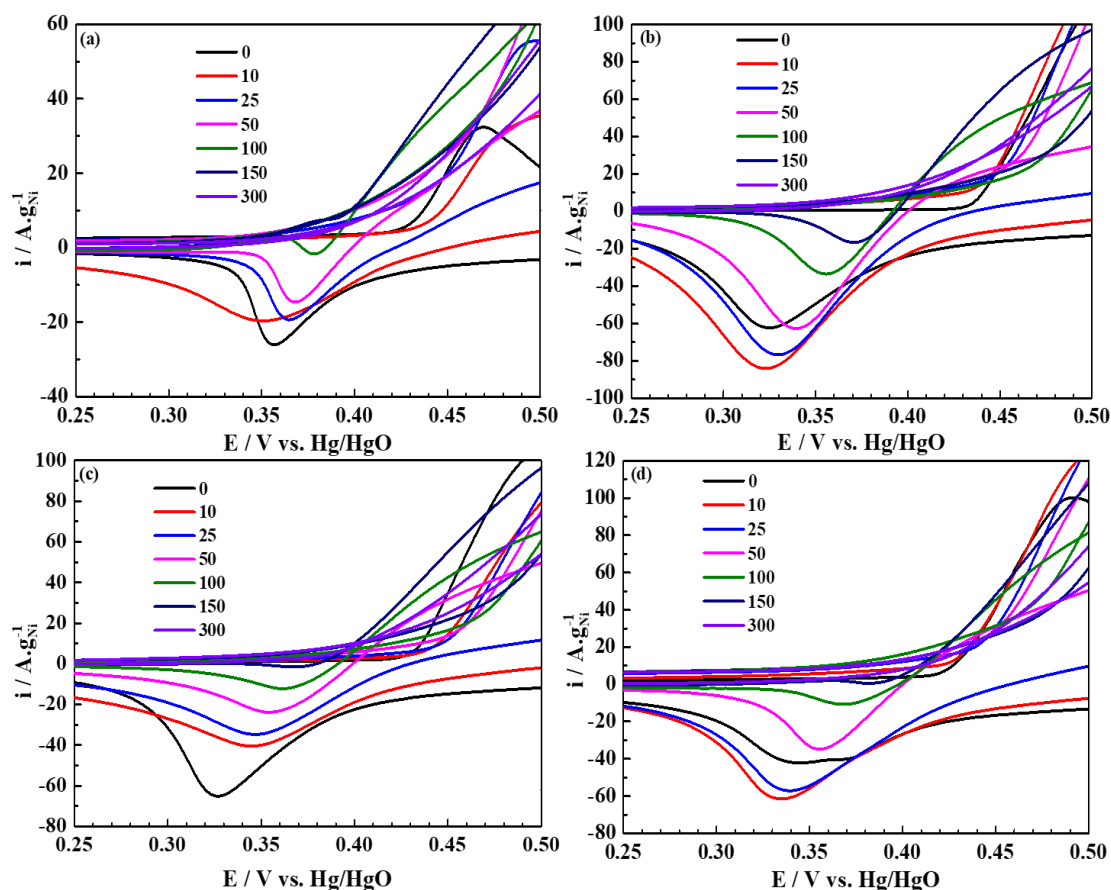


Figure C1. Cyclic voltammograms of (a) Ni, (b) Ni₉₅Pd₅ (c) Ni₉₀Pd₁₀ and (d) Ni₈₀Pd₂₀ in 1M KOH + x mM glycerol (x = 10, 25,..., 300) at 50 mVs⁻¹.

Figure C2 shows the resulting current– time CA response, in which the potential was stepped up from 0.34 to 0.54 V vs. Hg/HgO, while collecting spectra at each potential in increments of 10 min for 30 min as illustrated in Figure 5.7 (a- h).

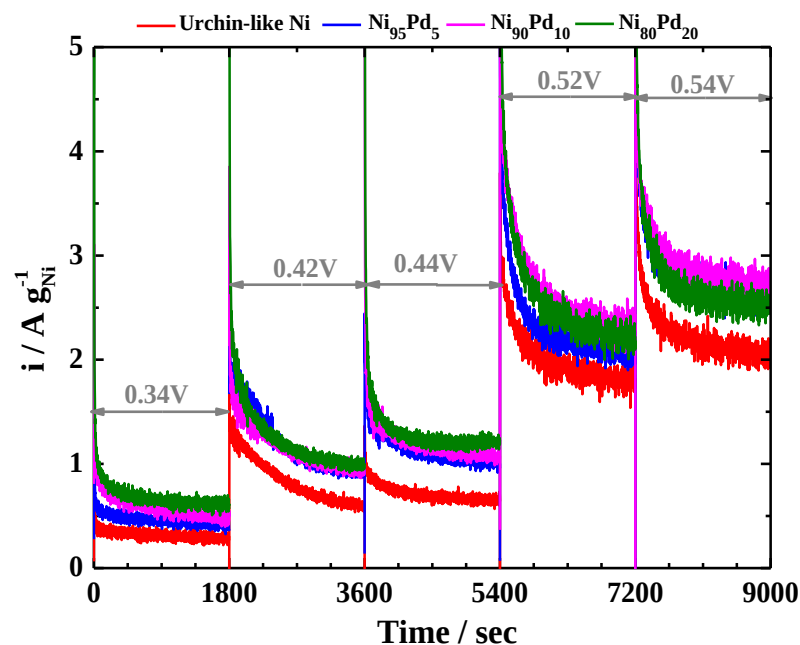


Figure C2. CA profile in 1M KOH+0.1M glycerol at different potentials, as specified by the double arrows for PM-IRRAS spectra.

Figure C3 illustrates the tracking level of CO₂ background at different time intervals before the actual measurements are initiated. The CO₂ level (negative peak at 2345 cm⁻¹) in surface and bulk species spectra are removed during purging dry air.

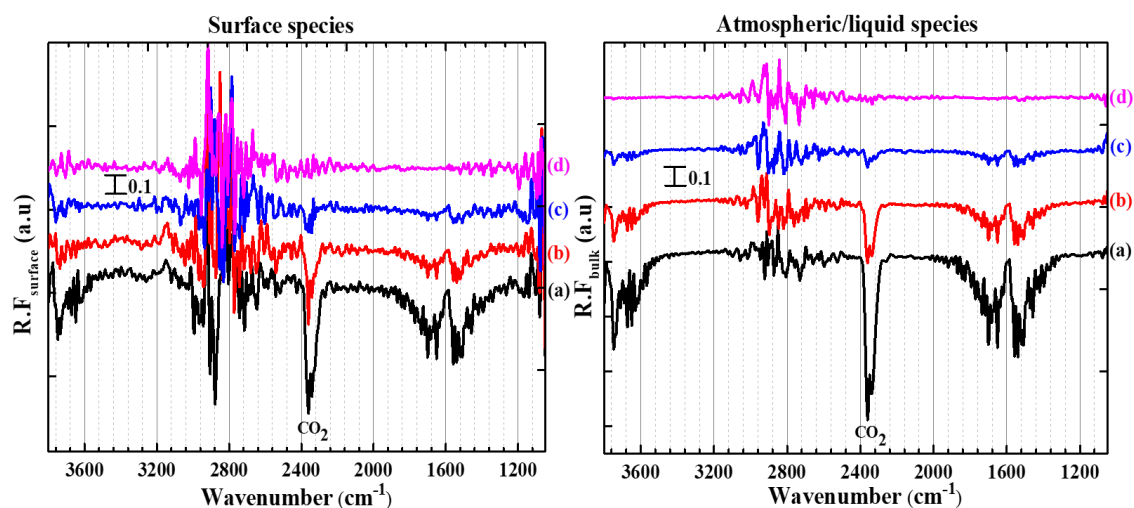


Figure C3. CO₂ tracking level background PM-IRRAS spectra of Ni-based catalyst in 1M KOH+0.1 M glycerol at open circuit potential (OCP); (a) 1.5 hrs., (b) 1 hr., (c) 30 min, and (d) 3min before measurements were initiated.

Chapter 6

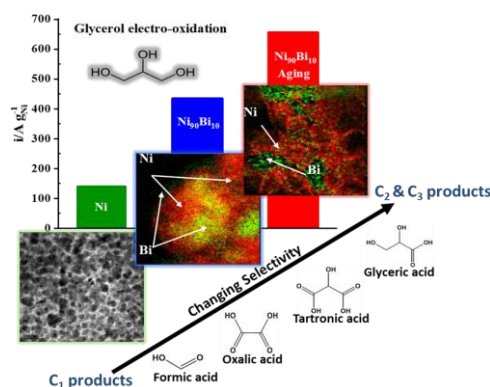
6 Modification of Nickel Surfaces by Bismuth: Effect on Electrochemical Activity and Selectivity Towards Glycerol

Based on the paper:

Houache M. S. E., Hughes K., Safari R., Botton G. A., Baranova E. A., ACS Applied Materials & Interfaces, 2020, 12(13), 15095-15107

Abstract

Herein we study the effect of adding Bismuth to Ni-nanostructured catalysts ($\text{Ni}_x\text{Bi}_{1-x}$, $x = 100 - 90$ at. %) for glycerol electrooxidation in alkaline solution by combining physiochemical, electrochemical and in-situ infrared spectroscopy techniques, as well as continuous electrolysis with HPLC product analysis. The addition of small quantities of Bi (< 20 at. %) to Ni nanoparticles led to significant activity enhancement at lower overpotentials, with $\text{Ni}_{90}\text{Bi}_{10}$ displaying the over 2-fold increase compared to Ni. Small quantities of bismuth actively affected the reaction selectivity of Ni by suppressing the pathways with C–C bond cleavage, hindering the production of carbonate and formate and improving the formation of tartronate, oxalate and glycerate. Furthermore, the effect of aging on $\text{Ni}_x\text{Bi}_{1-x}$ catalysts was investigated, resulting in a structural modification from the Ni-Bi double-shell/core structure to Bi decorated on folded Ni sheet, thus enhancing their activity twice after two weeks aging. NiBi catalysts are promising candidates for glycerol valorization to high-value added products.



6.1 Introduction

Biodiesel is recognized as a renewable alternative to conventional fossil diesel. Its global production increased significantly and produced a surplus of glycerol waste, which is a by-product (10 wt.%) of the biodiesel production.¹ The urgent need for new applications of glycerol has therefore inspired researchers from various scopes to investigate on this topic.²⁻⁵ In this context, electrochemical technologies are one of the promising approaches in using glycerol on anodes in the upcoming utilizations: (i) direct

glycerol fuel cell (DGFC): main purpose is producing electrical energy and (ii) electrolysis: generating valuable chemicals on the anode with cathodic H₂ generation or CO₂ electro-reduction processes.^{3,4} These value-added chemicals without C-C-C bond cleavage have a higher price than glycerol in a ratio of 500 in the case of tartronic acid, as it could be utilized in pharmaceutical and industrial manufacturing.⁶

Many studies have been published about glycerol electrooxidation reaction (GEOR) on noble metals, mainly in alkaline media and using different morphologies, promoters and supports.⁶ Based on their results, the authors demonstrated that the modification of the surface composition with a specific quantity of adatoms could improve the electrocatalytic activity and selectivity of a given electrode. Specifically, the adsorption effect of p-group metal promoters i.e. bismuth (Bi)⁷⁻¹², antimony (Sb)¹²⁻¹⁶, tin (Sn)¹⁷⁻²⁰ and lead (Pb)^{21,22}, on platinum and palladium electrodes toward glycerol electrooxidation has been widely investigated. However, the promotion role of Bi on Pd or Pt catalysts towards alcohol oxidation is still under debate. Hence, several interpretations for the Bi promoters have been proposed: (i) the formation of an alloy²³⁻²⁵, (ii) corrosion inhibition of the metal catalysts²⁵, (iii) active site blockage^{26,27}, (iv) formation of Bi-OH_{ads}^{28,29} as new active center and (v) interaction with the enediol intermediate structure.^{30,31}

Although our research will be focused on NiBi un-supported materials, it is worthwhile to indicate various published manuscripts using noble nanoparticles that inspired us to develop this research. Coutanceau's group utilized carbon supported Pd, Pt, PdBi, PtBi and PdPtBi NPs and *in situ* FTIR measurements to study GEOR in alkaline media.^{32,33} They observed lower overpotential values with different selectivity, depending on the electrode potential. Based on the long-term electrolysis and HPLC analysis, they detected oxalate and formate at high potentials (>0.8 V vs.RHE), whereas at lower potentials the reaction products were mainly dihydroxyacetone, tartronate and glycerate. The same group synthesized controlled shapes of Pd NPs (cubes, spheres and octahedrons) and modified their surfaces by Bi adsorption.⁸ The electrochemical results did not illustrate any significant alteration in activity with Bi addition; however, *in situ* spectroscopy displayed modification in the GEOR pathways. Recently, *Fernández et al.*,³⁰ reported an increase of polycrystalline platinum (Pt_p) activity by 5-fold when 10⁻⁵ M of Bi ions were added to the solution. Bi-decorated Pt surface has suppressed the triple

carbon breakage, hindering the carbon monoxide formation, resulting in an enhancement of glycerate and dihydroxyacetone (DHA) formation in alkaline and acidic media, respectively. Additionally, in acidic media a couple of studies by *Koper et al.*,^{34,35} were carried out on the performance of Pt electrodes modified by Bi for GEOR. In a first study, the authors reported a carbon supported Pt electrode that, after pre-treatment in a Bi saturated solution, is capable of oxidizing glycerol to DHA with 100% selectivity.³⁴ In this study, they showed that Bi blocks the pathway for primary alcohol oxidation and favors the oxidation of the secondary alcohol. Further investigations into the role of bismuth's irreversible adsorption on Pt single-crystal electrodes has on the oxidation of glycerol indicated that on Pt (111) electrode, Bi has a beneficial effect, improving the activity for the reaction by preventing the adsorption of CO₂. Whereas on Pt (100) Bi modification promotes a strong adsorption of glycerol resulting in an activity reduction.³⁵ Besides, interaction of Bi with a key intermediate in the isomerization reaction between glyceraldehyde and DHA increases the selectivity to DHA on Pt (111), but on Pt (100), since this intermediate does not exist, there is no change in the tendency towards glyceraldehyde formation.³⁵

Ni-based materials have been utilized as an electro-catalyst for oxidation of different organic and inorganic molecules such as, ethanol³⁶, methanol³⁷, glycerol^{36,38} and ammonia.³⁹ Particularly Ni nano-catalysts for GEOR were studied in a few publications and the oxidation products in alkaline medium have been identified using in-situ infrared spectroscopy and HPLC analysis, with glycerate, tartronate, glycolate, oxalate and formate as main reaction products.^{38,40-42} Furthermore, studies with Ni-M catalysts (M = Pd, Fe, Co) have showed that the catalytic performance and the distributions of the products is affected by composition of the catalyst.^{40,43} Based on literature, no work has been done on Ni-Bi catalysts for glycerol electrooxidation, however, the influence of Bi on the electro-catalytic performance of Ni to glucose oxidation was reported recently.⁴⁴

Although there are several previous studies on Bi-modified Pt-group metal electrocatalysts for GEOR, which are expensive and scarce. Therefore, our present work shifts towards cheaper and more abundant non-noble Ni_xBi_{1-x} (x = 100, 98, 95 and 90 at.%) nano-catalysts. Various physicochemical and electrochemical measurements were carried out on Ni_xBi_{1-x} catalysts in combination with *in-situ* polarization modulation

infrared-reflection absorption spectroscopy (PM-IRRAS) and high-performance liquid chromatography (HPLC) measurements for reaction product analysis.

6.2 Experimental section

6.2.1 Materials

Nickel (II) chloride hexahydrate (99.999%, Sigma-Aldrich) and sodium borohydride ($\geq 98\%$, ACROS). Bismuth chloride (99.99%) and ethanol (99%) were both supplied by Fisher Scientific. Ultrapure de-ionized water was utilized to prepare all solutions.

6.2.2 Preparation of $\text{Ni}_x\text{Bi}_{1-x}$ nanoparticles

At room temperature, $\text{Ni}_x\text{Bi}_{1-x}$ ($x = 100, 98, 95, 90$ at.%) nanoparticles (NPs) were synthesized by sodium borohydride (NaBH_4) in the presence of ethanol. Initially, the nickel chloride hexahydrate ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$) salt precursor was dissolved in ethanol for 30 min until it was homogenized. For bi-metallic, bismuth chloride (BiCl_3) precursor was dissolved in ethanol using similar approach. Then, the aqueous solutions of NiCl_2 and BiCl_3 were stirred and diluted to 50 mL by ethanol. The combined solution was mixed in the air environment for 10 minutes to ensure the solution was homogenous. A 2 wt.% of Sodium borohydride was then dissolved in minimal quantities of ethanol with 100% stoichiometric excess was dropped slowly to the reagents. The resulting solution was kept mixing for 30 min to assure a complete reduction of the salt precursors. Finally, $\text{Ni}_x\text{Bi}_{1-x}$ catalysts were rinsed with ethanol three times and centrifuged for 15 minutes per wash at (6000 rpm). The samples were dried overnight in a freeze dryer to remove all residual ethanol.

6.2.3 Physicochemical characterization

The detailed procedures of different physicochemical techniques (XRD, TEM, XPS, SAED, HAADF, EDS and EELS) were reported previously.^{38,45}

6.2.4 Electrochemical and in-situ PM-IRRAS measurements

The detail procedure of electrochemical characterization and IR spectroscopy measurements and interpretation equations were reported previously.^{38,45,46}

6.2.5 Continuous electrolysis measurements

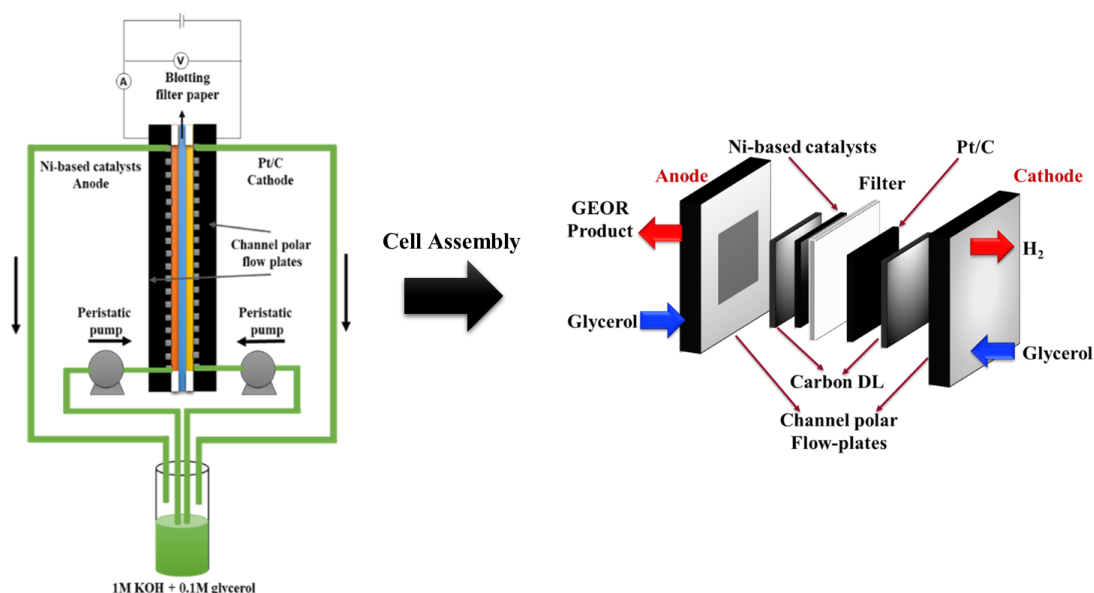
GEOR electrolysis measurements were carried out in a 25 cm² membraneless electrolysis cell comprised of unsupported (Ni, Ni₉₀Bi₁₀ and Ni₉₀Bi₁₀aging) anode (2 mg_{Ni_xBi_{1-x}}.cm⁻²) and a Pt/C cathode (2 mg_{Pt}.cm⁻²), both detached by a filter paper (WhatmanTM) and expanded Teflon gasket (DICHATOMATIK CANADA INC.), then mechanically compressed in the GEOR cell. Both compartments were fed continuously at 50 rpm (flow rate = 1.6 ml/sec) with 100 ml solution containing 1 M KOH and 0.1 M glycerol. The current was obtained for 6 hrs. at cell potential of (1.3, 1.4 and 1.55 V), using Hokuto Denko HA-303 potentiostat equipped with LabView software. Scheme 6.1 illustrates representation diagram of GEOR electrolysis measurements. A 600 µl aliquot was taken at (30 min, 1hr, 2hrs, 3hrs and 6hrs), these 5 samples were analyzed by High Performance Liquid Chromatography (HPLC) instrument, equipped with ion-exclusion column (Aminex HPX-87H), UV–Vis detector ($\lambda = 210$ nm) followed by a refractive index detector (IOTA2). The column was heated to 50 °C and the analytes were separated with diluted sulfuric acid (5 mM H₂SO₄) used as eluent. The expected standards were prepared from DL-glyceric acid (20% in water, TCI), formic acid (99%), glycolic acid (99%), oxalic acid (99%), tartronic acid ($\geq 97\%$) and DL-lactic acid (85%) were supplied by Sigma–Aldrich. The standards were dissolved in 1M KOH with varying concentrations from 0.02 M to 0.12 M (with increments of 0.02 M) and neutralized with 5mM H₂SO₄. The glycerol conversion and product selectivity are calculated by the following equations ⁴⁷:

Conversion of glycerol

$$= 1 - \left(\frac{\text{concentration of glycerol at certain time}}{\text{Initial concentration of glycerol}} \right) \times 100\% \quad (6.1)$$

Selectivity of one C₃, C₂ or C₁ product

$$= \left(\frac{\text{moles of C}_3, \text{ C}_2 \text{ or C}_1 \text{ product}}{\text{total moles of C}_3, \text{ C}_2 \text{ or C}_1 \text{ product}} \right) \times 100\% \quad (6.2)$$



Scheme 6.1. Representation diagram of GEOR electrolysis cell designed for the potentiometry measurements

6.3 Results and discussion

6.3.1 Synthesis and structural characterization of $\text{Ni}_x\text{Bi}_{1-x}$ NPs

Figure 6.1a shows representative TEM images of the as-prepared unsupported Ni NPs. The morphology of the NPs is predominantly spherical with a size distribution of 9.2 ± 2.4 nm, in accordance with 100 selected particles (Figure 6.1b). Moreover, selected area electron diffraction (SAED) analysis reveals a set of full rings, indicating that the spherical Ni nanoparticles have high crystallization degree (Figure 6.1c). The XRD pattern of spherical Ni as displayed in Figure 6.1d consists of four characteristic peaks at approximately 33.78° , 44.65° , 59.99° and 70.68° 2θ corresponding to $\beta\text{-Ni}(\text{OH})_2$ (100), Ni (111), $\beta\text{-Ni}(\text{OH})_2$ (110) and $\beta\text{-Ni}(\text{OH})_2$ (103), respectively.⁴⁸ To gain further information about the chemical composition and surface electronic state of Ni NPs, Figure 6.1e, shows the Ni 2p XPS spectrum. It can be seen that the as-prepared Ni surface consists of oxides and hydroxides and no metallic Ni was detected. The peaks at 873.8 and 856.1 eV correspond to $\text{Ni}(\text{OH})_2$ with two additional satellite peaks positioned at 880 and 861.9 eV.^{49,50}

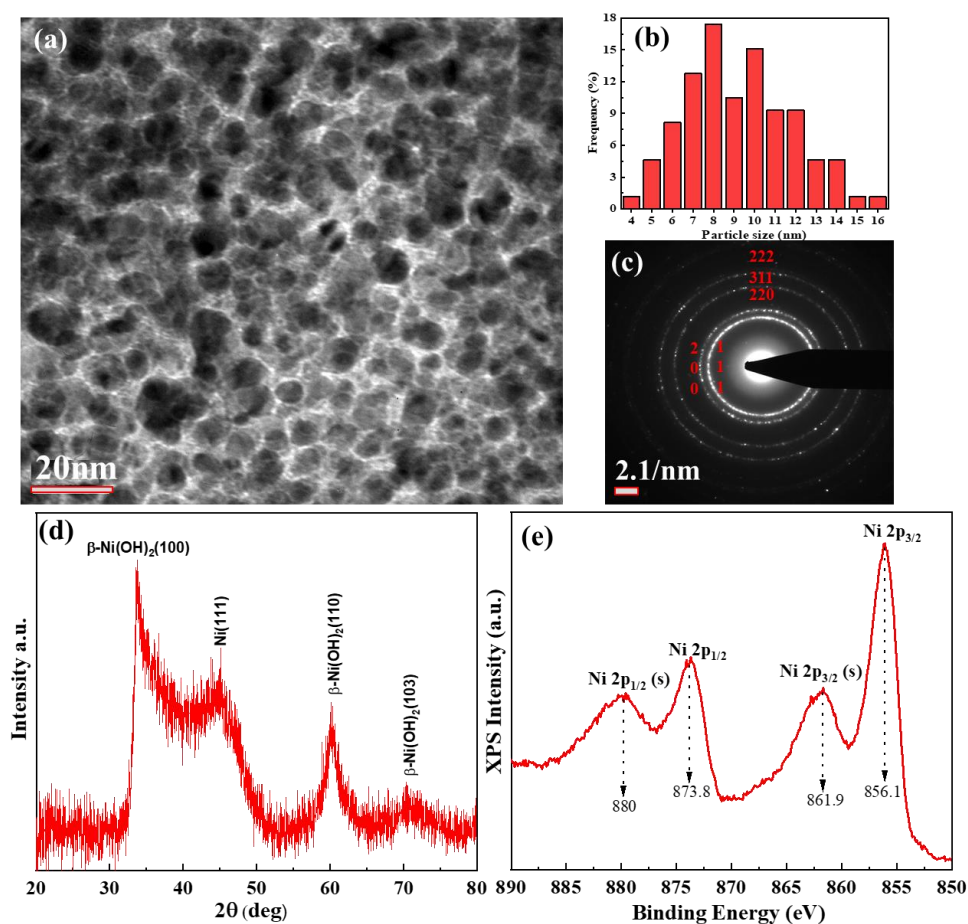


Figure 6.1. (a) TEM image of spherical Ni nanoparticles, (b) Ni particle size distribution histograms, (c) Marked SAED patterns, (d) XRD pattern and (e) High resolution XPS spectrum for the Ni 2p peak.

The $\text{Ni}_x\text{Bi}_{1-x}$ NPs with different composition ($\text{Bi} = 2, 5$ and 10 at.%) were prepared with a similar methodology to the spherical Ni nanoparticles. As will be discussed later, the $\text{Ni}_{90}\text{Bi}_{10}$ catalyst showed the highest activity towards GEOR. Hence, the physicochemical characterizations of this material are shown in Figure 6.2, while the characterization of other samples is illustrated in the supporting information (Figure D1 in SI). The TEM micrograph of $\text{Ni}_{90}\text{Bi}_{10}$ (Figure 6.2a) revealed the presence of two types of particles. Small spherical particles with mean size of 4.7 ± 1.17 nm (Figure 6.2b), decorating the surface of the latter with some aggregates in range of 15–40 nm, which could be due to strong attractive magnetic force between colloids.⁴⁵ Nevertheless, the presence of Bi reduced the catalyst size by almost half compared to spherical Ni.

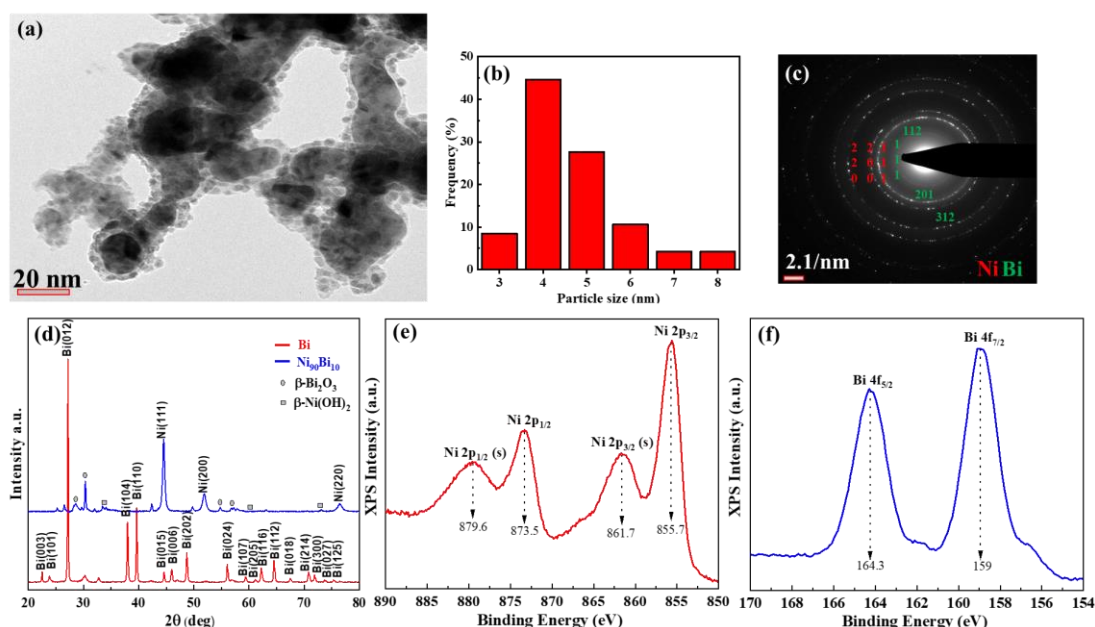


Figure 6.2. (a) TEM image of spherical $\text{Ni}_{90}\text{Bi}_{10}$ nanoparticles, (b) Particle size distribution histograms, (c) Marked SAED patterns, (d) XRD pattern of Bi and $\text{Ni}_{90}\text{Bi}_{10}$, XPS spectrum for (e) Ni 2p and (f) Bi 4f.

Moreover, the SAED pattern in Figure 6.2c illustrated annular Ni face-centered cubic (*fcc*) and rhombohedral Bi diffraction rings, corresponding to a polycrystalline feature of the 3D structure. The XRD patterns are displayed in Figure 6.2d for the as-prepared pure Bi and $\text{Ni}_{90}\text{Bi}_{10}$. The pure bismuth 2θ values are in agreement with (JCPDS # 85–1329) data, confirming 18 characteristic peaks in the rhombohedral system.⁵¹ For $\text{Ni}_{90}\text{Bi}_{10}$ catalyst, in addition to the three representative peaks of the *fcc* Ni structure at approximately 44.54, 51.78 and 76.4° 2θ , other peaks were observed indicating the presence of $\beta\text{-Ni}(\text{OH})_2$ and Bi_2O_3 . XRD peaks corresponding to Bi_2O_3 are in agreement with (PDF-Nr.: 03-065-2366), revealing that it crystallizes in the monoclinic system and all the bismuth peaks disappeared.⁵² Figure 6.2 (e-f) presents XPS high resolution spectra of Ni 2p and Bi 4f regions, respectively. The Ni 2p region shows four main peaks at the binding energy of 855.7, 861.7, 873.5 and 879.6 eV, corresponding to Ni 2p_{3/2}, Ni 2p_{1/2} and two satellite peaks, respectively.^{49,50} The position of the peaks indicates that Ni surface is oxidized similar to the surface of monometallic Ni NPs. For the Bi 4f region, only two strong peaks were detected at 159 eV (Bi 4f_{7/2}) and 164.3 eV (Bi 4f_{5/2}), these values correspond to Bi³⁺ in Bi_2O_3 .⁵³ However, Ni 2p values are slightly shifted by (0.4 eV) to a lower binding energy compared to Ni. This negative shift could be attributed to the presence of Bi_2O_3 , which may influence the chemical environment of Ni-(OH)₂.

Figure 6.3a depicts the STEM-energy dispersive spectroscopy (EDS) mapping images for $\text{Ni}_{90}\text{Bi}_{10}$ to provide a visual representation of its elemental distribution. The Ni (shown in red) and O (shown in yellow) elements are well distributed in the selected area of $\text{Ni}_{90}\text{Bi}_{10}$ catalysts. However, the element Bi (green) is only present in more specific area of the catalyst, signifying the presence of large clusters in the sample, probably due to the synthesis methodology. EDS spectra are also in agreement with the elemental composition of $\text{Ni}_{90}\text{Bi}_{10}$, confirming the presence of the characteristic peaks of nickel, bismuth and oxygen. Furthermore, the spatial distribution of Ni, Bi and O ions gained from STEM-EELS analysis is mapped in Figure 6.3b. The core@shell structuration of the $\text{Ni}_{90}\text{Bi}_{10}$ NPs is clearly visible, with Bi ions exclusively located in the core region and Ni ions mostly confined in the shell region. This confirms the existence of the (Bi, O)-rich core, which acts as a heterogeneous nucleation agent for the (Ni,O)-rich outer shell to grow, resulting in smaller NPs compared to monometallic spherical Ni. It is important to observe that Bi is not solely in the core of the nanostructures. There is a small presence of Bi on the Ni shell, indicating the possibility of a Bi-core NiBi double-shell structure. The STEM-EELS spectrum images (Figure D2 in SI) also confirms the presence of the Ni $L_{2,3}$ signal at ~ 855 and Bi- $M_{4,5}$ signal at ~ 2600 eV. As mentioned earlier our catalysts consist of Ni and $\text{Ni}(\text{OH})_2$, as evidenced by XRD, SAED and XPS. For clarity, we are naming our catalysts Ni particles.

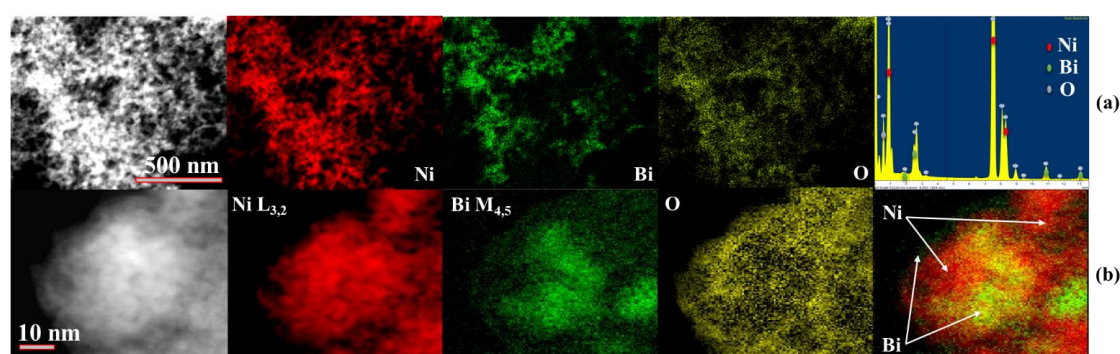


Figure 6.3. (a) HAADF-STEM image, STEM-EDS mapping images for Ni, Bi and O elements and EDS spectrum of $\text{Ni}_{90}\text{Bi}_{10}$ (b) STEM-EELS Map of Ni- $L_{3,2}$, Bi- $M_{4,5}$ and O.

6.3.2 Electrochemical characterizations

Figure 6.4a shows stable cyclic voltammograms (CVs) of $\text{Ni}_x\text{Bi}_{1-x}$ ($x = 100, 98, 95, 90$ at. %) in 1M KOH at 50 mV s^{-1} . In the case of data normalization for $\text{Ni}_x\text{Bi}_{1-x}/\text{C}$ materials, it is complex to evaluate the electro-active surface areas (ECSA) with the use

of a bi-metallic as the estimation involves many uncertainties.⁵⁴ Therefore, the currents were normalized per mass of the active Ni phase as illustrated in Figure 6.4. The comparison of current densities per the geometric area of the GC (0.196 cm²) is shown in Figure D3 in SI. The surface redox process of nickel in alkaline media is well established.⁵⁵⁻⁵⁷ The pair of peaks corresponds to Ni^{II}/Ni^{III} redox process, where anodic peak at ~ 0.55 V is due to β -NiOOH formation and the cathodic peak corresponds to its reduction to β -Ni(OH)₂. The addition of Bi results in more reversible redox process, as the separation between anodic and cathodic peak decreases from 0.59 to 0.54 and 0.33 to 0.27 for Ni and Ni₉₀Bi₁₀, respectively. Moreover, Ni_xBi_{1-x} catalysts showed higher current densities for Ni^{II}/Ni^{III} redox peak compared to Ni. This could be elucidated by the synergistic effect between Ni and Bi on each other's redox electrochemistry. Furthermore, the addition of bismuth had a positive effect on oxygen evolution reaction (OER). The current growth due to OER is initiated at ~ 0.67 and 0.7 V vs. Hg/HgO for Ni₉₀Bi₁₀ and spherical Ni, respectively. This phenomenon is likely due to the Ni-Bi double shell-core structure, which includes highly dispersed Bi clusters on the outer Ni shell, affecting the formation of the Ni^{III} phase. CVs of mono-metallic bismuth in the presence and absence of glycerol are shown in (Figure D4 in SI) as a reference. It can be seen that two anodic peaks at -0.5 and -0.34V vs. Hg/HgO are related with the oxidation of metallic Bi to Bi³⁺ according to the following equation:



where, the first anodic peak corresponds to the formation of a thin layer of Bi(OH)₃ sites at the electrode surface and the second peak is due to the thickening of the oxidized product Bi³⁺. (ii) A sharp cathodic peak at -0.85 V vs. Hg/HgO corresponds to the reduction of Bi³⁺.^{30,44}

CVs of Ni_xBi_{1-x} catalysts in the glycerol containing solution are shown in Figure 6.4b. Glycerol oxidation takes place in the region of NiOOH formation, in agreement with previous results of GEOR on Ni-based electrodes.^{38,45} The Ni₉₀Bi₁₀ showed the highest mass activity and the peak value reached (436.5 A.g⁻¹_{Ni} or 92.6 mA.cm⁻²), which is much higher than that of spherical Ni (122.4 A.g⁻¹_{Ni} or 28.9 mA.cm⁻²). The activity follows the order: Ni₉₀Bi₁₀ > Ni₉₅Bi₅ > Ni₉₈Bi₂ > Ni as shown in (Figure D3f in SI). The onset potential of GEOR with Ni_xBi_{1-x} catalysts occurred at a more negative value (~ 45 mV) compared to the spherical Ni catalyst, indicating an enhancement in oxidation

kinetics. In all of these catalysts, it has been seen that the GEOR clearly starts after the formation of β -NiOOH species, which is an electrochemically active phase for the oxidation of glycerol and other organic molecules.^{39,58-60}

The promotional role of the Bi atom is further shown in (Figure 6.4c). Linear sweep voltammetry (LSV) tests clearly indicate that glycerol electro-oxidation on the Bi-containing catalysts starts at lower onset potentials of ~ 0.44 V and attains higher current densities than on Ni. Chronoamperometry (CA) measurements carried out for 3600 sec at 0.48 and 0.52 V vs. Hg/HgO are shown in Figure 6.4 d-e. For all catalysts, the current shows an initial increase and rapid decay followed by stabilization at ~ 5.1 and $6.7 \text{ A g}_{\text{Ni}}^{-1}$ and ~ 12.8 and $20.3 \text{ A g}_{\text{Ni}}^{-1}$ for Ni and Ni₉₀Bi₁₀ at 0.48 and 0.52 V, respectively. Moreover, Ni₉₀Bi₁₀ had an initial current density of $\sim 120 \text{ A g}_{\text{Ni}}^{-1}$ with a drop-in activity to $\sim 45 \text{ A g}_{\text{Ni}}^{-1}$ after 8 min, likely attributed to current decay (Figure 6.4e). This phenomenon can be contributed to the active sites blockage by some reaction intermediates as well as to mechanical degradation of the catalyst ink deposited on glassy carbon.

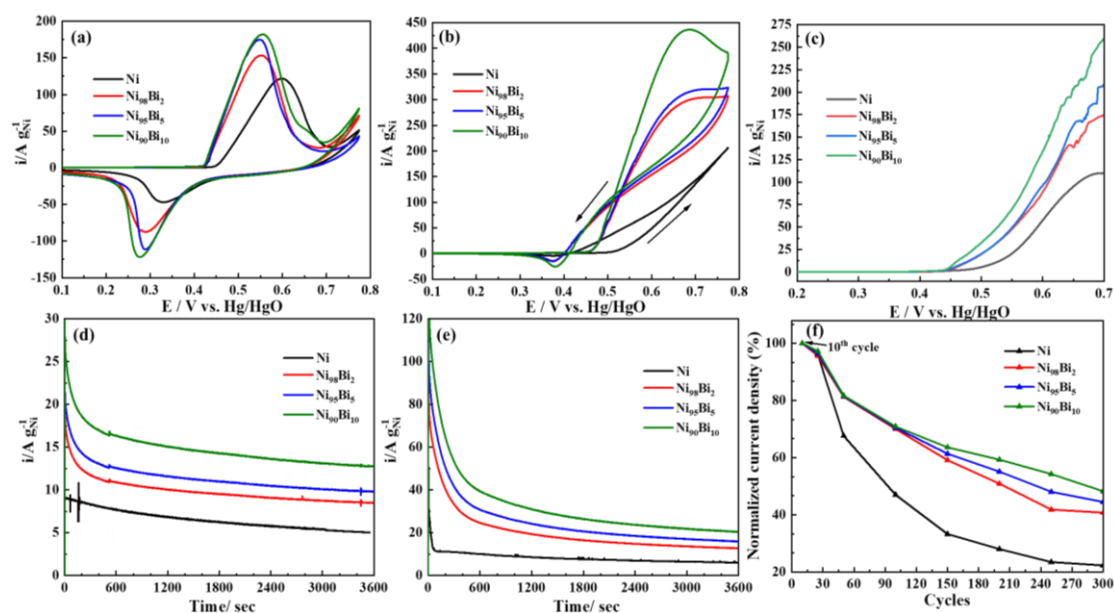


Figure 6.4. Cyclic voltammograms of Ni-based catalysts Ni_xBi_{1-x} performed in (a) 1 M KOH solution and (b) 1M KOH + 0.1M glycerol solution at scan rate of 50 mV s^{-1} . (c) Linear sweep voltammetry (LSV) at 1 mV s^{-1} . (d-e) CA tests at potential of 0.48 and 0.52 V vs. Hg/HgO for 60 min. (f) Normalized current density percentage vs CV cycles.

The durability tests for the four Ni-based catalysts towards GEOR were performed by running 300 consecutive CV cycles in 1 M KOH + 0.1 M glycerol. As

illustrated in (Figure 6.4f), $\text{Ni}_{90}\text{Bi}_{10}$ exhibited the highest mass activity among the four catalysts. In the same manner as the chronoamperometry measurements, all Ni-based catalysts showed decrease in the current density, which may be contributed to either electrode degradation or electrode poisoning, or both. After 300 CVs, the retained activity percentage of $\text{Ni}_x\text{Bi}_{1-x}$ ($x = 100, 98, 95, 90$ at. %) follows the order: $\text{Ni}_{90}\text{Bi}_{10}$ (48.2%) > $\text{Ni}_{95}\text{Bi}_5$ (44.5%) > $\text{Ni}_{98}\text{Bi}_2$ (40.7%) > Ni (22.3%). Based on the above analysis, we conclude that the $\text{Ni}_{90}\text{Bi}_{10}$ double shell-core structure exhibited the superior activity performance compared to the other three catalysts.

6.3.3 Aging of $\text{Ni}_x\text{Bi}_{1-x}$ electrocatalysts

All $\text{Ni}_x\text{Bi}_{1-x}$ catalysts were subjected to aging studies for 2 weeks, where the as-prepared catalyst “ink” performance was tested with time. We observed the change in the ink color that went from black (for as prepared) to green (after aging) (Figure D5 in SI). The electrochemical measurements on the aged $\text{Ni}_x\text{Bi}_{1-x}$ catalysts with different aging time are shown in Figure 6.5a-c. After 2 weeks of aging process, the current density of all $\text{Ni}_x\text{Bi}_{1-x}$ catalysts increased almost two times compared to the fresh samples, however no significant change in the overpotential was observed. As shown below, this could be attributed to the structural deformations and morphology change of the NiBi catalysts. Instead of being encased within the Ni-O shell, the Bi particles are exposed towards the surface of Ni-O sheets. This spatial distribution of Ni and Bi and higher percentage of $\text{Ni}(\text{OH})_2$ and $\text{Bi}(\text{OH})_3$ are favorable towards GEOR.

At the same time, the cathodic peak at ~ 0.34 V increases with aging process time remained almost constant after 2 weeks for all the catalysts. This indicate the change in the oxidation mechanism from indirect to direct electron transfer mechanism; where glycerol molecules penetrate the film of nickel hydroxide and get oxidized by the OH^- ions trapped in the structure. In this case, Ni^{III} species is not consumed during the reaction and the reduction peak will be present on the cyclic voltammetry. In addition, CA tests carried out at 0.48 and 0.52 V vs. Hg/HgO for 3600 sec has also been employed to investigate the stability of aged- $\text{Ni}_x\text{Bi}_{1-x}$ catalysts. As result, minimal activity changes were observed for the aged $\text{Ni}_x\text{Bi}_{1-x}$ catalysts compared to fresh samples as shown in Figure 6.5d. Under these quasi-stationary measurement conditions, the following order in activity was found: $\text{Ni}_{90}\text{Bi}_{10} > \text{Ni}_{95}\text{Bi}_5 > \text{Ni}_{98}\text{Bi}_2 > \text{Ni}$. Since $\text{Ni}_{90}\text{Bi}_{10}$ exhibited best catalytic activity towards GEOR, its structural morphology and elemental distribution

were investigated after two-week aging process using STEM, SAED, EDS mapping and EELS as shown in (Figure 6.6a-c).

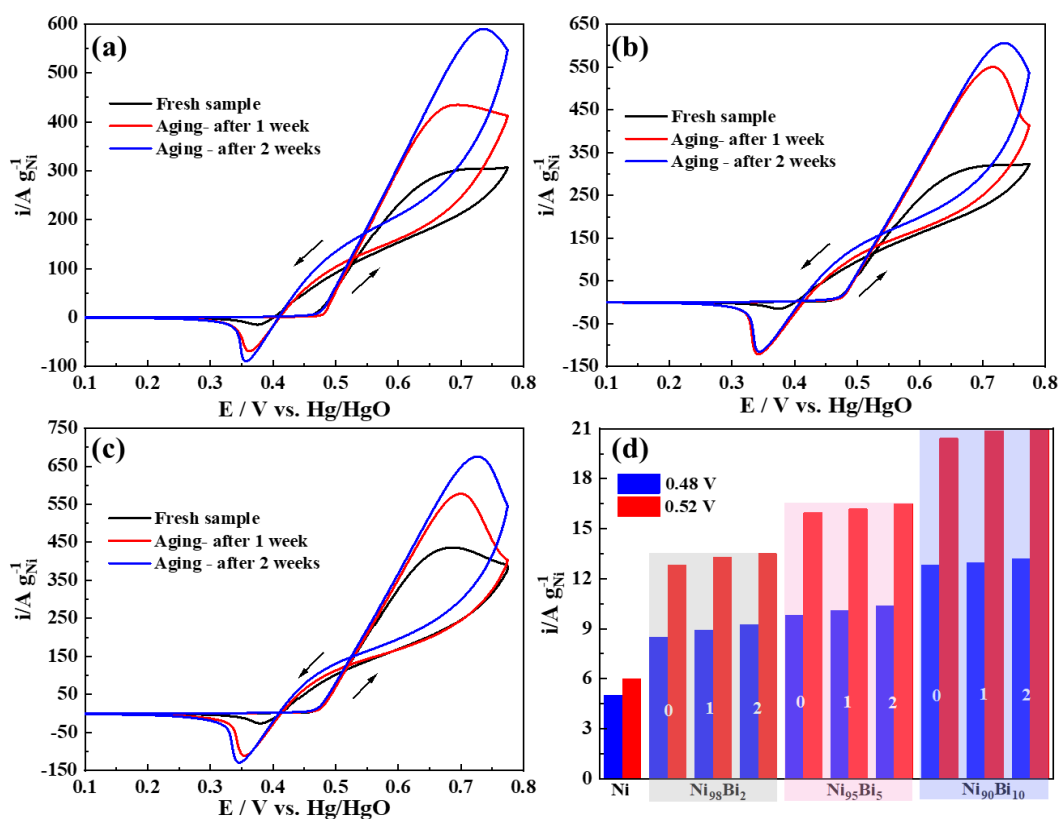


Figure 6.5. Cyclic voltammograms of $\text{Ni}_x\text{Bi}_{1-x}$ catalysts in 1 M KOH + 0.1 M glycerol: (a) $\text{Ni}_{98}\text{Bi}_2$ (b) $\text{Ni}_{95}\text{Bi}_5$, (c) $\text{Ni}_{90}\text{Bi}_{10}$ at scan rate of 50 mV sec^{-1} . (d) Histogram of retained mass activities of different Ni-based catalysts after 60 min CA tests, while 0, 1 and 2 corresponds to fresh, aging after 1 week and 2 weeks, respectively.

The STEM image (Figure 6.6a) depicts that $\text{Ni}_{90}\text{Bi}_{10}$ -aging after two weeks adopted a nanoflakes-like morphology differing markedly from that seen for the mono- and bi-metallic $\text{Ni}_x\text{Bi}_{1-x}$ catalysts. SAED pattern confirms the formation of Ni-*fcc* and rhombohedral Bi diffraction rings, forming higher crystallization degree than fresh $\text{Ni}_{90}\text{Bi}_{10}$. The elemental mapping in Figure 6.6b confirms the presence of well dispersed, small Ni (red), Bi (green) and O (yellow). Moreover, the catalyst also exhibited an interesting spatial elemental distribution of Ni, Bi and O by STEM-EELS analysis in Figure 6.6c. Forming folded thin sheet for Ni and O ions, while Bi ions settling down all over the Ni-O sheet. This aging behavior modified the shape of $\text{Ni}_{90}\text{Bi}_{10}$ from NiBi double-shell/core structure to Bi decorated on folded Ni sheet. The STEM-EELS spectrum images (Figure D5 in SI) also confirms the presence of the Ni $L_{2,3}$ signal at ~ 855 and Bi- $M_{4,5}$ signal at ~ 2600 eV.

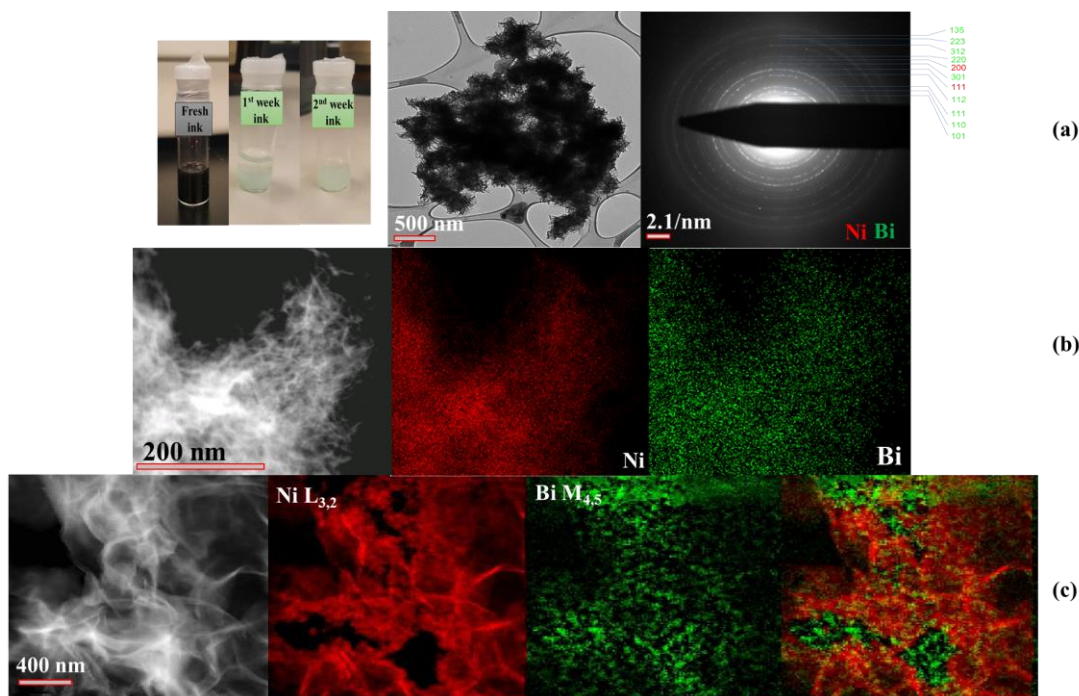
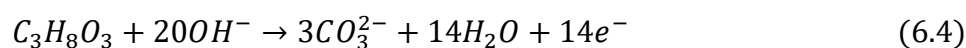


Figure 6.6. Photograph of $\text{Ni}_{90}\text{Bi}_{10}$ ink after aging process, STEM image and marked SAED patterns (b) HAADF-STEM images and STEM-EDS mapping of $\text{Ni}_{90}\text{Bi}_{10}$ after aging (c) EELS Map of $\text{Ni-L}_{2,3}$ and $\text{Bi-M}_{4,5}$.

6.3.4 In-situ PM-RRAS

The in situ-spectroelectrochemical measurements have been carried out to investigate the reaction products and intermediates of GEOR on nano-sized Ni-based catalysts, Figure 6.7 and (Figure D6 in SI) illustrate sets of *in-situ* PM-IRRAS spectra in the wavenumber range from 2500 cm^{-1} to 1010 cm^{-1} corresponding to the GEOR on Ni, $\text{Ni}_{95}\text{Bi}_5$, $\text{Ni}_{90}\text{Bi}_{10}$, $\text{Ni}_{95}\text{Bi}_5$ -aging-2w and $\text{Ni}_{90}\text{Bi}_{10}$ -aging-2w catalysts. The spectra were obtained simultaneously with CAs between 0.34 and 0.54 V vs. Hg/HgO for 30 min as summarized in Figure D7, (SI). Our previous work illustrated the advantageous of PM-IRRAS compared to regular IRRAS technique, distinguishing the oxidation species on the electrode surface (Figure 6.7 – right hand side) and the bulk species in electrolyte within the cavity between CaF_2 prism and the deposited Ni-based catalyst on glassy carbon (Figure 6.7 – left hand side).^{45,46} No Complete electrooxidation of glycerol to carbonate could be achieved by cleaving C-C-C, according to reaction:



However, the obtained PM-IRRAS spectra are complex and various features related to the formation of incomplete oxidation products are observed. These reaction products

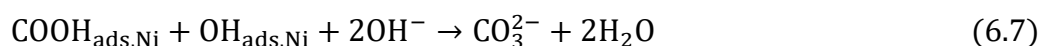
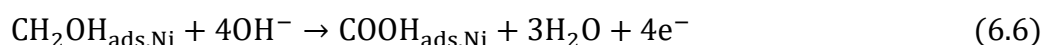
include those in which no C-C-C bond cleaved as tartronate, two-carbon products as oxalate, or even one-carbon products such as formate.

Table D1 summarizes the partial oxidation products from the main peaks detected in the PM-IRRAS spectra. Generally, the observed features are associated to stretching or bending vibration modes of aldehydes, ketones, alcohols, carboxylic acids, carboxylates, enols and carbonates, excluding a signal at $\sim 1920\text{ cm}^{-1}$ that is an artifact.⁶¹

For Ni-based catalysts, the stretch mode at $\sim 1585\text{ cm}^{-1}$ is assigned to different asymmetric COO- group, i.e. oxalate, glycerate, mesooxalate, tartronate ions and without the exclusion of H-O-H stretching mode of water.^{38,40-41} Furthermore, this band could also be attributed to acyl intermediate species ($\nu(\text{C}=\text{O})_{\text{acyl}}$) as reported by *McManus et al.* when glyceraldehyde was thermally decomposed on Pt (111) surface.^{62,63} Based on our PM-IRRAS spectra (Figure 6.7 and Figure D6), glyceraldehyde only illustrates intense band in the crowded region bellows 1300 cm^{-1} , making its identification by PM-IRRAS almost impossible, this behavior is due to the superimposition of bands from several compounds. An additional pathway noticed for the Ni-based catalysts is the formation of glycolate ($\text{C}_2\text{H}_3\text{O}_3^-$). This species indicates that the C-C-C bond has been broken into two fragments according to⁶⁴



Forming glycolate ion (1076 and 1355 cm^{-1}), while the CH_2OH fragment adsorbed on Ni was further oxidized to yield formate or carbonate as the final product in alkaline media.



Formate ion occurs at (1355 , 1386 and 1585 cm^{-1}) and the peak at (1390 - 1420 cm^{-1}) is originated by carbonate formation (Figure 6.7). A small absorption peak at $\sim 2352\text{ cm}^{-1}$ (asymmetric stretching) has been detected on the spectra with all catalysts, indicating the production of CO_2 . However, the peak intensity at 0.34 V remains unaltered with increasing potential, except for Ni in (Figure 6.7b). The presence of CO_2 during GEOR in alkaline media is an indication of an OH^- depletion in thin layer configuration (i.e. between the CaF_2 prism and the working electrode) due to pH change.⁶⁵

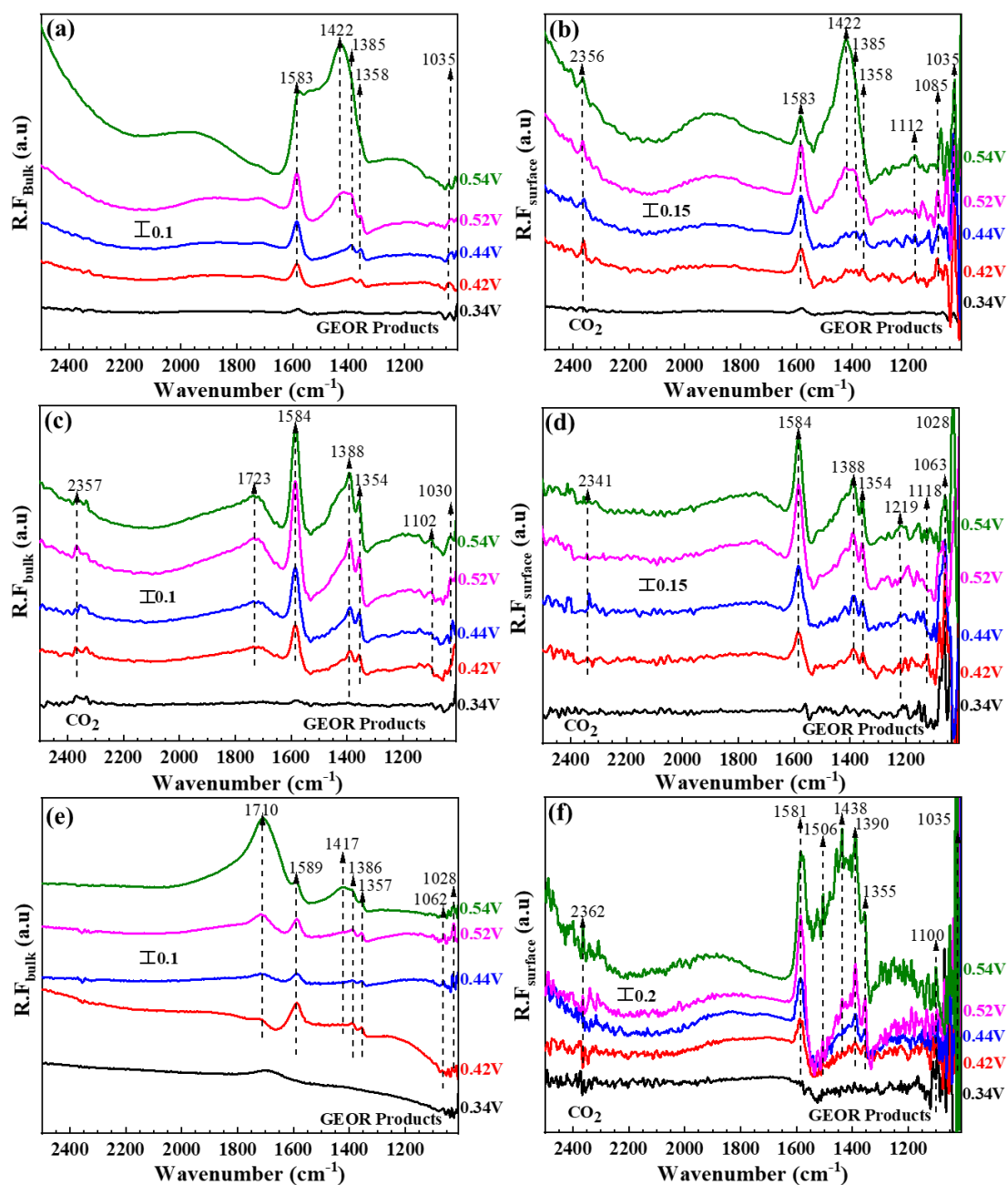


Figure 6.7. PM-IRRAS spectra during GEOR on (a,b) Ni (c,d) Ni₉₀Bi₁₀ and (e,f) Ni₉₀Bi₁₀-aging-2w in 1M KOH+0.1 M glycerol at five potentials. The left-hand spectra show oxidation species in the bulk solution, while the right-hand spectra show oxidation species on the surface.

Figure 6.7 c-f and Figure SI D6 show that spectra of Ni_xBi_{1-x} (x= 95 and 90 at%) before and after aging have similar qualitative band structure compared to Ni NPs. However, a remarkable change in selectivity was distinguished. A broad band of ~1720 cm⁻¹ with characteristic of the C=O stretching vibration of a C-COO⁻ could indicate non-adsorbed aldehydes and carboxylic acids namely: (tartronate, glycolate and glyoxylate).

Similar trends were observed using single crystal Pt (111)^{63,66,67}, polycrystalline Pt and Au⁶⁸ for GEOR in alkaline media. It is clear that the carbonyl groups at $\sim 1720\text{ cm}^{-1}$ is mainly available in the bulk solution but not near/or on the electrode surface, which also highlights the beneficial of using PM-IRRAS technique compared to regular IRRAS.

Another important difference between the Ni and NiBi catalysts appears at $\sim 1420\text{ cm}^{-1}$, where the presence of Bi decreases the CO_3^{2-} intensity. This indicates that bi-metallics are less prone to break the triple C bond of glycerol than Ni NPs, thus increasing the selectivity towards C3 compounds.

6.3.5 HPLC measurements

The catalysts of Ni, Ni₉₀Bi₁₀ and Ni₉₀Bi₁₀-aging-2w with best GEOR performance were used to compare and determine the conversion and product distributions of GEOR in 1 M KOH + 0.1M glycerol. Figure 6.8 and Figure D9- D11 in ESI display quantification of reaction products performed by HPLC over Ni-based catalysts under different applied potential of 1.3, 1.4 and 1.55 V and temperatures (room temperature (RT) and 50 °C) for 6 hours. Before HPLC analysis, seven related compounds including oxalate, tartronate, glycerate, glycolate, lactate, formate and glycerol were calibrated as shown in (Figure D12-D17, in SI).

After 30 min of continuous electrolysis (Figure 6.8 a, c, e), all Ni_xBi_{1-x} catalysts showed that the lowest applied potential (1.3 V) resulted in the highest selectivity towards glycerate and low glycerol conversion. Specifically, for Ni in Figure 6.8a, the selectivity of glycerate reduces with increasing anode potential and rises with increasing temperature, leading to maximum value of 49.6% and 60.2% at 1.3 V for RT and 50 °C, respectively. In contrast, formate selectivity has a contrary trend, resulting in a maximum value of 72% and 48.1% at 1.55 V for RT and 50 °C, respectively. Whereas, a negligible amount of oxalate and tartronate was observed (< 4.2%). Compared to Ni, the Ni₉₀Bi₁₀ and Ni₉₀Bi₁₀-aging-2w catalysts show a better tendency to produce oxalate and tartronate. Notably, a maximum oxalate and tartronate selectivity of 18.8% and 23.5% were detected at 1.3 V and 50 °C for Ni₉₀Bi₁₀ and Ni₉₀Bi₁₀-aging-2w as illustrated in Figure 6.8 c,e, respectively; which are 4.5 and 5.6 times of those of the Ni catalyst. The production of formate is largely reduced, e.g., when the potential is 1.55 V and 50 °C, the formate selectivity on Ni, Ni₉₀Bi₁₀ and Ni₉₀Bi₁₀-aging-2w are 48.1%, 38.6%, and 25.4%, while the

glycolate and lactate selectivity have almost similar trend with no significant change in the production. The selectivity of 3-carbon products especially tartronate and glycerate are much higher for $\text{Ni}_{90}\text{Bi}_{10\text{-aging-2w}} > \text{Ni}_{90}\text{Bi}_{10} > \text{Ni}$ throughout the potential range (1.3–1.55 V). The fact that the formation of C_3 products are much higher in Ni-Bi than in Ni could be justified by the presence of Bi disfavoring the formation of multiple bonded intermediates by decreasing the probability of finding neighboring Nickel sites.³⁰ To further confirm the dominant effect of temperature and applied potential towards glycerol conversion and product distribution, we extended the reaction time to 6 hours throughout the anode potential range as elucidated in (Figure 6.8b, d, f and Figure D9-D11 in SI). It is apparent that the selectivity of each product changed during the whole reaction period, indicating that the reaction time has also a significant influence on the product distribution.

Increasing the reaction time of continuous electrolysis from 30 min to 6 hours, resulted in gradually decreasing the concentration of glycerate (C_3) to formate (C_1). As illustrated in (Figure 6.8b and Figure D9e), by applying a higher potential of 1.55 V at 50 °C, the glycerol conversion continuously increased with the elongation of reaction time, reaching 55.4% after 6 h. While, the selectivity of formate increased to 79.1% on monometallic Ni by breaking the C–C bond of C_3 molecules.

On other hand, we observed that $\text{Ni}_{90}\text{Bi}_{10}$ and $\text{Ni}_{90}\text{Bi}_{10\text{-aging-2w}}$ have better selectivity towards C_3 products than Ni (Figure 6.8 d,f) and (Figure D10 and D11 in SI). When the time elongated, the selectivity difference is enlarged between bimetallic Ni-Bi and monometallic Ni by an average of ($\sim 2.3\text{x}$) for $\text{Ni}_{90}\text{Bi}_{10}$ and ($\sim 3\text{x}$) for $\text{Ni}_{90}\text{Bi}_{10\text{-aging-2w}}$. This means a 10 at.% of Bi selectively positioned on Ni NPs was more beneficial than Ni in promoting the C_3 selectivity. The reason could be ascribed to the role of blocking effect of Bi on specific Ni sites by changing the adsorption species and preventing the formation of poisonous species based on the so-called third-body effect.³¹ Alternative explanation, since bismuth has higher affinity for oxygen, in which Bi adatoms adsorb oxygen to form Ni-Bi-OH species on the surface, acting as a co-catalyst in order to protect Ni from over-oxidation.⁶⁹

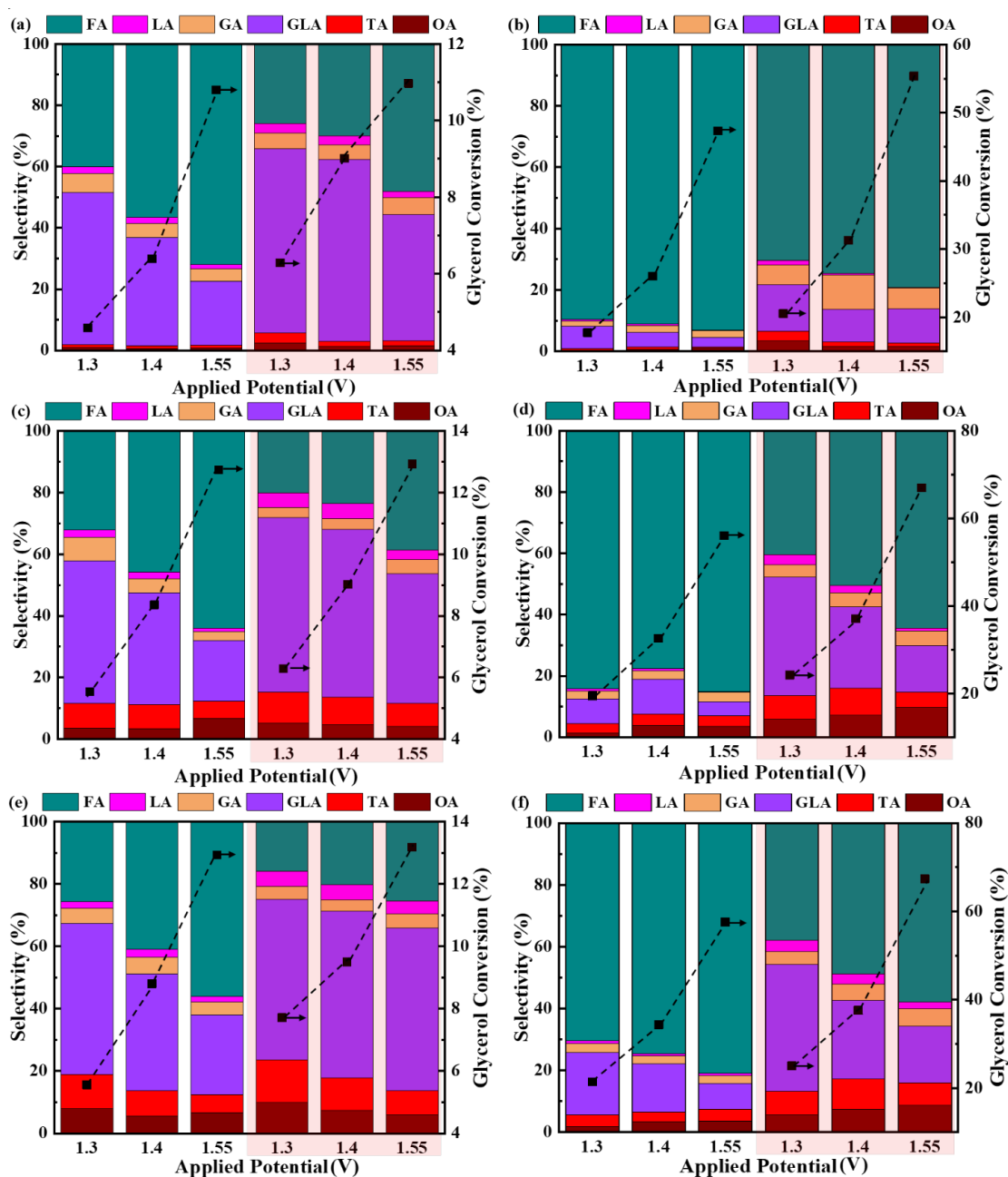
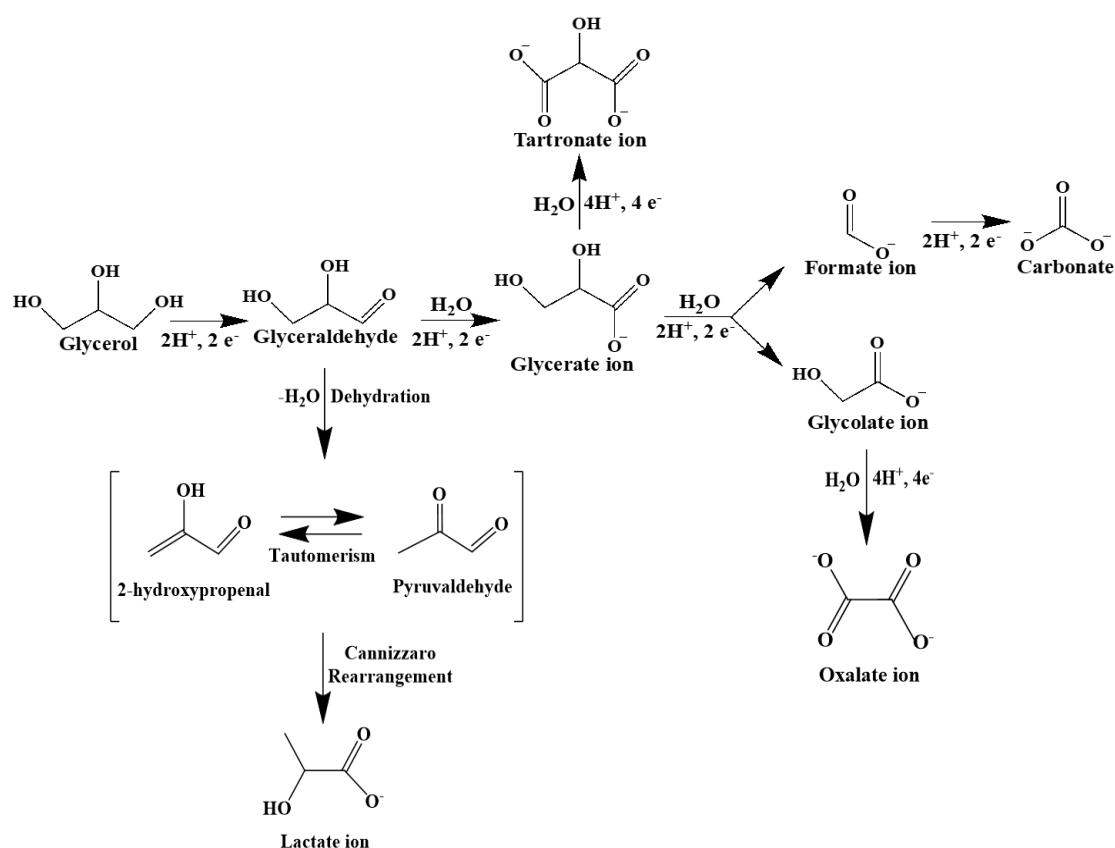


Figure 6.8. Product distributions and glycerol conversion (dashed line) under different applied potentials and temperatures over the (a,b) Ni, (c,d) Ni₉₀Bi₁₀ and (e,f) Ni₉₀Bi₁₀-aging-2w, in a 1M KOH+0.1 M glycerol. The left-hand figures illustrate product distributions after 30 min, while the right-hand illustrates products after 6 hrs. Green: formate; Pink: lactate; Orange: glycolate; Violet: glycerate; Red: tartronate and Brown: oxalate. The red shaded border represents temperature at 50 °C.

Based on the in-situ PM-IRRAS and HPLC results, the proposed reaction pathway on NiBi bimetallic catalysts for GEOR is illustrated in Scheme 6.2. Glycerol is initially oxidized to glyceraldehyde. Then the reactions undertake either metal-catalyzed oxidation to glycerate, tartronate and triple C bond cleavage products such as (glycolate,

oxalate, formate and carbonate) or base-catalyzed dehydration from glyceraldehyde to 2-hydroxypropenal, which tautomerizes to form pyruvaldehyde and then goes with Cannizzaro rearrangement to lactate formation.⁷⁰ In summary, addition of 10 at.% of Bi influences the selectivity by hindering the C-C breakage of the glycerol than the monometallic Ni, leading to improved production of C₃ products at different applied potential and temperature. Based on the open literature for PGM free catalysts, our Ni_xBi_{1-x} materials show the highest selectivity towards C₃ products (glycerate and tartronate) as illustrated in (Table D2 in SI).



Scheme 6.2. Proposed reaction pathways for GEOR in alkaline media on Ni_xBi_{1-x} catalysts.

6.4 Conclusion

In this work, Ni_xBi_{1-x} (x = 100, 98, 95 and 90 at.%) nanoparticles were studied for glycerol electrooxidation in 1 M KOH. A series of electrochemical measurements have revealed that Ni₉₀Bi₁₀ displayed high mass activity and stability towards GEOR compared to the monometallic Ni. This is due to the Ni-Bi double shell-core structure, which includes highly dispersed Bi clusters on the outer Ni shell, affecting the formation of the Ni^{III} phase. The effect of catalyst aging showed modification of the structural shape from the

Ni-Bi double-shell/core structure to Bi decorated on folded Ni sheet and enhancing their activity twice after two weeks aging. In-situ PM-IRRAS measurements during chronoamperometry showed that addition of the small quantities of Bi (≤ 10 at. %) to Ni significantly altered the product selectivity of GEOR facilitating tartronate production, which is attributed to C=O stretching at 1718 cm^{-1} . Whereas HPLC analysis reveals that Bi adatom actively influences the reaction products by suppressing the pathways with C–C bond cleavage, hindering the production of formate and improving the production of tartronate, oxalate and glycerate at different applied potential and temperature. Overall, this work indicates that bimetallic Ni-Bi can serve as a potential catalyst with better control of products in the electrolysis system while generating higher current density.

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Supplementary Information D: Chapter 6

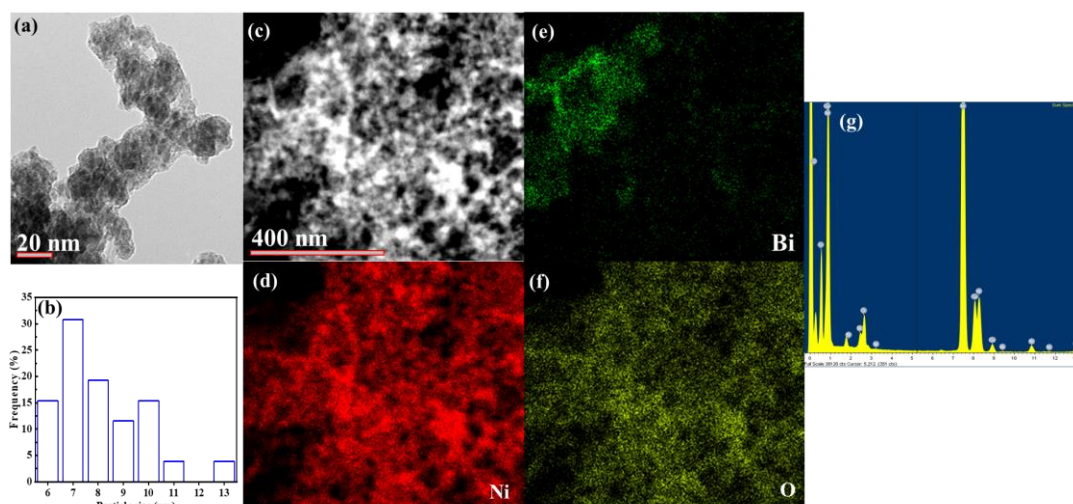


Figure D1. (a) STEM bright-field image of $\text{Ni}_{98}\text{Bi}_2$ nanoparticles, (b) Particle size distribution histograms, (c) HAADF-STEM image, (d-f) STEM-EDS mapping images for Ni, Bi and O elements, respectively and (g) EDS spectrum of $\text{Ni}_{98}\text{Bi}_2$.

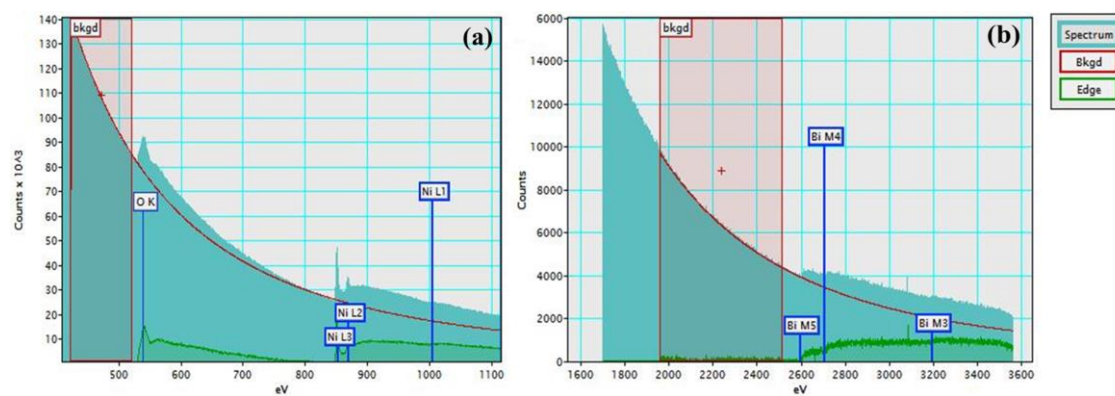


Figure D2. $\text{Ni}_{90}\text{Bi}_{10}$ EELS Spectrum Obtained at High Spatial Resolution of a) O-K and Ni-L_{3,2}L₁ and b) Bi-M_{5,4}M₃.

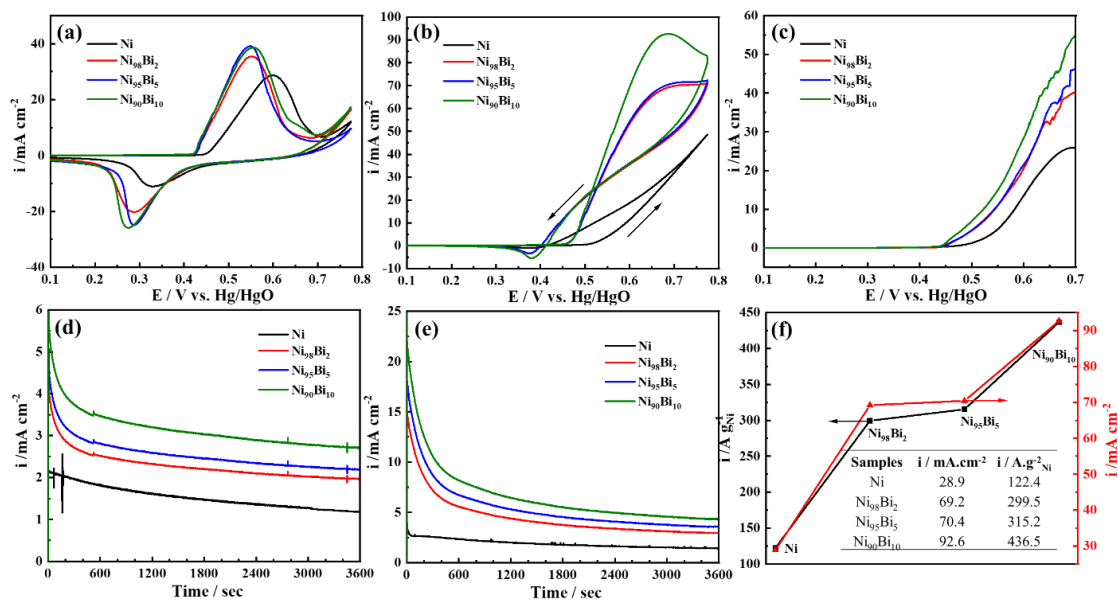


Figure D3. Cyclic voltammograms of Ni-based catalysts Ni_xBi_{1-x} performed in (a) 1 M KOH solution and (b) 1M KOH + 0.1M glycerol solution at scan rate of 50 mV s⁻¹. (c) Linear sweep voltammetry (LSV) at 1 mV s⁻¹. (d-e) CA tests at potential of 0.48 and 0.52 V vs. Hg/HgO for 60 min. (f) Comparison of current density after normalization to the Ni mass and the geometric surface area of the GC (0.196 cm²).

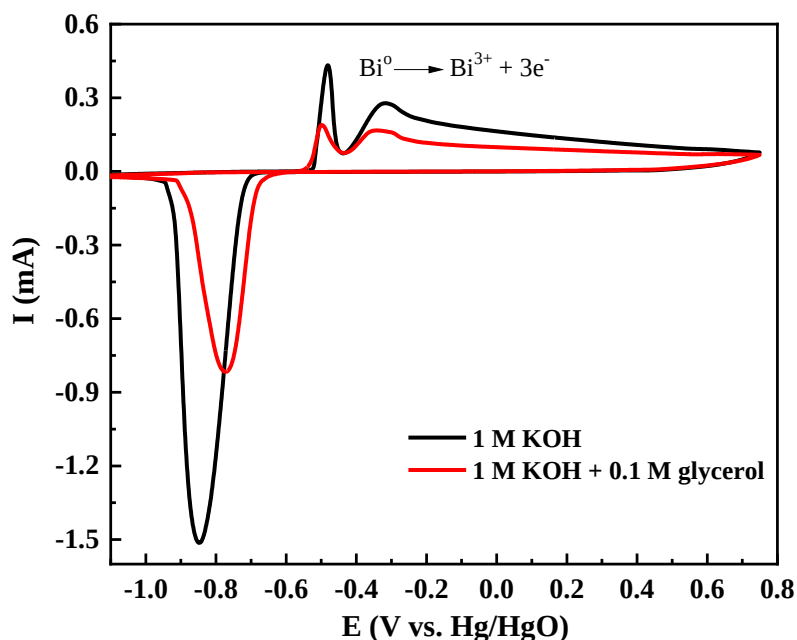


Figure D4. Cyclic voltammograms of Bi catalyst in 1 M KOH (black line) and 1M KOH + 0.1M glycerol (red line) at scan rate of 50 mV sec⁻¹.

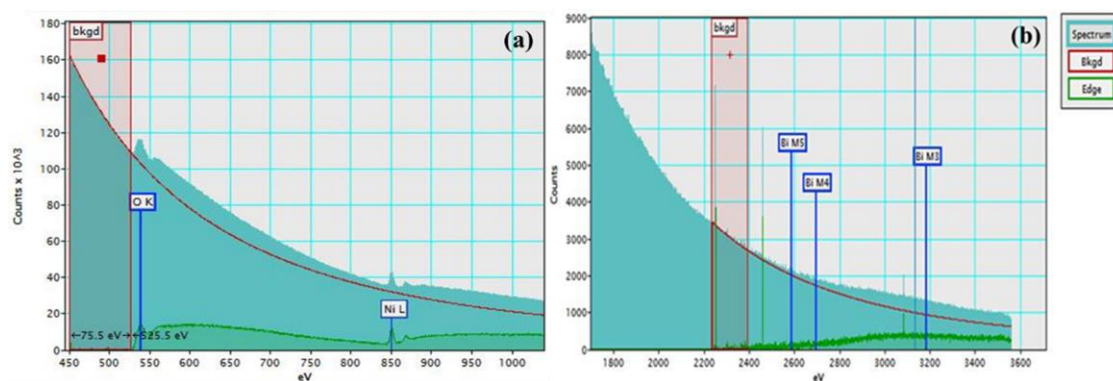


Figure D5. Ni₉₀Bi₁₀ after aging EELS spectrum obtained at high spatial resolution of a) O-K and Ni-L_{3,2}L₁ edges and b) Bi-M_{5,4}M₃ edges.

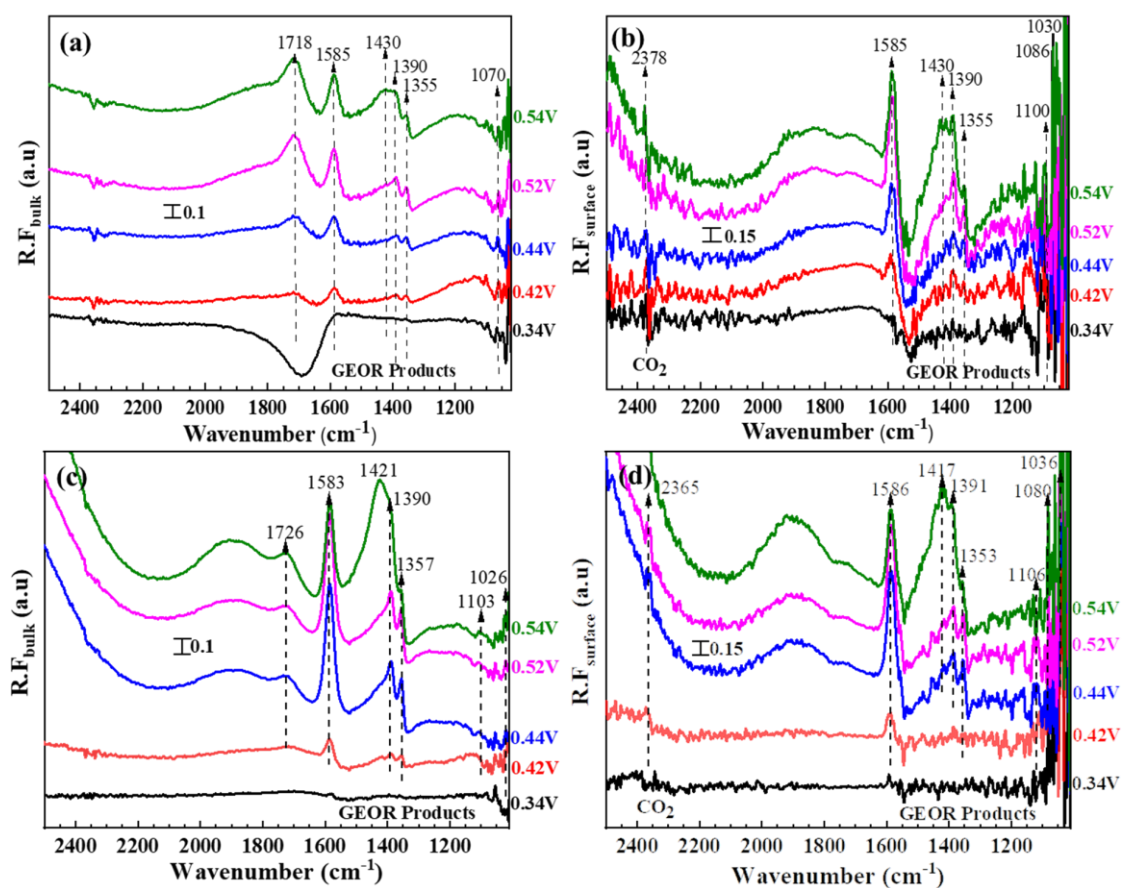


Figure D6. PM-IRRAS spectra during glycerol electro-oxidation on (a,b) Ni₉₅Bi₅ and (c,d) Ni₉₅Bi₅-aging-2w in 1M KOH+0.1 M glycerol at various potentials as indicated in the figure. The left-hand spectra illustrate oxidation species in the thin cavity/bulk solution, while the right-hand spectra illustrate oxidation species on the surface.

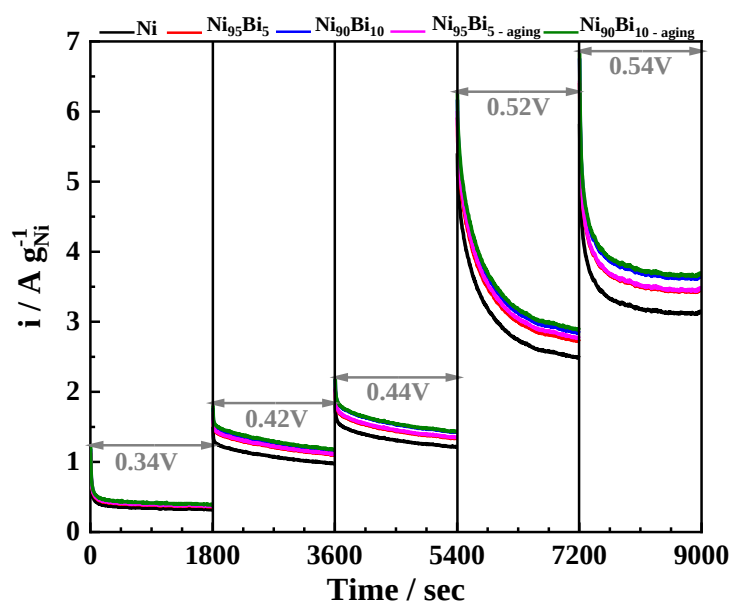


Figure D7. CA profile in 1M KOH+0.1M glycerol at different potentials, as specified by the double arrows for PM-IRRAS spectra.

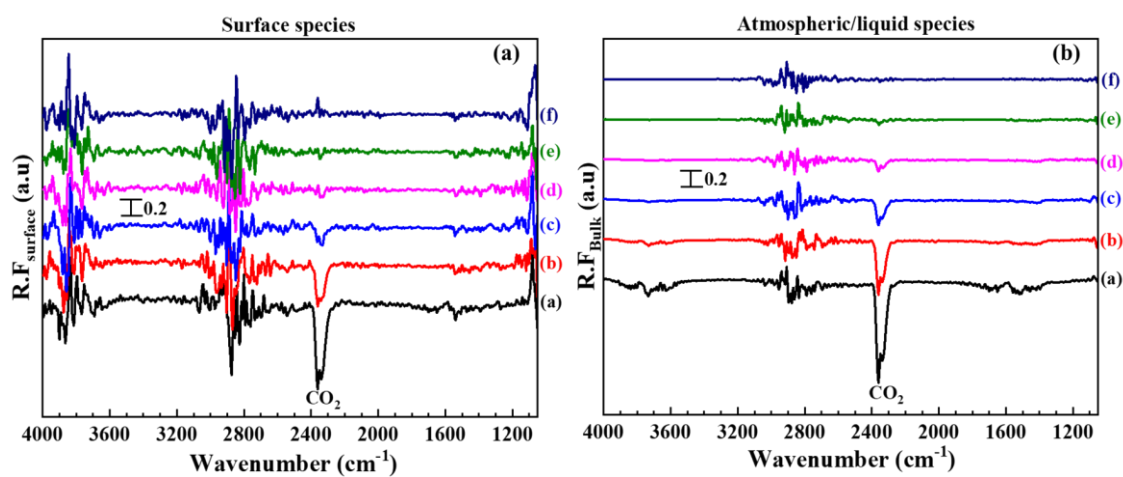


Figure D8. CO₂ tracking level background PM-IRRAS spectra of Ni-based catalyst in 1M KOH+0.1 M glycerol at open circuit potential (OCP); (a) 2.5 hrs., (b) 2 hrs., (c) 1.5 hrs., (d) 1 hr., (e) 30 min, and (f) 3min before measurements were initiated

Table D1. Assignment of the main bands in the spectra of the figure 6.7 (a-f) and SI 6.6 (a-d)

Wavenumber (cm ⁻¹)					Assignment
Ni	Ni ₉₅ Bi ₅	Ni ₉₀ Bi ₁₀	Ni ₉₅ Bi ₅ aging	Ni ₉₀ Bi ₁₀ aging	
1035 ^{b,s}	1030 ^{b,s}	1028 ^s / 1030 ^b	1026 ^b / 1036 ^s	1028 ^b / 1035 ^s	ν (C-O) of alcohols
1085 ^s	1070 ^s / 1086 ^b	1063 ^s	1080 ^s	1062 ^{b,s}	ν (C-O) of alcohols
1112 ^s	1100 ^s	1102 ^b / 1118 ^s	1103 ^b / 1106 ^s	1100 ^{b,s}	ν (C-O) of alcohols
		1219 ^s			ν (C-O) of carboxylic acids, ν (C-O) of aliphatic ketones, δ(OH) of alcohols
1358 ^{b,s}	1355 ^{b,s}	1345 ^{b,s}	1353 ^s / 1357 ^b	1355 ^s / 1357 ^b	ν (O-C-O) _s of carboxylates; ν (C-C) of aliphatic ketones, δ(OH) of alcohols
1385 ^{b,s}	1390 ^{b,s}	1388 ^{b,s}	1390 ^{b,s}	1386 ^b / 1390 ^s	ν (O-C-O) _s of carboxylates and carbonate; δ(CH ₃) _s of methyl groups; δ(OH) of alcohols
1422 ^{b,s}	1430 ^{b,s}		1417 ^s / 1421 ^b	1417 ^b / 1438 ^s	ν (O-C-O) _s of carboxylates and carbonate; δ(OH) of alcohols
				1506 ^s	δ(CH ₂) scissor vibration
1583 ^{b,s}	1585 ^{b,s}	1584 ^{b,s}	1583 ^b / 1586 ^s	1581 ^s / 1589 ^b	ν (O-C-O) _{as} of carboxylates; ν (C≡C) of enols
	1718 ^b	1723 ^b	1726 ^b	1710 ^b	ν (C=O) carboxylic acids, aldehydes and ketones
2356 ^s	2378 ^s	2341 ^s / 2357 ^b	2365 ^s	2362 ^s	ν (O=C=O) _{as}

Subscripts indicate the type of oxidation species: b – in thin cavity/bulk solution, s – on the surface.

Notation used for mode description: ν – stretching; δ – deformation.

Subscripts illustrate the type of mode: s – symmetric, as – asymmetric.

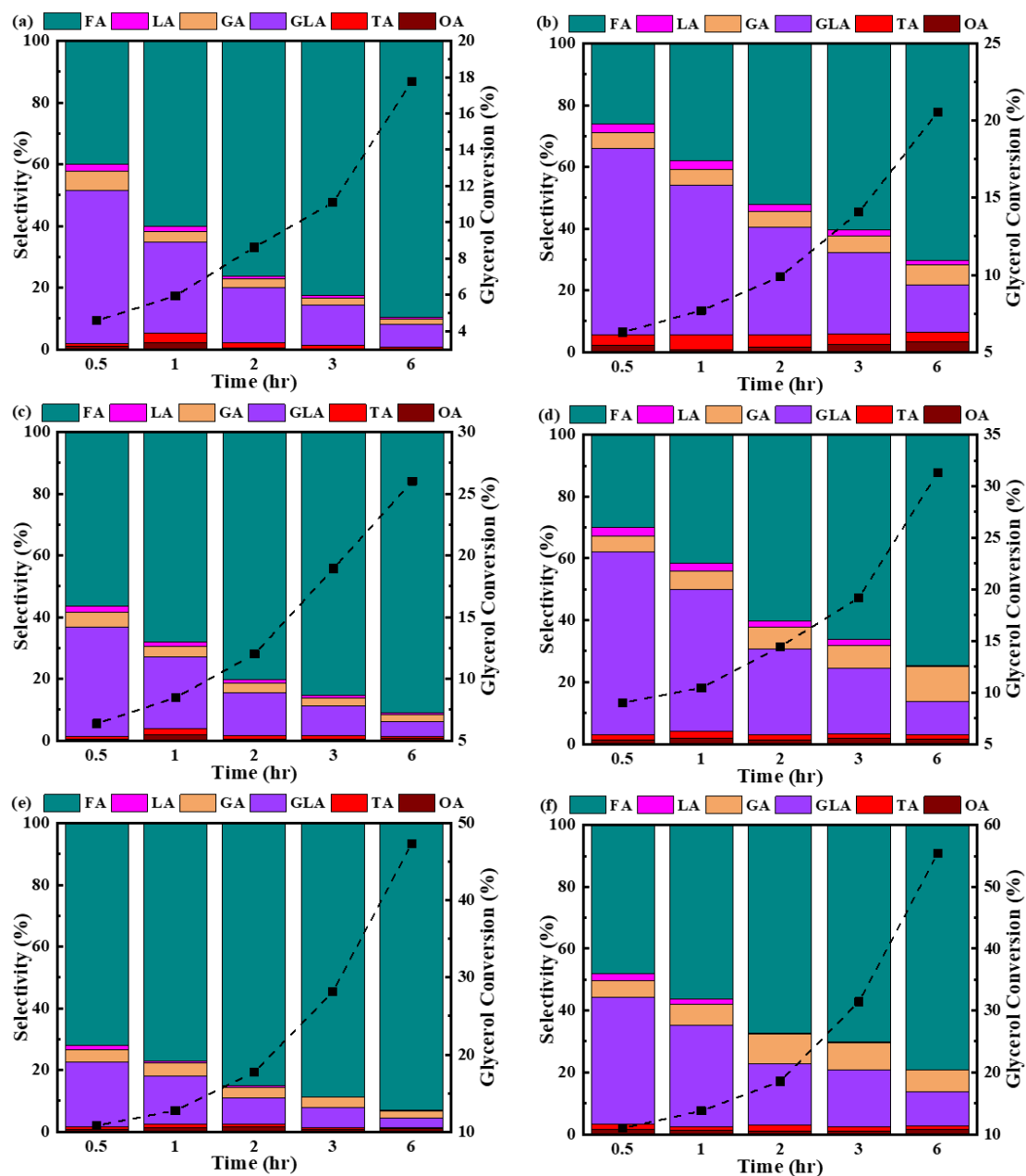


Figure D9. Product distributions and glycerol conversion (dashed line) on Ni at different applied potentials for different reaction time (a,b) 1.3 V, (c,d) 1.4 V and (e,f) 1.55 V, in a 1M KOH+0.1 M glycerol. The left-hand figures illustrate product distributions at room temperature, while the right-hand illustrates products at 50 °C. Green: formate; Pink: lactate; Orange: glycolate; Violet: glycerate; Red: tartronate and Brown: oxalate.

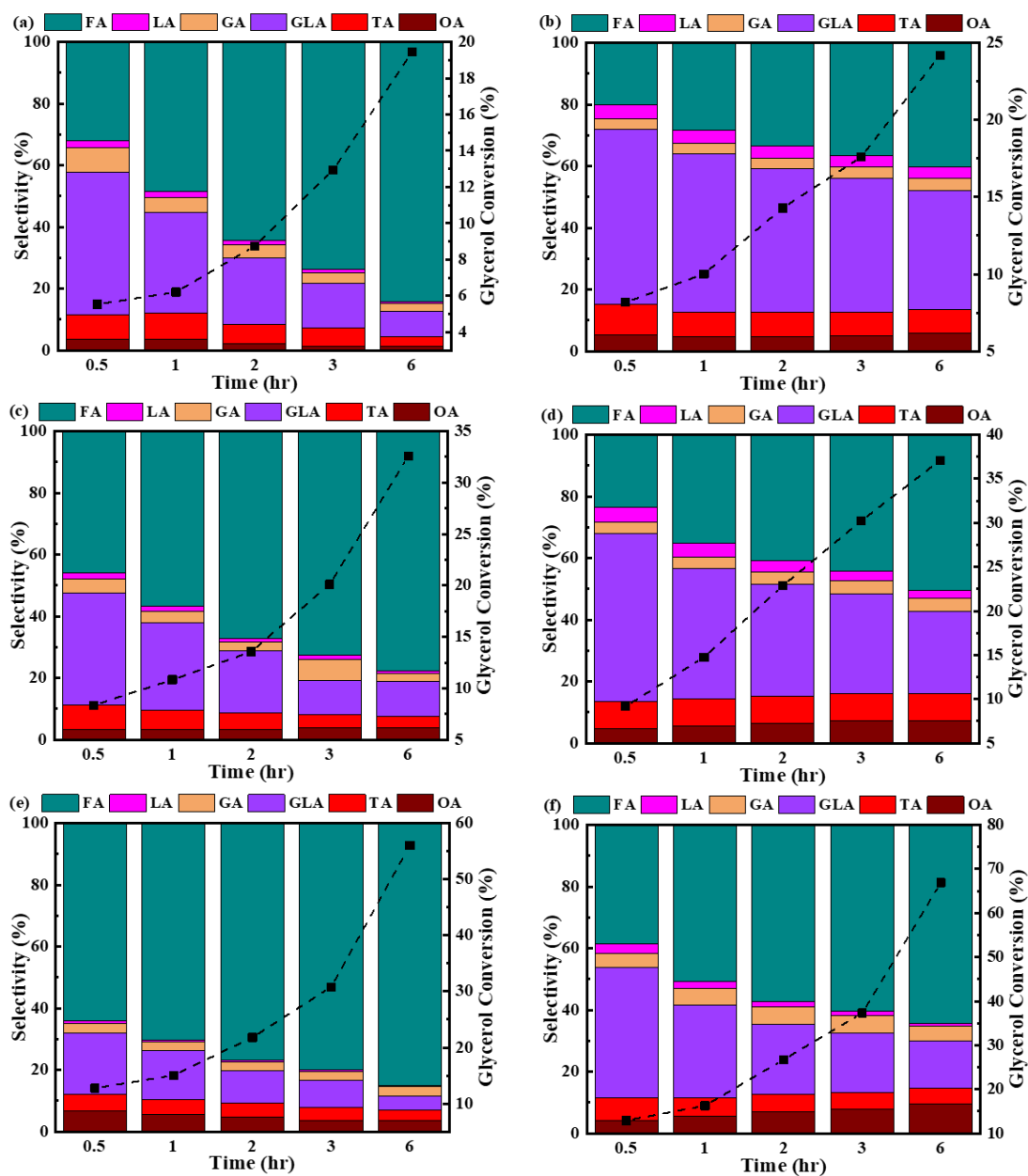


Figure D10. Product distributions and glycerol conversion (dashed line) on $\text{Ni}_{90}\text{Bi}_{10}$ at different applied potentials for different reaction time (a,b) 1.3 V, (c,d) 1.4 V and (e,f) 1.55 V, in a 1M KOH+0.1 M glycerol. The left-hand figures illustrate product distributions at room temperature, while the right-hand illustrates products at 50 °C. Green: formate; Pink: lactate; Orange: glycolate; Violet: glycerate; Red: tartronate and Brown: oxalate.

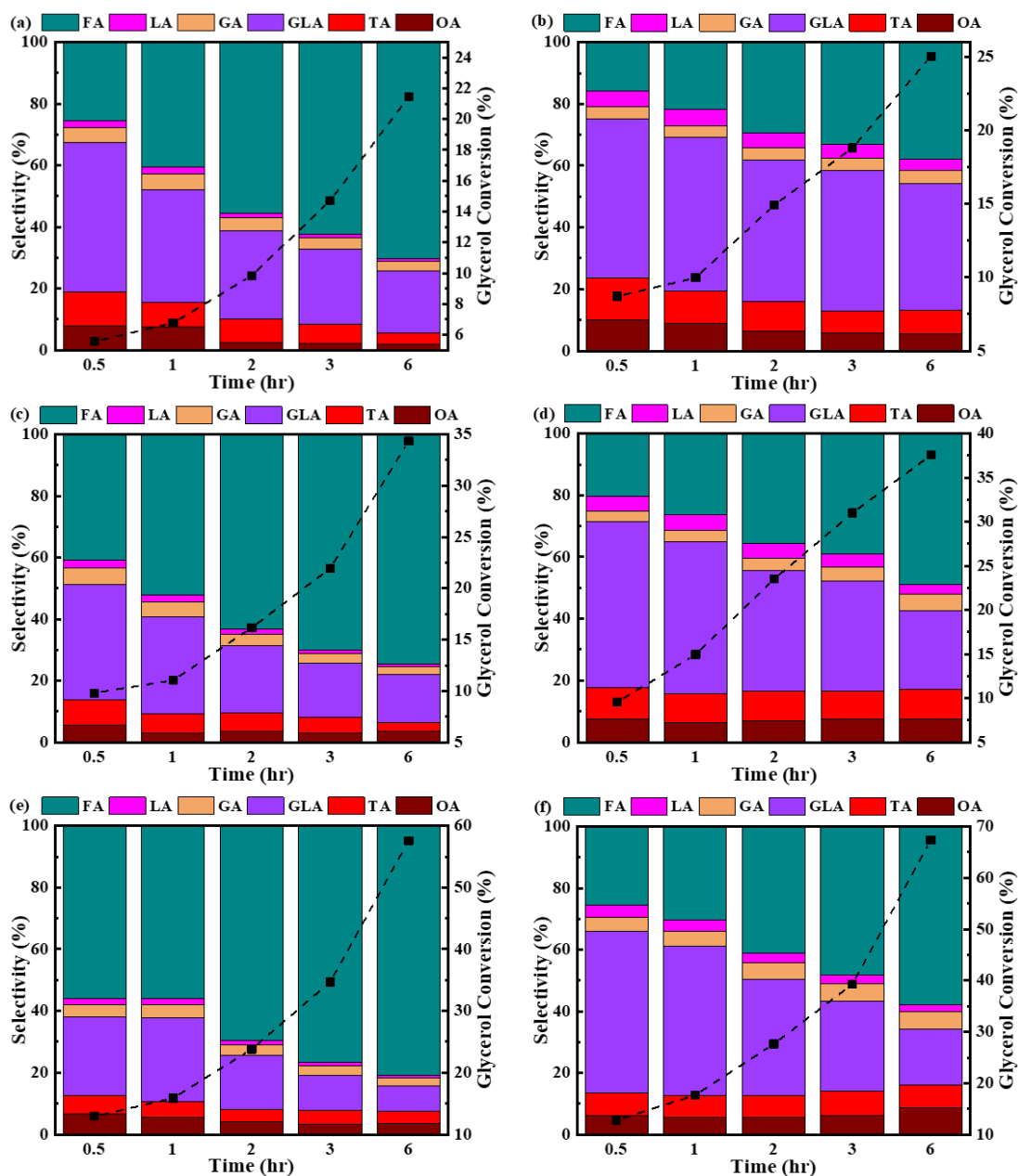


Figure D11. Product distributions and glycerol conversion (dashed line) on Ni₉₀Bi₁₀-aging-_{2w} at different applied potentials for different reaction time (a,b) 1.3 V, (c,d) 1.4 V and (e,f) 1.55 V, in a 1M KOH+0.1 M glycerol. The left-hand figures illustrate product distributions at room temperature, while the right-hand illustrates products at 50 °C. Green: formate; Pink: lactate; Orange: glycolate; Violet: glycerate; Red: tartronate and Brown: oxalate.

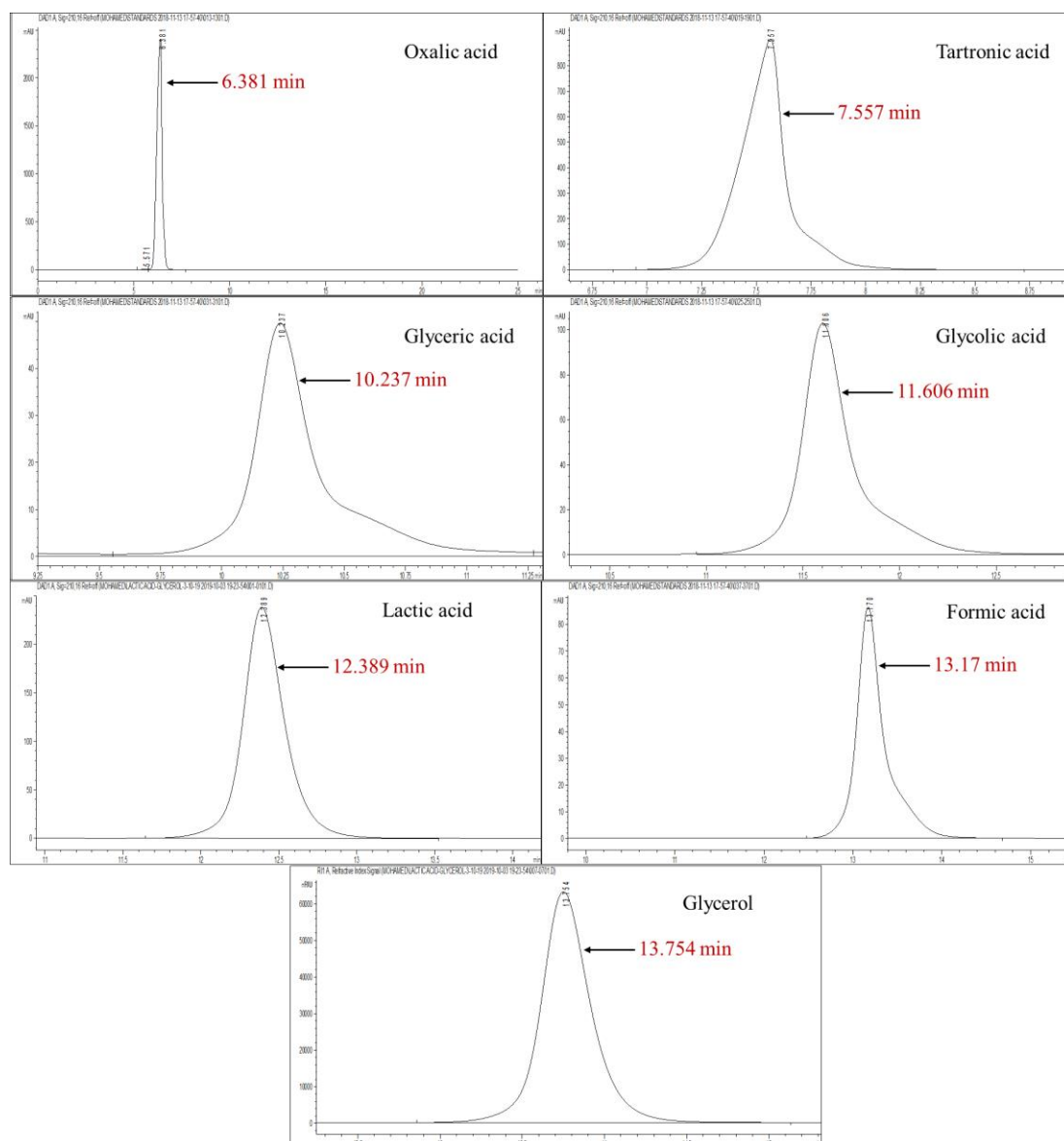


Figure D12. Chromatograms of the standards using DAD (diode array detector) UV/Vis detector at 210 nm for GEOR products and refractive index signal for glycerol. Each sample consist of 1 M KOH with 0.12M of the chosen analyte.

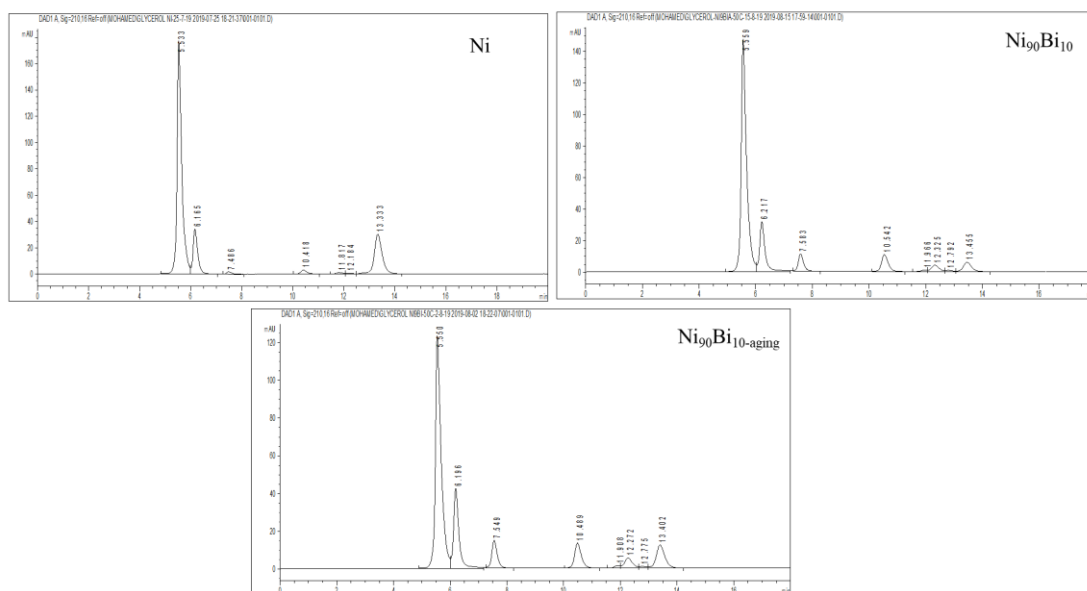


Figure D13. Chromatograms of the samples using DAD (diode array detector) UV/Vis detector at 210 nm for GEOR products at 1.3 V in a 1M KOH + 0.1 M glycerol after 30 min electrolysis.

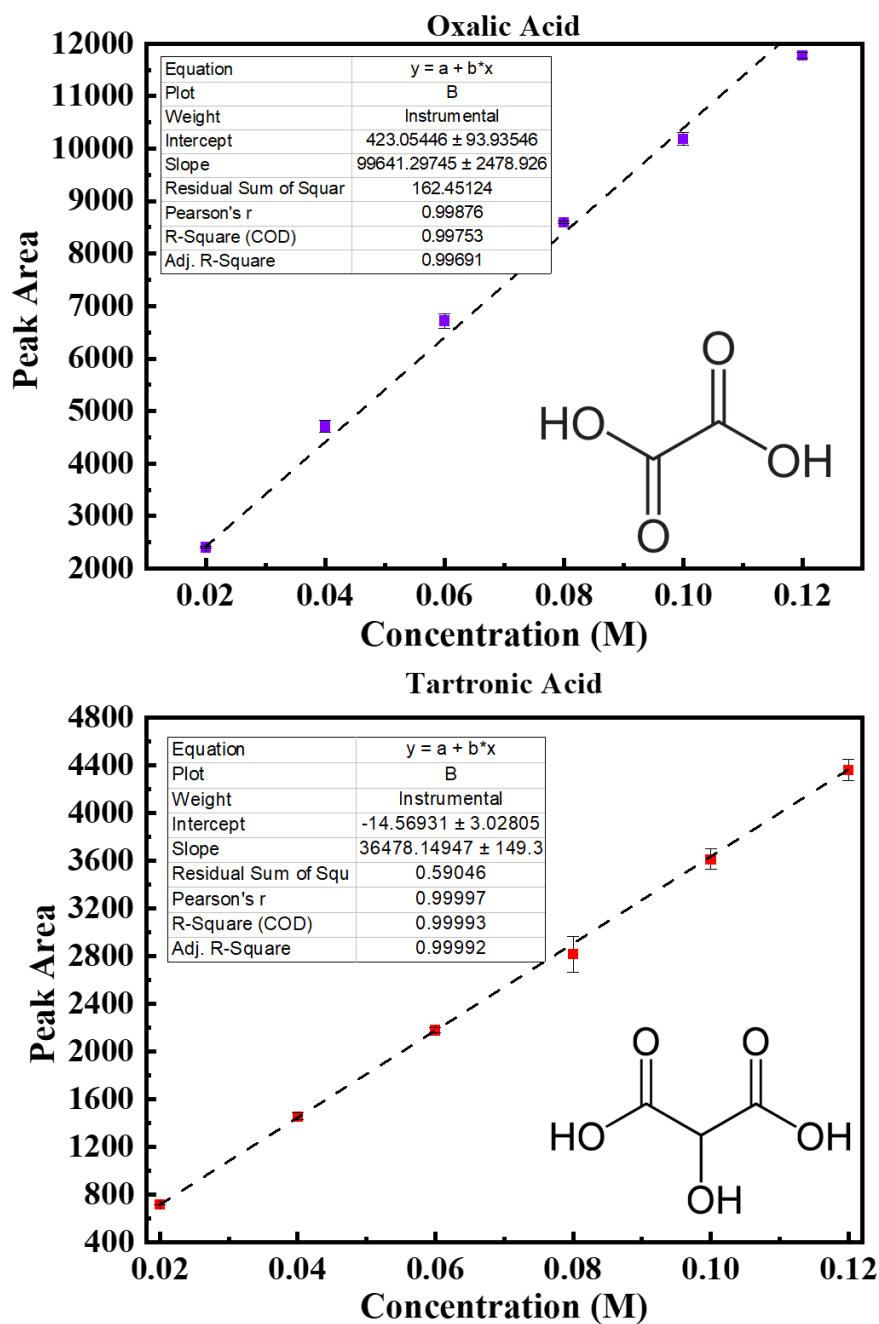


Figure D14. Calibrated curves of oxalic and tartronic acids determined from HPLC with retention time of 6.23 and 7.58 min, respectively using DAD (diode array detector) UV/Vis detector 210 nm.

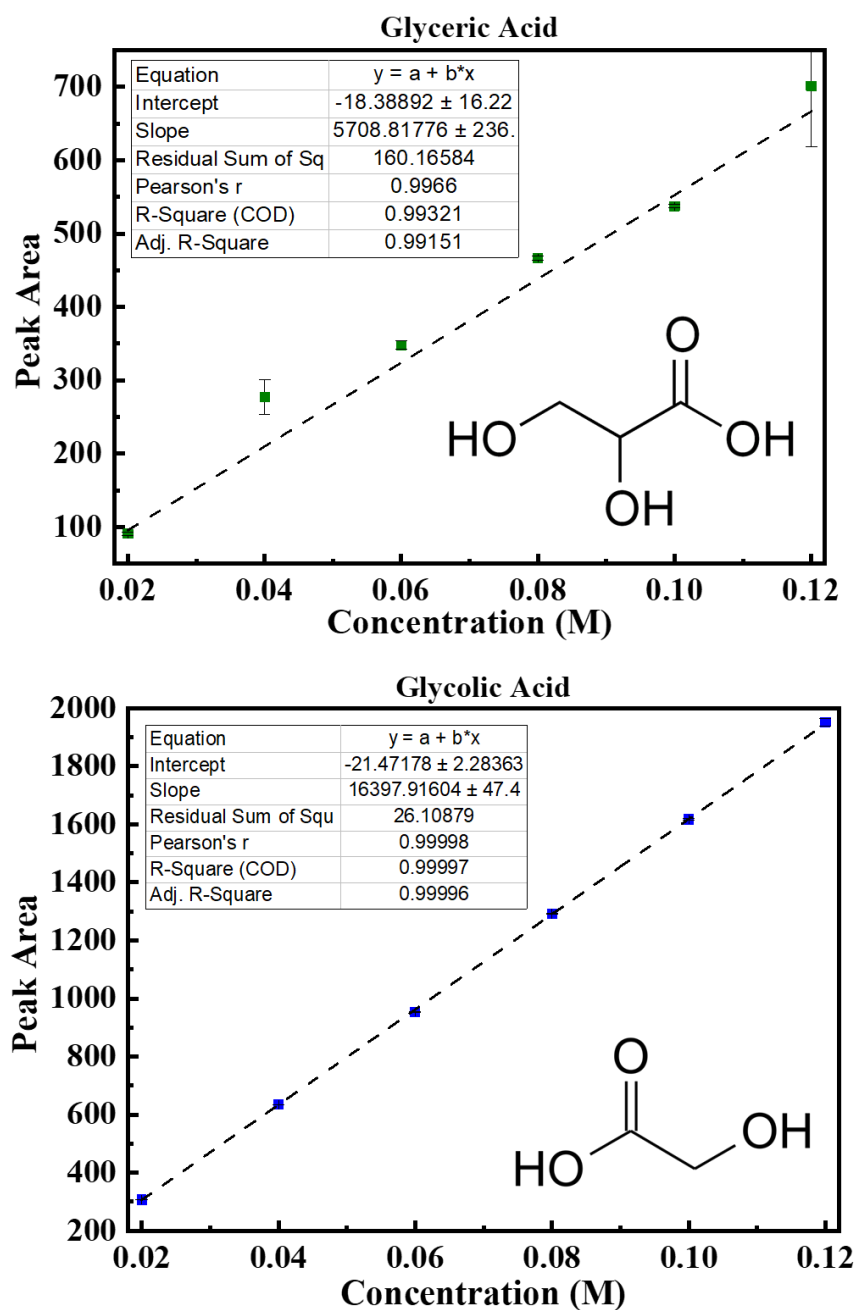


Figure D15. Calibrated curves of glyceric and glycolic acids determined from HPLC with retention time of 10.41 and 11.81 min, respectively using DAD (diode array detector) UV/Vis detector 210 nm.

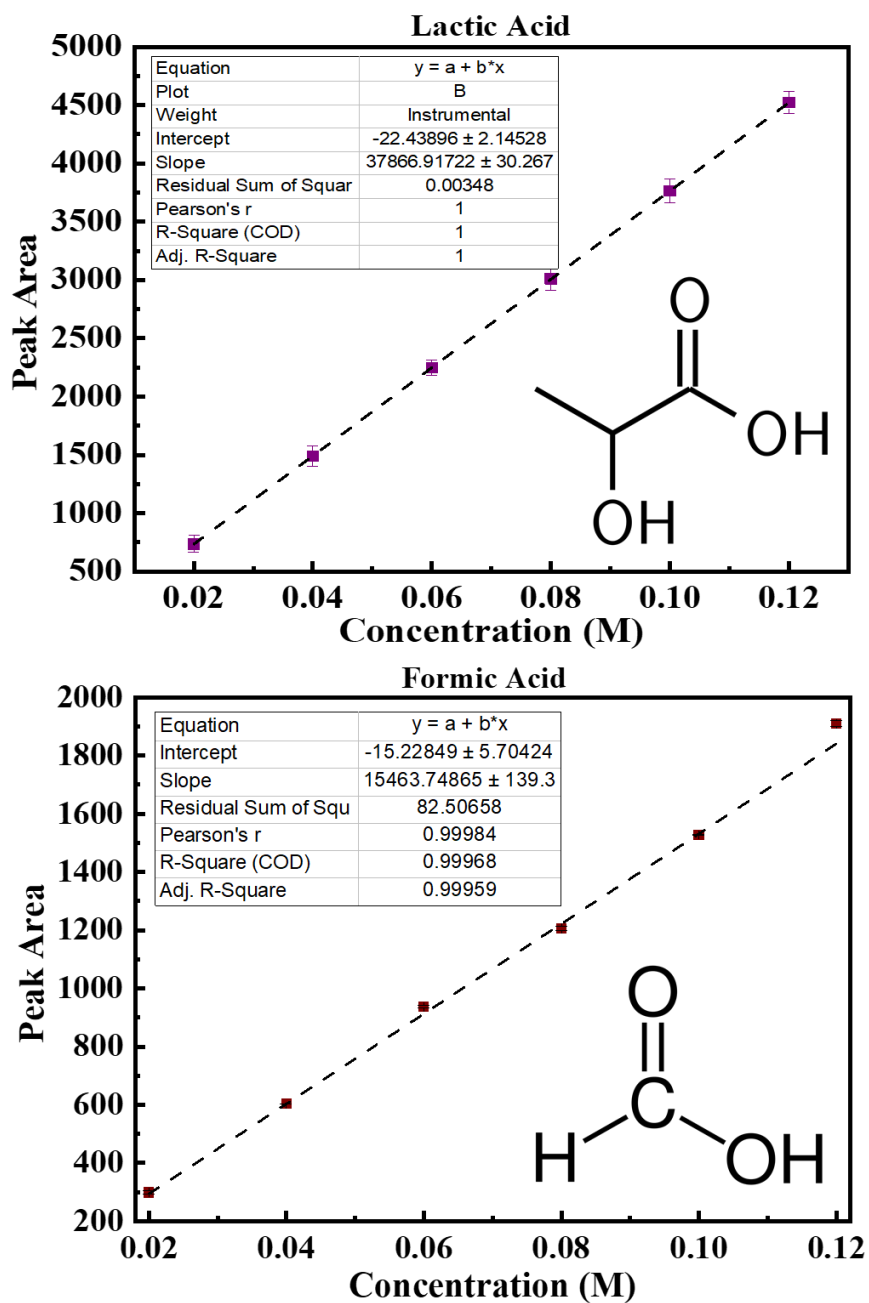


Figure D16. Calibrated curves of lactic and formic acids determined from HPLC with retention time of 12.39 and 13.47 min, respectively using DAD (diode array detector) UV/Vis detector 210 nm.

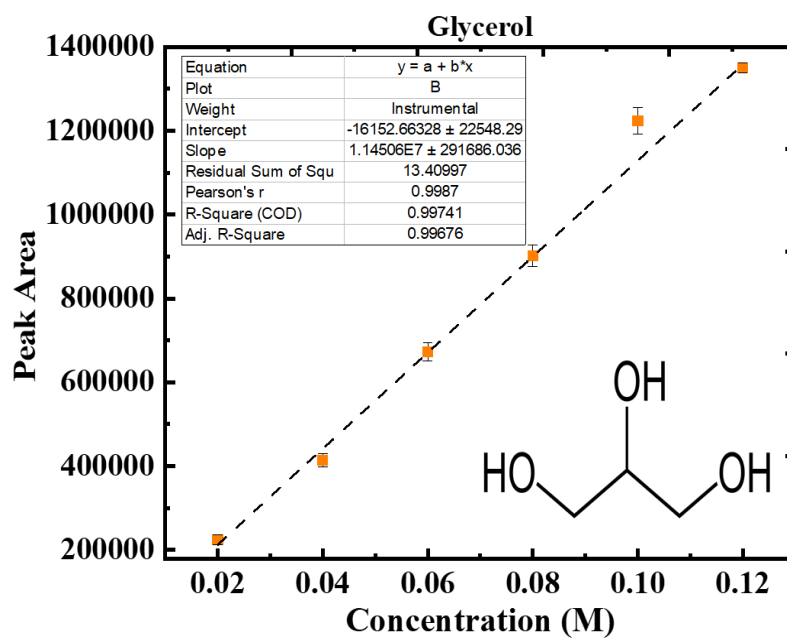


Figure D17. Calibrated curves of glycerol determined from HPLC with retention time of 13.74 using refractive index signal.

Table D2. Comparison of performance reported in the open literature for PGM free catalysts.

Catalyst	Synthesis	Electrolyte	E _{onset} vs. RHE (V)	Conditions	Selectivity	Ref.
Spherical Ni	Heatless NaBH ₄ reduction	0.1 M glycerol + 1 M KOH	1.375	CA -1.4 V; 30 min	OX: 0.6%, TA: 0.85% GA: 4.75%, GLYC:35.3%, LA:2%, FA:56.5% ^h	This work
Ni ₉₀ Bi ₁₀			1.33		OX: 3.3%, TA: 7.9% GA: 4.5%, GLYC:36.3%, LA:2.1%, FA:45.8% ^h	
Ni ₉₀ Bi ₁₀ -after aging			1.33		OX: 5.5%, TA: 8.2% GA: 5.4%, GLYC:37.5%, LA:2.5%, FA:40.9% ^h	
Ni/C	Commercial	0.1 M glycerol +	1.43	CA - 0.7 V vs. Hg/HgO; 3 h	DHA: 1.5% GLYD: 3.1%, GLYC: 29.8%, HPA: 17.9%, GA: 28.2%, OX: 4.1% ^h	1
ALD (TiO ₂)-Ni/C	Commercial/TiO ₂ deposition	0.1 M KOH	1.39		DHA: 4%, GLYD: 0.9%, HPA: 10.1%, TA, 3.7%, GLYC: 24%, OX: 4.8%, FA: 1.4% ^h	
Bulk Ni	Commercial	0.1 M glycerol +	1.37	CA - 0.42 to 0.54 V vs. Hg/HgO; 30 min	GLYD, carbonyl species, carboxylates ^p	2
Bulk Ni-after treatment		1 M KOH	1.33			
Co ₃ O ₄ /GPE	Electrodeposition / annealing in air	0.5 M glycerol + 1 M KOH	1.3	CA - 0.6 V vs. Hg/HgO; 24 h	FA ⁿ	3
Urchin Ni	Modified Polyol Method	0.5 M glycerol +	1.3	CA - 0.42 to 0.54 V vs. Hg/HgO; 30 min	GLYD, carbonyl species, carboxylates ^p	4
Ni ₈₀ Pd ₂₀		1 M KOH	1.21			
Ni/C	Impregnation/Reduction method	0.1 M glycerol +	1.3	CA - 1.6 V vs. RHE; 8 h	FA: 32.2%, GA: 11.5%, GLYC: 0.5 mM ^h	5
NiCo/C			1.44		FA: 7.5%, GA: 4.5%, GLYC: 0.25 mM ^h	
NiFe/C		0.1 M NaOH	1.2		FA: 4%, GA: 3.7%, GLYC: 0.1 mM ^h	
NiFeCO/C			1.25		FA: 34.1%, GA: 10.3%, GLYC: 0.2 mM ^h	
Bulk Ag	Commercial	1 M glycerol + 0.1 M NaOH	0.8	CA - 1.125 V vs. RHE; 14 h	FA, GA, GLYC ^h	6

Abbreviations: tartronic acid (TA), dihydroxyacetone (DHA), glyceraldehyde (GLYD), glyceric acid (GLYC) and hydroxypyruvic acid (HPA), glycolic acid (GA), oxalic acid (OX), lactic acid (LA) and formic acid (FA)

Subscripts illustrate the type of detection technique: (h) HPLC, (n) NMR and (p) PM-IRRAS

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Chapter 7

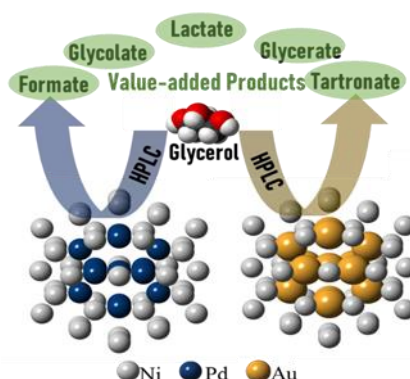
7 Influence of Pd and Au on Electrochemical Valorization of Glycerol over Ni-rich Surfaces

Based on the paper:

Houache M. S. E., Shubair A., Sandoval M. G., Safari R., Botton G. A., Jasen P. V. Jasen, González E. A., Baranova E. A., (In preparation for submission).

Abstract

Herein we synthesized bi-metallic Pd@Ni and Au@Ni core-shell like nanoparticles for glycerol electrooxidation reaction (GEOR) in alkaline media. Catalytic activity and stability were evaluated via various electrochemical measurements. Among different atomic ratios, Ni₈₀Pd₂₀ and Ni₉₀Au₁₀ nanoparticles display the highest current densities of 543 and 504 A.g⁻¹_{Ni}, which are ~ 4.5 and 4.2 times higher than spherical Ni, respectively. The GEOR products were analyzed by High Performance Liquid Chromatograph in a continuous electrolysis combined with chronoamperometry at different applied potentials and temperatures. The addition of auxiliary metals (<20 at.%) to Ni nanoparticles led to a remarkable glycerate selectivity of ~ 73.1% and 65.7% for Ni₈₀Pd₂₀ and Ni₉₀Au₁₀ catalysts at 1.3 V and 50 °C, respectively. Notably, after 6 hours of electrolysis Pd@Ni and Au@Ni tend to suppress the C-C bond cleavage to yield more C₁ products, compared to Ni at any applied potentials and temperatures. We also performed DFT calculation for the core@shell icosahedral (Ih₁₃, Ih₅₅) and decahedral (Dh₅₄) systems. Our results indicate that both bimetallic systems are more stable and reactive than Ni NP. Pd@Ni and Au@Ni NPs are mixed shell with an excess energy of -0.41 eV and -0.24 eV, respectively, and their work function decrease with respect of Ni NP. In all of our bimetallic systems the core@shell develop negative@(positive) net charge.



7.1 Introduction

Glycerol electrooxidation reaction (GEOR) is a viable and efficient way of converting an excess of glycerol, a by-product of biodiesel production¹⁻³, to value added chemicals.⁴⁻⁶ GEOR was proposed over two decades ago, however there are still several

questions that remain to be answered before this process could see practical application. The central issue is a type of electrocatalytic material and the nature of the active sites that in turn dictate the catalytic activity and selectivity towards value added products.⁴ There are several possible reaction pathways for the partial electro-oxidation of glycerol, which result in various products: glycerate, tartronate, hydroxypyruvate, glycolate, oxalate, dihydroxyacetone, mesoxalate and formate⁷⁻¹⁰, therefore development of efficient and stable electrocatalysts with high selectivity to the desired products has been a central topic of GEOR research in recent years.

Several noble platinum-, palladium- and gold-based catalysts have been developed.¹¹⁻¹⁵ Results showed that gold outperforms the other noble metals in alkaline media due to its relatively high anti-poisoning capabilities and large capacity to adsorb hydroxyl ions, which promote the oxidation reaction.¹⁶ *Maumau et al.* tested Au/C which showed to have high current density and anti-poisoning ability to surface oxides compared to Pd/C.¹⁷ Similarly, gold disk electrodes exhibited nine times higher current density than palladium disks.¹⁸ Regarding selectivity, the main products formed on noble metals like Pd, Pt and Au have been shown to be glycerate ions, mesoxalate and/or tartronate with a unique selectivity to hydroxypyruvate ion on gold.^{19,20} In addition, AuPt alloy showed a unique selectivity to lactic acid (73%), which is a valuable product used in several industries.⁸

Among the non-noble metals, nickel is the most common metal used in electrochemical technologies: rechargeable batteries, fuel cells, sensors, alkaline water electrolysis and supercapacitors,²¹⁻²³ due to its high current densities and good stability in alkaline media²⁴. However, limited numbers of studies explored Ni and Ni-based electrocatalysts for GEOR.²⁵⁻²⁹ *Oliveira et al.* reported, that the region of nickel oxyhydroxide formation (NiOOH), which forms at ($\sim 1.4\text{V}$ vs RHE) is the active phase for GEOR on Ni nanoparticles.²⁵⁻²⁷ The main products were formate with minor amounts of glycolate, glycerate, tartronate, and oxalate on carbon supported Ni, NiCo and NiFe.²⁷ In our recent report, we synthesized Ni-Bi double-shell/core structure that showed a 2-fold enhanced GEOR activity when compared to monometallic Ni.²⁸ The addition of 10 atomic (at.) % of Bi improved the formation of C₃ products by suppressing the C-C bond cleavage. In another study from our group, we prepared Ni-Pd double-shell/core nanoparticles (NPs) using a modified polyol method. NiPd nanoparticles of various

composition showed higher electrocatalytic activity towards GEOR than mono-metallic Ni due to a synergistic effect between the two metals, however, the reaction pathway and selectivity were similar to that of monometallic Ni.²⁹

Theoretical methods for studying properties of bimetallic particles have become an important tool, which allows predicting reactivity, stability and magnetic properties of nano clusters. Several authors studied the structural properties, stability, anisotropy, strain, mixing energies, magnetic properties and chemical order of NPs formed by metals of the groups 10 and 11.³⁰⁻³⁶ The NPs present a size-dependent evolution of their structure and properties. The geometric shape and the energetic stability of NP could drastically change with size.³⁰ Also, the accumulation of strain at the atomic level and its subsequent release can be responsible for the symmetry breaking that make possible the different size- and composition-dependent transitions between the core@shell arrangements.³¹

*Zhu et al.*³⁷ investigated the structural and electronic properties of the icosahedral Pd_{55-n}Ni_n (n = 0-55) clusters using DFT. These authors found that the core-shell Ni₁₃@Pd₄₂ cluster is the most stable structure. Their electronic property analysis reveals that the interaction between Pd-4d and Ni-3d orbitals makes the main contribution and a strong d-d self-interaction among the 3d orbitals of the Ni atoms. They also found that with an increasing number of Ni atoms, the d-band center of the surface Pd atoms shift far away from the Fermi level, while the root mean squared d-band width broadens. This feature is also observed in the partial DOS of the surface Pd atoms. The charges are partially transferred from Pd to Ni in the bimetallic cluster and partially from Ni atoms on the top sites to Ni atoms in the core.

In a recent publication, *Shnedlitz et al.*³⁸ investigated the in-situ impact of oxygen, an inevitable trace gas the clusters are exposed to during transmission electron microscopy (TEM) measurements, on the phase transition from Ni-Au to Au-Ni core-shell clusters. Temperature-programmed, high-resolution TEM studies are accompanied by a computational modeling approach with the aim to identify the effect of O₂ adsorption on the observed phase transition. Theory as well as experiment leads to the conclusion that the inevitable oxygen presence during TEM measurements, an Au-Ni core-shell system becomes thermodynamically preferred at elevated temperatures, even before a full oxidation of the reactive metal takes place. In terms of reaction kinetics, the process of Ni diffusion to the surface is catalyzed by the mere presence of oxygen. So, for future

applications of bimetallic nanoparticles in this size regime as catalysts, it needs to be taken into consideration that gas adsorption onto the protective noble metal shell can destabilize the core-shell structure by an enhancement of intermetallic diffusion.

Herein, we synthesize bimetallic nickel rich catalysts $\text{Ni}_x\text{Au}_{1-x}$ [$x = 100, 98, 95$, and $90 \text{ at.}\%$] and $\text{Ni}_x\text{Pd}_{1-x}$ [$x = 100, 95, 90$ and $80 \text{ at.}\%$] catalysts using a sodium borohydride method, which could be easily scaled up. The structure, morphology, and composition of the catalysts were characterized by transmission electron microscopy (TEM), X-ray diffraction (XRD), X-ray photoelectron microscopy (XPS), energy-dispersive X-ray spectroscopy (EDS) and electron energy loss spectroscopy (EELS). In addition, the electrochemical performance was evaluated by cyclic voltammetry (CV), chronoamperometry (CA), linear sweep voltammetry (LSV) and durability test (cycling for 300 cycles) in alkaline media. Product distributions of GEOR were also analyzed by HPLC in a membraneless continuous electrolysis cell (25 cm^2) at different applied potentials and temperatures. Furthermore, to shed light on the experimental observations, a series of Density Functional Theory (DFT) calculations on smaller, finite model systems has been carried out. To this end, we calculated the excess energy, electronic structure, d band center, work function (WF) and strain between core-shell layers.

7.2 Experimental section

7.2.1 Material synthesis

The $\text{Ni}_x\text{Au}_{1-x}$ ($x = 100, 98, 95$, and $90 \text{ at.}\%$) and $\text{Ni}_x\text{Pd}_{1-x}$ ($x = 100, 95, 90$ and $80 \text{ at.}\%$) catalysts were synthesized via wet chemical synthesis. The detailed methodology was reported in our previous work.²⁹ Briefly, the metal precursor salts nickel (II) chloride hexahydrate (ALDRICH Chemistry, 99.999% purity), gold (III) chloride (ACROS Organics, 99% purity) and palladium (II) chloride (ALDRICH Chemistry, $\geq 99.9\%$ purity) were dissolved in ethanol solvent in a controlled weight percentage ratio. After complete dissolution, the sodium borohydride powder (ACROS Organics, 98+% purity), which is the reducing agent, was added to the mixture. Finally, the samples were centrifuged and freeze dried.

7.2.2 Physicochemical and electrochemical characterizations

Various physicochemical procedures (TEM, SAED, XRD, XPS, HAADF, EDS, EELS) were implemented. In addition, different electrochemical tests (CV, LSV, CA) were conducted. The detailed procedures were thoroughly explained elsewhere.²⁹

7.2.3 Chromatographic analysis of products

Continuous electrolysis cell (25 cm²) coupled with chronoamperometry was utilized to detect product distributions for GEOR. The HPLC measurement and standard calibration details were previously reported along with calculations.²⁸

7.2.4 Theoretical modeling and calculations

To develop several finite size models to complement experimental characterization we perform DFT calculations on these models using the VASP code.³⁹ The calculations are spin polarized since most systems have interesting magnetic properties. According to the experimental results for the NPs, we focus on icosahedral and decahedral clusters. We studied the 13- and 55-atoms icosahedral (Ih₁₃ and Ih₅₅, respectively) and 54-atoms decahedral (Dh₅₄) nanoparticles. The 13 atoms systems were studied in order to validate our theoretical methodology. These results are discussed in the supporting information and compared with other experimental and theoretical findings from literature. The 55-atoms icosahedral NP serves as a model system resembling the experimental finding, with an almost spherical shape and (111) faces terminations. Also, the NPs with icosahedral structure have good stability.^{34,40-42} From the point of view of surface energy, this structure is a highly strained non-crystalline one with a quasi-spherical shape and close-packed surface, which optimizes the surface energy well. In addition, the icosahedral NPs are obtained by packing together twenty tetrahedrons sharing a common vertex. This packing causes the high internal strain of the structure and the efficient minimization of the surface energy, which favored this structure at small sizes.^{34,40,41} The decahedral structure also has (111) faces termination. In both systems the composition of bimetallic NP is in the range of that synthesized experimentally. More information on the schematic models is given in Figure E1 in SI. The Ih₁₃-, Dh₅₄- and Ih₅₅-NPs are configured as core_m@shell_n systems, i.e., M_m@Ni_n (as mentioned before Ni_xM_{1-x}) particles (M = Au and Pd), where “m” is the number of M-atoms in the core and “n” is the number of Ni-atoms in the shell. In this work, we study the Ih₁₃-M₁@Ni₁₂, Ih₅₅-M₁@Ni₅₄, Ih₅₅-M₁₃@Ni₄₂ and Dh₅₄-M₇@Ni₄₇ systems.

7.3 Results and discussion

7.3.1 Physicochemical characterization of $\text{Ni}_x\text{M}_{1-x}$ NPs

The morphological features of as prepared $\text{Ni}_x\text{M}_{1-x}$ ($\text{M} = \text{Pd}$ and Au) NPs were investigated by TEM. Figure 7.1a and 7.2a shows representative micrographs of $\text{Ni}_{90}\text{Pd}_{10}$ and $\text{Ni}_{90}\text{Au}_{10}$ nanoparticles, respectively. TEM reveals almost spherical nanosized particles possessing irregular aggregate shapes, with average particles sizes in the range of 3-5 nm. For these materials, the high rates of agglomeration could be elucidated by the strong attractive magnetic force between colloids during the synthesis procedure.²⁹ Nevertheless, the presence of the second metal Pd or Au, have approximately halved the average catalyst size compared to our previously reported spherical Ni (9.2 ± 2.4 nm).²⁸

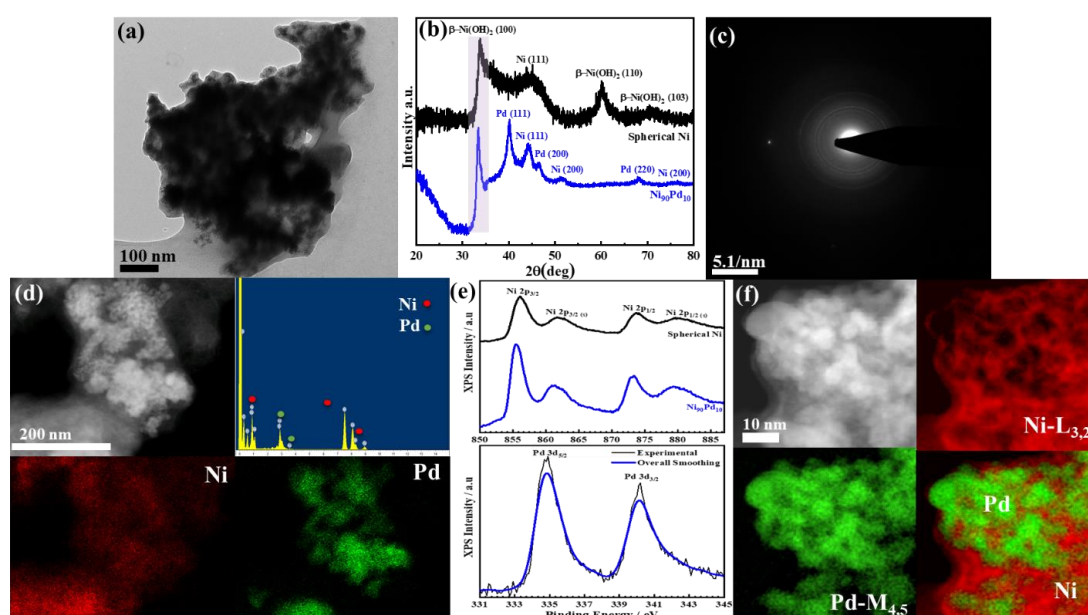


Figure 7.1. Morphology and structure characterizations of $\text{Ni}_{90}\text{Pd}_{10}$ nanostructures. (a) TEM image, (b) XRD patterns, (c) SAED patterns, (d) Dark Field-STEM image, EDS elemental spectrum and mapping of Ni and Pd, (e) XPS Ni 2p and Pd 3d spectrum and (f) HAADF-STEM images and EELS Mapping of $\text{Ni}_{90}\text{Pd}_{10}$ catalyst.

Moreover, XRD pattern was conducted to identify the crystal structure of nanosized $\text{Ni}_{90}\text{Pd}_{10}$ and $\text{Ni}_{90}\text{Au}_{10}$ catalysts. As shown in Figure 7.1b and 7.2b, the peaks displayed distinct face-centered cubic (fcc) structure of Pd(111) and Au(111), respectively, with the presence of Ni(111) and $\beta\text{-Ni}(\text{OH})_2(100)$. The corresponding selected area electron diffraction (SAED) pattern (Figure 7.1c and 7.2c) revealed a set of full rings, indicating that the bi-metallic nanoparticles have high polycrystalline nature, which is in agreement with our XRD data. However, the diffraction rings were not indexed due to close

proximity of Ni to Pd and Au. The spatial distributions of Pd and Au elements in Ni-rich NPs were characterized by the STEM-energy dispersive spectroscopy (EDS) mapping as depicted in Figure 7.1d and 7.2d, respectively. The Z-contrast images illustrate that Ni (red) is uniformly distributed in the selected area. However, Pd and Au (green) are present in a large cluster in more specific area of the nanosized NPs. The EDS spectra are also in good correlation with the elemental composition of $\text{Ni}_{90}\text{Pd}_{10}$ and $\text{Ni}_{90}\text{Au}_{10}$. The physicochemical characterizations of other samples ($\text{Ni}_{80}\text{Pd}_{20}$ and $\text{Ni}_{95}\text{Au}_5$) are illustrated in the supporting information (Figure E2 and E3).

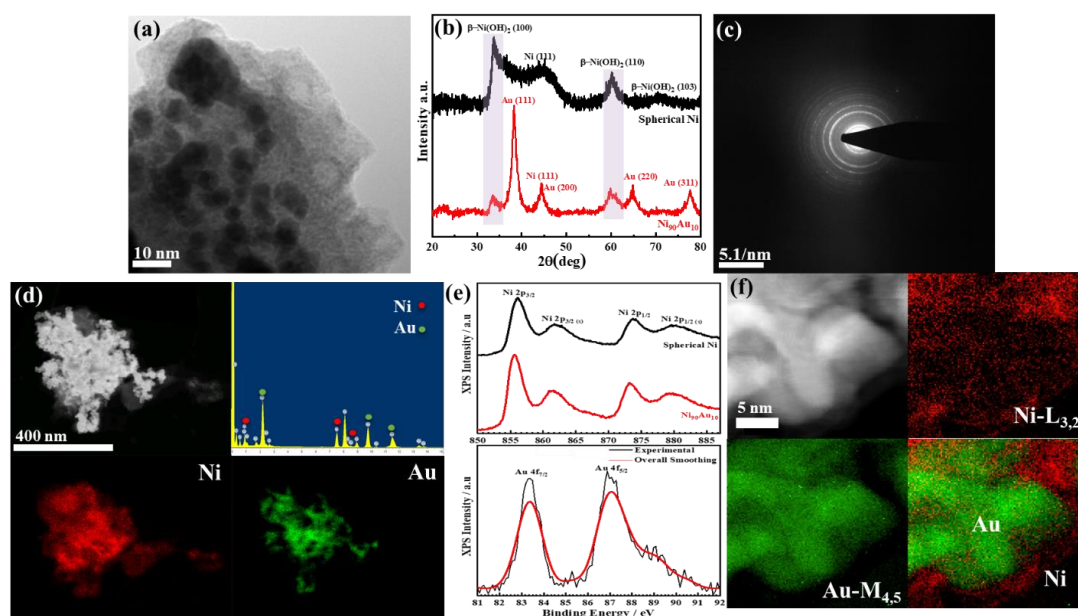


Figure 7.2. Morphology and structure characterizations of $\text{Ni}_{90}\text{Au}_{10}$ nanostructures. (a) TEM image, (b) XRD patterns, (c) SAED patterns, (d) Dark Field-STEM image, EDS elemental spectrum and mapping of Ni and Au, (e) XPS Ni 2p and Au 4f spectrum and (f) HAADF-STEM images and EELS Mapping of $\text{Ni}_{90}\text{Au}_{10}$ catalyst.

To gain additional information about the surface electronic state and chemical composition of $\text{Ni}_x\text{M}_{1-x}$ catalysts, Figure 7.1e and 7.2e, depict the XPS spectra of Pd 3d and Au 4f core level regions, respectively, along with Ni 2p XPS spectrum. Monometallic Ni shows Ni 2p_{3/2} and Ni 2p_{1/2} peaks with binding energies at 856.1 and 873.9 eV, respectively, and two satellite peaks positioned at 861.9 and 880.0 eV. The position of the peaks corresponds to the formation of $\text{Ni}(\text{OH})_2$ phase with the 17.8 eV binding energy distance.^{43,44} For $\text{Ni}_{90}\text{Pd}_{10}$ and $\text{Ni}_{90}\text{Au}_{10}$ samples, one can observe similar peaks corresponding to Ni 2p with a shift of 0.5 eV compared to Ni, which indicates that the chemical environment of Ni^{2+} is affected. Figure 3e (lower spectrum), the Pd 3d spectrum

is positioned between 331-345 eV with two doublets Pd 3d_{5/2} (334.8 eV) and Pd 3d_{3/2} (340.1 eV) in Figure 7.1e. The peaks position and the full width at half maximum (FWHM) of the peaks demonstrate the formation of a pure metal Pd (Pd (0)) with the 5.3 eV binding energy distance.^{45,46} In Figure 7.2e, the two XPS peaks located at binding energies of 83.4 and 87.1 eV (spin-orbital splitting of 3.7 eV) were attributed to Au 4f_{7/2} and Au 4f_{5/2}, respectively, these values are in good correlation with the reported values for pure metal gold (Au(0)).^{45,47} Furthermore, the chemical microstructures of Ni_{1-x}M_x surfaces were also mapped using STEM-EELS analysis. Figs. 7.1f and 7.2f illustrate the elemental distribution of (Ni L_{2,3} and Pd-M_{4,5}) and (Ni L_{2,3} and Au-M_{4,5}) within the Ni₉₀Pd₁₀ and Ni₉₀Au₁₀ NPs, respectively, which were extracted from different signals centered at ~855, 400 and 2200 eV for Ni L_{2,3}, Pd-M_{4,5} and Au-M_{4,5}, (Figure E4). The corresponding STEM-EELS map of Ni-M clearly shows that Pd and Au (green) ions are mostly located in the core region and non-uniform thin layer of Ni (red) ions are segregated on the surface forming a shell. This indicates the formation of M-core@Ni shell-like structures, with Au and Pd serving as seeds during the NPs synthesis.²⁹

7.3.2 Electrochemical characterization

Figures 7.3a and 7.4a. show cyclic voltammograms (CVs) of Ni_xPd_{1-x} (x = 100, 95, 90 and 80 at. %) and Ni_xAu_{1-x} (x = 100, 98, 95 and 90 at. %) catalysts in a N₂-purged 1M KOH solution at 50 mV s⁻¹. The current densities of unsupported Ni_xM_{1-x} were normalized per mass of active nickel species, to avoid uncertainties involved in calculation of the electrochemical active surface areas (ECSA) of Ni-based materials.²⁸ The comparison of current densities per the geometric area (0.196 cm²) is given in Figure E5.

The CVs in the absence of glycerol were consistent with voltammogram profiles reported in the literature for Ni-rich catalysts.²⁴⁻²⁷ On monometallic Ni, the anodic peak (~0.59V) and the cathodic peak (~0.33V) correspond to the surface redox process of β-NiOOH/β-Ni(OH)₂.²⁸ For Ni₈₀Pd₂₀, a peak in the cathodic region centered at ~ -0.33 V (Figure 7.3a inset) represents the reduction of PdO active sites available on the surface²⁹, whereas for Ni₉₅Pd₅ and Ni₉₀Pd₁₀, this peak is negligible, demonstrating Pd is mostly segregate in the core. Similarly, no reduction peak of quasi-2D oxide state of Au was observed as shown in Figure 7.4a. Addition of Pd and Au enhanced the current density of the Ni²⁺/Ni³⁺ peak. It can be noted that the Ni₈₀Pd₂₀ and Ni₉₀Au₁₀ catalysts have higher

$\text{Ni}^{\text{II}}/\text{Ni}^{\text{III}}$ redox peak ($\sim 3 \times$) followed by a more reversible redox process compared to monometallic Ni as shown in Figure 7.3a and 7.4a. Probably the reason for the low activity of pure Ni, its low conductivity, as it is mostly present as oxide. You can clearly see how $\text{NiOOH}/\text{Ni}(\text{OH})_2$ peaks are separated for Ni. Moreover, the presence of palladium and gold had a positive outcome in improving the conductivity as well as the oxygen evolution reaction (OER). The OER current growth was initiated at $\sim 0.71 \text{ V}$ vs. Hg/HgO for Ni compared to $\sim 0.67 \text{ V}$ for $\text{Ni}_{80}\text{Pd}_{20}$ and $\text{Ni}_{90}\text{Au}_{10}$. This phenomenon could be explained by either the synergistic effect between Pd and Au on Ni redox electrochemistry or the $\text{M}_{1-x}\text{Ni}_x$ core-shell structure, resulting in a larger active surface area due to the smaller particle size.

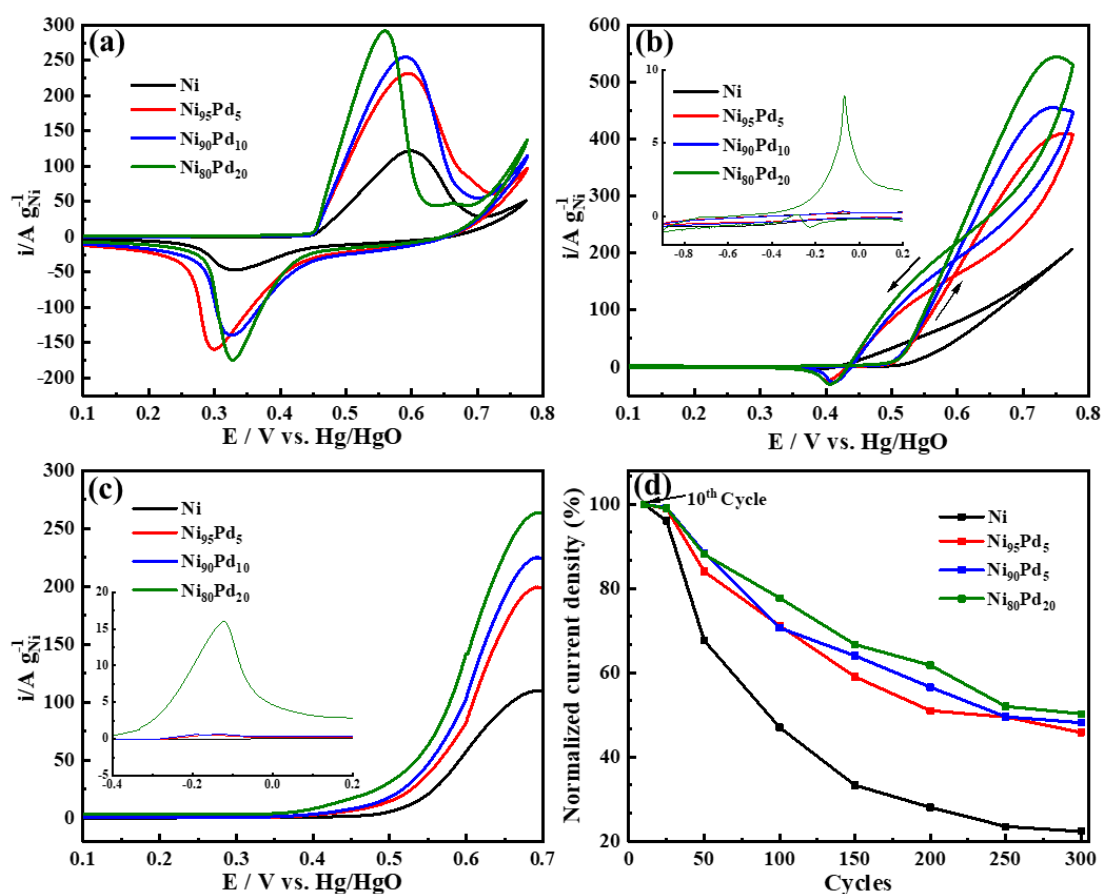


Figure 7.3. Cyclic voltammograms of Ni-based catalysts $\text{Ni}_x\text{Pd}_{1-x}$ performed in (a) 1 M KOH electrolyte and (b) 1M KOH + 0.1M glycerol solution at scan rate of 50 mV s^{-1} . (c) Linear sweep voltammetry at 1 mV s^{-1} and (d) Normalized current density percentage vs CV cycles.

In the presence of glycerol, various electrochemical characterizations were utilized to study the GEOR activity and stability as depicted in Figure 7.3 b-d and 7.4 b-d. CVs of unsupported $\text{Ni}_x\text{M}_{1-x}$ catalysts demonstrated a continuous enhancement in GEOR activity

and negative shift of onset potential with increase in Pd and Au content. For the set of catalysts studied, Ni₈₀Pd₂₀ and Ni₉₀Au₁₀ exhibited the highest mass current densities of 543 A.g⁻¹_{Ni} and 504 A.g⁻¹_{Ni}, respectively compared to 122.4 A.g⁻¹_{Ni} for Ni, as shown in Figure 7.3b and 7.4b. The onset potential of GEOR is negatively shifted by ~ 100mV and 50 mV for Ni₈₀Pd₂₀ and Ni₉₀Au₁₀ compared to spherical Ni, indicating an enhancement in oxidation kinetics. Moreover, these current densities are higher than the ones reported for Ni_xPd_{1-x}.²⁹ For Ni₈₀Pd₂₀ synthesized at high temperature using hydrazine as reducing agent showed a ~2.5x lower mass activity compared to our recent Ni₈₀Pd₂₀ catalyst produced by a heatless, easy to scale up method. Addition of Pd and Au are capable of promoting the activity of Ni much more than bismuth. For Bi promotion, the maximum current density obtained by Ni₉₀Bi₁₀ is 436.5 A.g⁻¹_{Ni}, lower than the data obtained in this report.²⁸

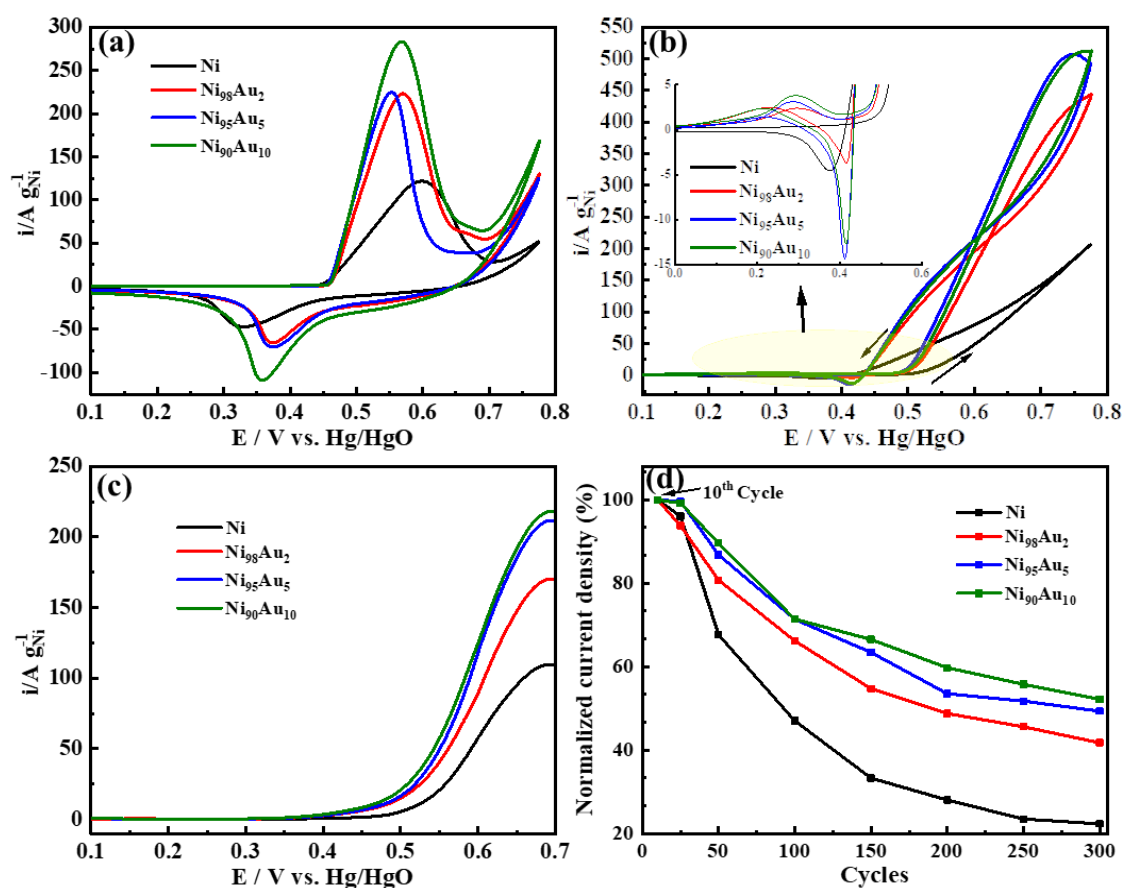


Figure 7.4. Cyclic voltammograms of Ni-based catalysts Ni_xAu_{1-x} performed in (a) 1 M KOH electrolyte and (b) 1M KOH + 0.1M glycerol solution at scan rate of 50 mV s⁻¹. (c) Linear sweep voltammetry at 1 mV s⁻¹ and (d) Normalized current density percentage vs CV cycles.

This enhancement of GEOR performance of Ni-rich catalysts is due to synergistic and electronic effects between the bi-phases of Ni-Pd and Ni-Au. It is worth to note that we observed an additional oxidation peak centered at ~ -0.1 V vs. Hg/HgO which attributed to GEOR on Pd sites for Ni₈₀Pd₂₀ (Figure 7.3b, inset).²⁹ Whereas, two additional oxidation peaks appeared at ~ 0.12 V vs. Hg/HgO ascribed to GEOR on Au sites, demonstrating that gold by itself has much lower overpotential compared to Ni.⁴⁸ Figure 7.4b, inset illustrates more intense peaks with higher Au content.

The increase in activity with addition of Pd and Au is further observed in the linear sweep voltammetry (LSV) test in Figure 7.3c and 7.4c. Clearly, bimetallic catalysts have lower onset potentials and higher mass current densities than on monometallic Ni. The durability tests of the unsupported Ni_xM_{1-x} catalysts were attained by running 300 consecutive CV cycles in 1 M KOH + 0.1 M glycerol. After 300 cycles in (Figure 7.3d and 7.4d), Ni₈₀Pd₂₀ and Ni₉₀Au₁₀ exhibited the highest activity and retained $\sim 51\%$ of their initial current density compared to $\sim 22\%$ for Ni. The drop of activity can be explained by mechanical degradation of the catalysts and/or surface blocking by intermediates. Based on the electrochemical analysis, we conclude that the M_{1-x}Ni_x core-shell-like structure displayed superior GEOR stability and activity performance than monometallic Ni.

7.3.3 Theoretical results

7.3.3.1 Stability and geometrical analysis

In order to analyze the results at varying composition, we calculate the normalized excess energy E^* (equation E2 in supporting information). The excess energy values for the considered systems are shown in Figure 5.7. As expected, all pure NPs have 0 eV. For the Ih₁₃ systems, the more stable configurations are Au₁@Ni₁Au₁₁ and Ni₁@Pd₁Ni₁₁. The configurations of Pd₁@Ni₁₂, Pd₁@Pd₁Ni₁₁, Ni₁@Pd₁₂ and Pd₁@Ni₁₂ present some morphological instability, although this does not mean that the cores have unstable configurations. The NPs have locally stable minima, whose energy is however much higher than the energy of the optimal configurations. These morphologies do not persist as the lowest-energy morphology when the proportion of core atoms increases in the nanoparticle, i.e., the term instability is referred to the overall core morphology and not to the local minimum corresponding to the centered core.³¹ In the case of Ih₅₅- and Dh₅₄-NPs, the Ni₁@Au₁Ni₁₁@Ni₄₂ (Layer1@Layer2@Layer3 - Figure E1) and Pd₁₃@Ni₄₂ systems were the more stable, respectively. The configurations Au₁₃@Ni₄₂ and Au₇@Ni₄₇

also present morphological instability.

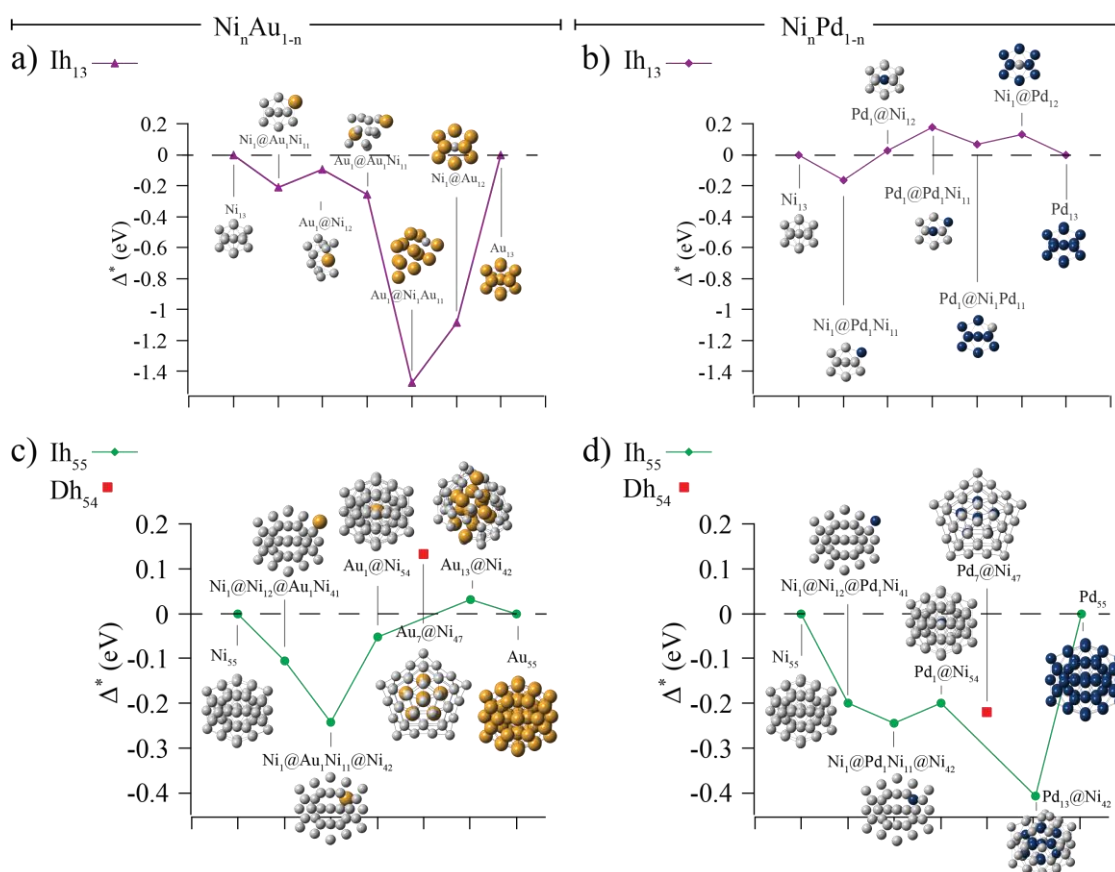


Figure 7.5. Excess energy values of the N_nM_{1-n} NPs for (a,b) the 13-atoms icosahedral systems (purple) and (c,d) 55-atoms icosahedral systems (green) and 54-atoms decahedral systems (red).

The morphological instability has a physical origin that is related to strain release. In Figure 7.6 optimized structures of the Ih_{13} , Dh_{54} and Ih_{55} NPs are shown. It can be seen that the $Au@Ni$ icosahedral systems have the most important strain percentage (e Layer #, # = 2, 3), which is consistent with a strong structural deformation and the formation of mixed shell systems (the equation for strain (Eq. E4) is presented in SI). This is consequence of the mismatch between the metal atomic radii. Also, in the system strain is reducing when the Ni shell diameter is higher than that of the Au core. For the $Pd@Ni$ icosahedral NP we found less strain and therefore less structural deformation, which is consistent with a similar atomic radius of these metals. Despite this, the presence of strain and the fact of the mixed shell system have negative excess energy indicate that the Pd could segregate to the shell, but in a less amount that in the case of the NP with Au in the core. In the decahedral NPs the strain values are smaller and they have less geometrical distortion, as a consequence of more open structure. These results agree with the range

of stable composition described in the experimental sections.

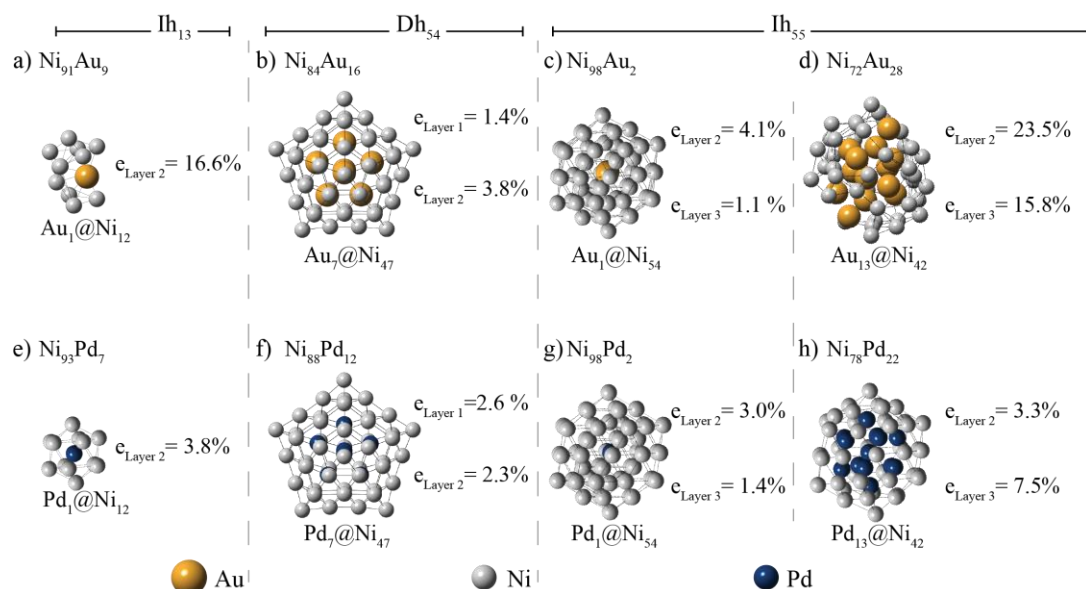


Figure 7.6. Optimized structures for theoretical core@shell nanoparticles. The labels above the NP system correspond to the estimated composition percentage of each metal.

7.3.3.2 Electronic structure

Regarding electronic structure, the d-band PDOS curves are shown in Figure 7.7. It can be seen that all systems are metallic. Also, with the exception of Au monometallic NP (see Figure 7.7a, both side), the spin up and spin down contributions are shifted and are asymmetrical which is consistent with a magnetic behavior.

The large magnetic moment value in the bare Ni₅₅ icosahedral system (47.7 μ_{BB}), suffer a slightly decrease when the central atom is substituted by an Au- or Pd-atom. When the all core atoms are replaced by Au or Pd atoms (i.e. the 13th central atoms in the core) the magnetic moment decreases about 5.7 μ_{B} or 4.3 μ_{B} , respectively as illustrated on the left-hand side of Figure 7.7c, e, g, i and k. In addition, the Pd₅₅ NP has the smallest magnetic moment of the icosahedral systems (Figure 7.7m, left-hand side) and the decahedral systems show similar behavior (Figure 7.7. right-hand side). The magnetic moment values for the monometallic systems agree with those reported by Wang *et al.*^{49,50} and Yang *et al.*⁵¹ The d-band center (ϵ_d) is an important factor for studying the systems reactivity, for this reason we calculate the values for the monometallic and bimetallic NP using Equation E5 in supporting information.

The ε_d values shown the following trend for icosahedral systems: $\text{Pd}_{55} < \text{Pd}_{13}@\text{Ni}_{42} < \text{Ni}_{55} < \text{Pd}_1@\text{Ni}_{54} = \text{Au}_1@\text{Ni}_{54} < \text{Au}_{55} < \text{Au}_{13}@\text{Ni}_{42}$ (Figure 7.7b, d, f, h, j, l and n on the left). For the decahedral NPs the order is $\text{Pd}_{54} < \text{Pd}_7@\text{Ni}_{47} < \text{Au}_{54} < \text{Ni}_{54} < \text{Au}_7@\text{Ni}_{47}$ (Figure 7.7b, d, f, h, and j on the right). It can be noted that these trends do not follow any linear relationship for the bimetallic systems with respect to reactivity. The d-band center value is based on the degree of filling, average energy and width of the localized d-band of the metal surface and how they interact with the adsorbate energy levels. In particular, there are two simple mechanisms for changing the chemical properties of the NP. First, the average bond length between the metal atoms in the shell surface is different from that of the monometallic particle, resulting in changes on the strain. Second, hetero-metallic bonding interactions (called the ‘ligand effect’) between the surface atoms and the substrate can result in a change of the surface electronic structure, thereby modify the surface chemical properties. This probes that the chemical reactivity cannot be analyzed only with the d-band center idea, because of the complex interplay between different parameters. Then, for a better understanding of NPs reactivity, charge transfer, work function (WF) and electronegativity must also be considered.

In these metallic systems, the information about the ability of the metal to gain or lose electrons could be provided from the WF and Fermi level (E_F) values. Electrons can freely exchange at the metal–metal interface.⁵² The different E_F values produce a net flow of electrons from the material with the lowest WF to that with the highest WF value, until the E_F values in both phases is equilibrated. During this process, some of transferred charge will be distributed on the surfaces, generating an electric field, although most of it will be retained at the metal contact interface, like a surface dipole. This reveals an outer potential difference between M and Ni metals that is directly proportional to the WF value difference.

The WF and E_F obtained for the studied systems is listed in Table E1. The Fermi levels trends of the nonmetallic systems are $\text{Pd} (-4.338 \text{ eV}) < \text{Au} (-4.307 \text{ eV}) < \text{Ni} (-3.487 \text{ eV})$ for the Dh_{54} , and $\text{Pd} (-3.835) < \text{Au} (-3.817 \text{ eV}) < \text{Ni} (-3.374 \text{ eV})$ for the Ih_{55} structures. The WF values are ordered as follows: $\text{Pd} (4.71 \text{ eV}) > \text{Au} (3.97 \text{ eV}) > \text{Ni} (3.75 \text{ eV})$ for the Ih_{13} , $\text{Pd} (5.09 \text{ eV}) > \text{Au} (5.06 \text{ eV}) > \text{Ni} (3.98 \text{ eV})$ for the Dh_{54} , and $\text{Au} (5.07 \text{ eV}) > \text{Pd} (4.88 \text{ eV}) > \text{Ni} (4.17 \text{ eV})$ for the Ih_{55} structures. Also, the WF values trend is $\text{Pd} (5.09 \text{ eV}) > \text{Au} (5.06 \text{ eV}) > \text{Ni} (3.98 \text{ eV})$ for the Dh_{54} , and $\text{Au} (5.07 \text{ eV}) > \text{Pd} (4.88$

eV) > Ni (4.17 eV) for the Ih₅₅ NP. In addition, the electronegativity order of the metallic elements is Au > Pd > Ni.

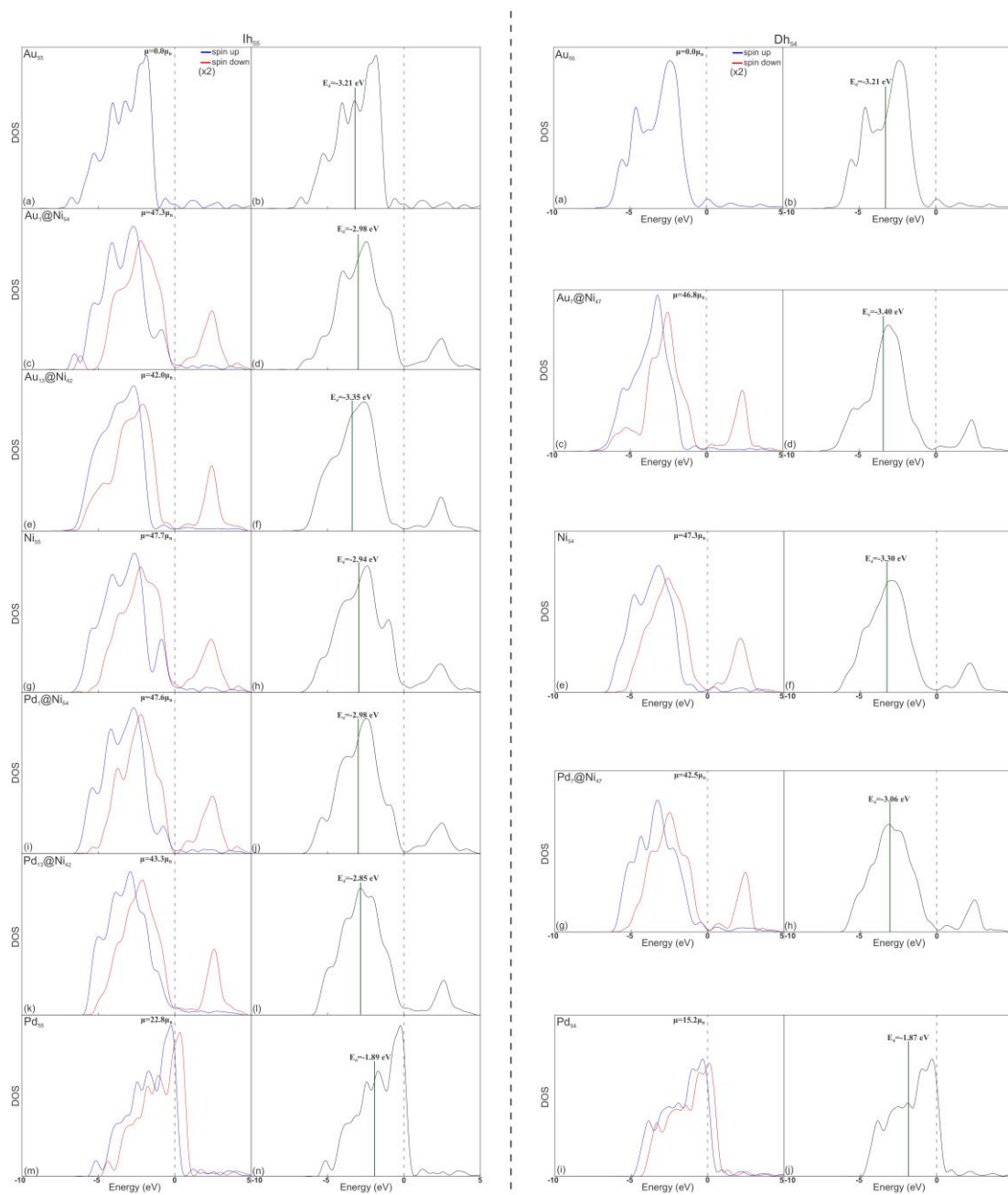


Figure 7.7. Curves of d-band PDOS for the 55-atoms icosahedral systems (left) and 54-atoms decahedral systems (right). The blue and red lines indicate the spin up and spin down contributions, respectively. The black line corresponds to the total d-band curve.

These values are consistent with the electron density transfer from Ni to other metals when they are in contact, as can be seen in Figure 7.8. In all of our bimetallic systems the core and the shell develop negative and positive net charge, respectively. Then, it is clear that the charge is transferred from the shell atoms to the core atoms, leading to a surface

shell being partially positive. In addition, a smaller WF value for $M_m@Ni_n$ NPs compared with mono-metallic Ni NPs, could indicate a higher reactivity.⁵³ Replacing the core of Dh_{54} Ni NP by Au- or Pd-atoms, increase the WF values about 0.08 or 0.09 eV. Finally, changing the central atom in Ih_{55} -Ni NP by Au- or Pd-atom induces a decrease in the WF of about 0.12 or 0.16 eV, while if the complete core is replaced by Au- or Pd-atoms the decrease is 0.13 and 0.24 eV, respectively. These results could indicate that the $Pd_{13}@Ni_{42}$ system is the most reactive. As previously mentioned by *Logsdail et al.*, the interfacial charge transfer effects are then dependent on the inherent material WF.⁵⁴

The layer-by-layer net charge distribution (upper part of each subfigure) and the distribution of charge onto the individual atoms in the cross section (lower part of each subfigure) of $M_m@Ni_n$ systems ($M = Au, Pd$) are shown in Figure 7.8.

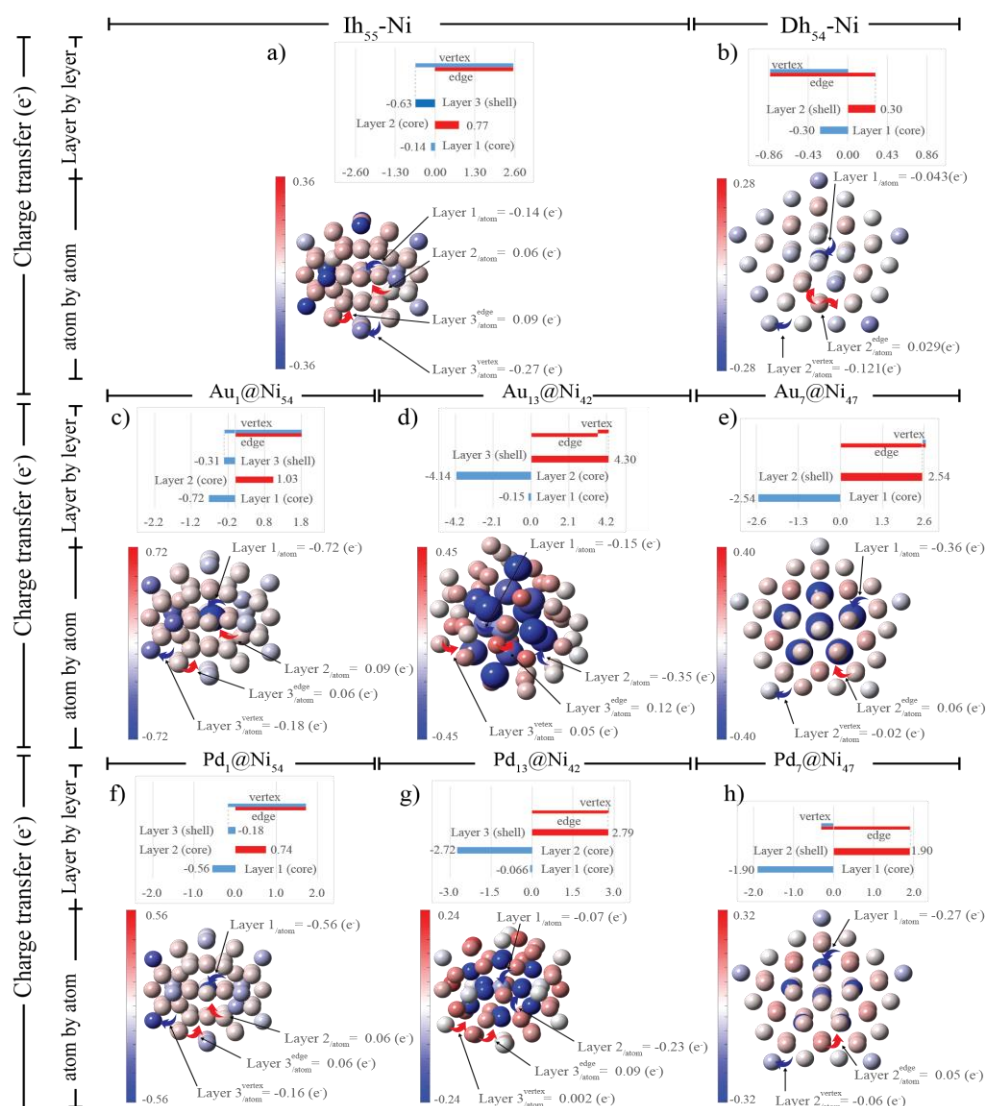


Figure 7.8. Densities charge distributions for Au@Ni and Pd@Ni NPs.

In this Figure, the charges have been normalized by the total amount of charge transferred from Ni to M of each particular system. It is clear from Figure 7.8 that the charge is not equally distributed onto the atoms within the same layer, and also is different between layers. As expected, by analyzing the number of electrons carriers (e^-) for each system, the layer by layer net charge distribution between the cross sections reveals that almost all of the charge transfer occurs at the nanoparticle metal–metal interface in all systems, i.e., the charge transfer is distributed within the metal phases, where the total charge is retained directly at the contact interface.⁵² As predicted by WF values, in the case of $\text{Ih}_{55}\text{-M}_1\text{@Ni}_{54}$ and $\text{Dh}_{54}\text{-M}_7\text{@Ni}_{47}$, mostly of the transferences occurs from Ni-atoms to M-atoms, but some of the charge is transferred to the Ni vertex atoms too, as a geometrical property (Figure 7.8c, f, e and h, respectively). In the case of $\text{Ih}_{55}\text{-M}_{13}\text{@Ni}_{42}$ systems the transference occurs from Ni-atoms to M-atoms and there is no charge concentrated in the vertex.

7.3.4 Electrolysis experiments and product distribution

The best performing $\text{Ni}_{80}\text{Pd}_{20}$ and $\text{Ni}_{90}\text{Au}_{10}$, as well as Ni electrocatalysts were further investigated under continuous electrolysis in 1 M KOH + 0.1 M glycerol for 6 hours at different applied potentials (1.3, 1.4 and 1.55 V), temperatures (R.T and 50°C), and KOH concentrations (0.1 and 1 M) in 0.1 M glycerol as shown in Figure E7 in SI. The quantitative analysis of products was carried out by HPLC by collecting 0.6 ml of the electrolyte solution every 1h. The comparison in glycerol conversions and product distributions of the catalysts are shown in Figure 7.9-7.10 and E8-E11 in supporting information. The calibration curves for the C_3 (glycerate, tartronate, and lactate), C_2 (glycolate and oxalate) and C_1 (formate) products were previously reported.²⁸ According to the HPLC results, the primary products are glyceric (GLA) and formic acid (FA) while, the secondary products are tartronic (TA), lactic (LA), glycolic (GA) and oxalic (OX) acids.

In Figure 7.9a-f, all catalysts showed the same trend in that the lowest applied potential (1.3 V) resulted in the highest selectivity towards GLA and lowest glycerol conversion (< 14%). Additionally, a rise in temperature resulted in higher selectivity to GLA consequently, less production of FA. These trends are consistent with our previous results for $\text{Ni}_{90}\text{Bi}_{10}$.²⁸ Noticeably, the addition of Pd and Au reduced the extent of the decrease in GLA selectivity when applying higher potentials, the glyceric acid production

in Ni, Ni₈₀Pd₂₀ and Ni₉₀Au₁₀ decreases by $\sim 2.4x$, $1.3x$, and $1.5x$, respectively as demonstrated in Figure 7.9a, c and e. The production of C₃ products especially glycerate is enhanced over the bi-metallic catalysts. Specifically, Ni₈₀Pd₂₀ achieved the highest GLA selectivity (73.02%) at 1.3 V and 50°C (Figure 7.9c), which represents the highest C₃/(C₁+C₂) achieved with Ni-rich catalysts to date.²⁵⁻²⁹ Tartronic acid production, a high-value added product⁵⁵, is seven times higher over bimetallic NiPd and NiAu catalysts compared to monometallic Ni at 1.3V and R.T. This enhancement in glycerate and tartronate selectivity on Ni₈₀Pd₂₀ and Ni₉₀Au₁₀ could be elucidated by the lower particle size of the bimetallic catalysts compared to monometallic Ni.^{56,57} Alternative explanation, the bimetallic catalysts have less of the electropositive Ni sites and thus less ability to C-C bond cleavage.⁵⁶ Furthermore, Ni₉₀Au₁₀ has the highest tendency to produce LA ($\sim 3x$) and GA ($\sim 2x$) compared to Ni at 1.4 V and R.T (Figure 7.9e). The fact that the addition of 10 at. % of Au to Ni-rich catalysts induces the production of lactate, indicated that Au increases the oxidative dehydration capacity of the catalyst favoring the reaction pathway leading to LA.⁵⁸ Also, the addition of gold modified the electronic configurations of Ni resulting in different reaction pathways that led to partially oxidized intermediates such as TA and GA.⁵⁶

It was previously noticed that time has a vital role on product distributions.²⁸ After 6 hours of continuous electrolysis, we observed that GLA concentration dropped gradually to FA and glycerol conversion increased progressively as shown in Figure 7.9 b,d,f and E8-E10 in SI. On the other hand, Ni₈₀Pd₂₀ and Ni₉₀Au₁₀ catalysts produced less C₁ products after 6 hours of electrolysis, compared to Ni. By applying a moderate potential of 1.4 V at 50°C, the selectivity to formate is much higher on monometallic Ni (74.5%) compared to Ni-Pd (42.6%) and Ni-Au (40.3%). Additionally, at higher potential of 1.55V, Ni₈₀Pd₂₀ had the highest selectivity of oxalic acid (6.9%) at 50°C as illustrated in Figure 7.9d. This observation indicates that the addition of a ≤ 20 at. % of Pd and Au prompts the C₃ selectivity and hinders the further oxidation of GLA to FA.

The effect of 0.1 M KOH concentration on product distributions of Ni₈₀Pd₂₀ and Ni₉₀Pd₁₀ was also investigated at 1.4 V as shown in Figure 7.10a-d and E11 in SI. For comparison, with time at room temperature, the glycerate production is reduced by (3.72x and 2.4x) at 1 M KOH vs. (1.6x and 1.23x) at 0.1M KOH for Ni₈₀Pd₂₀ and Ni₉₀Au₁₀, respectively. Similar trend is noticed at higher temperatures.

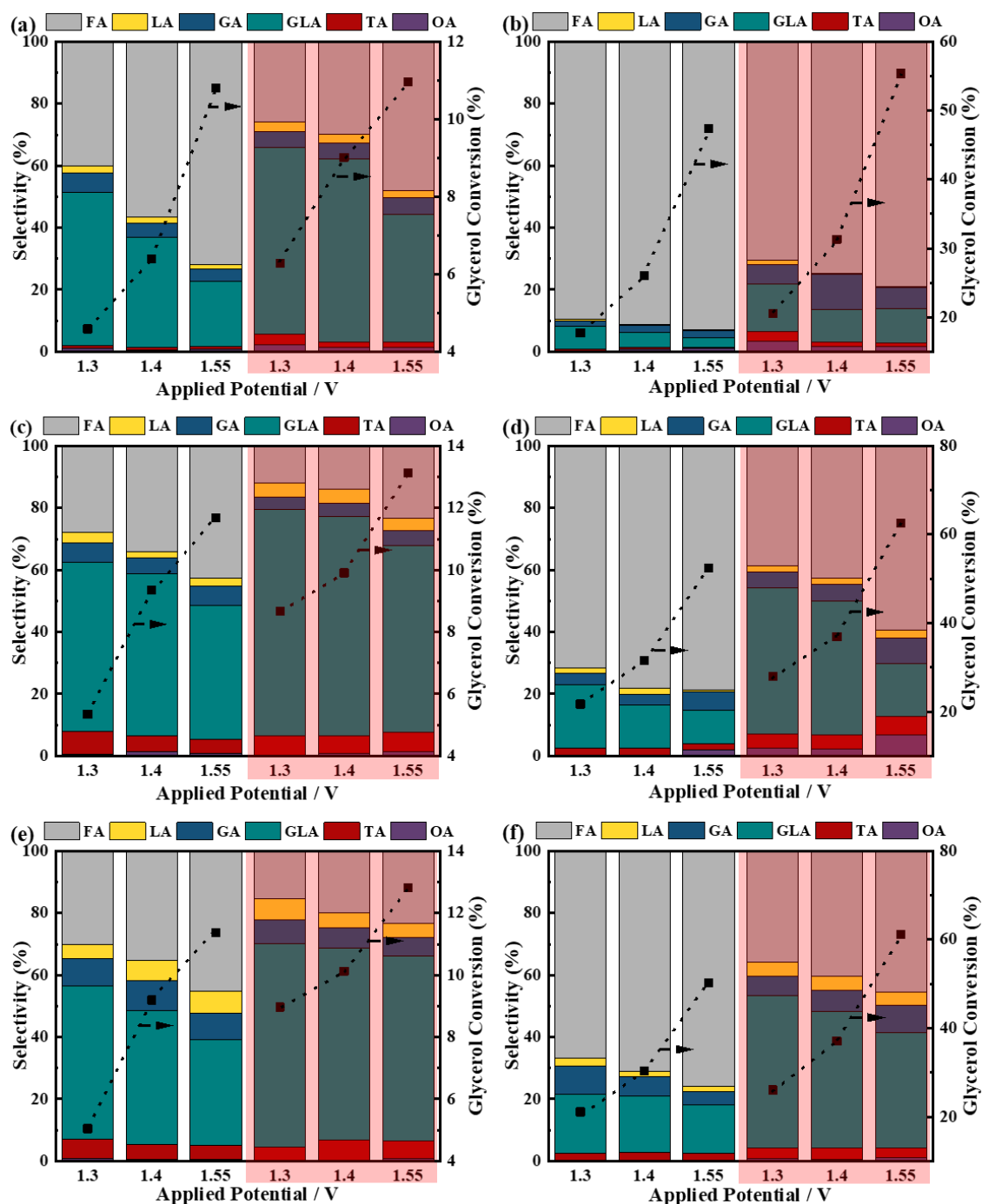


Figure 7.9. Product distributions and glycerol conversion (dashed line) under different applied potentials and temperatures over the (a,b) Ni, (c,d) Pd₂₀Ni₈₀ and (e,f) Au₁₀Ni₉₀ in a 1M KOH+0.1 M glycerol. The left-hand figures illustrate product distributions after 30 min, while the right-hand illustrates products after 6 hrs Gray: formate; Yellow: lactate; Navy: glycolate; Dark Cyan: glycerate; Wine: tartronate and Violet: oxalate. The red shaded border represents temperature at 50 °C.

Based on the HPLC results, the proposed reaction pathway on Ni, NiPd and NiAu catalysts for GEOR is initially oxidized by the primary alcohol electrooxidation (glyceraldehyde), which is in good agreement with our previous study.²⁸⁻²⁹ Further

oxidation is either metal-catalyzed to produce GLA, TA, GA, OX, FA and carbonate or base-catalyzed dehydration forming lactate after Cannizzaro rearrangement.⁵⁸

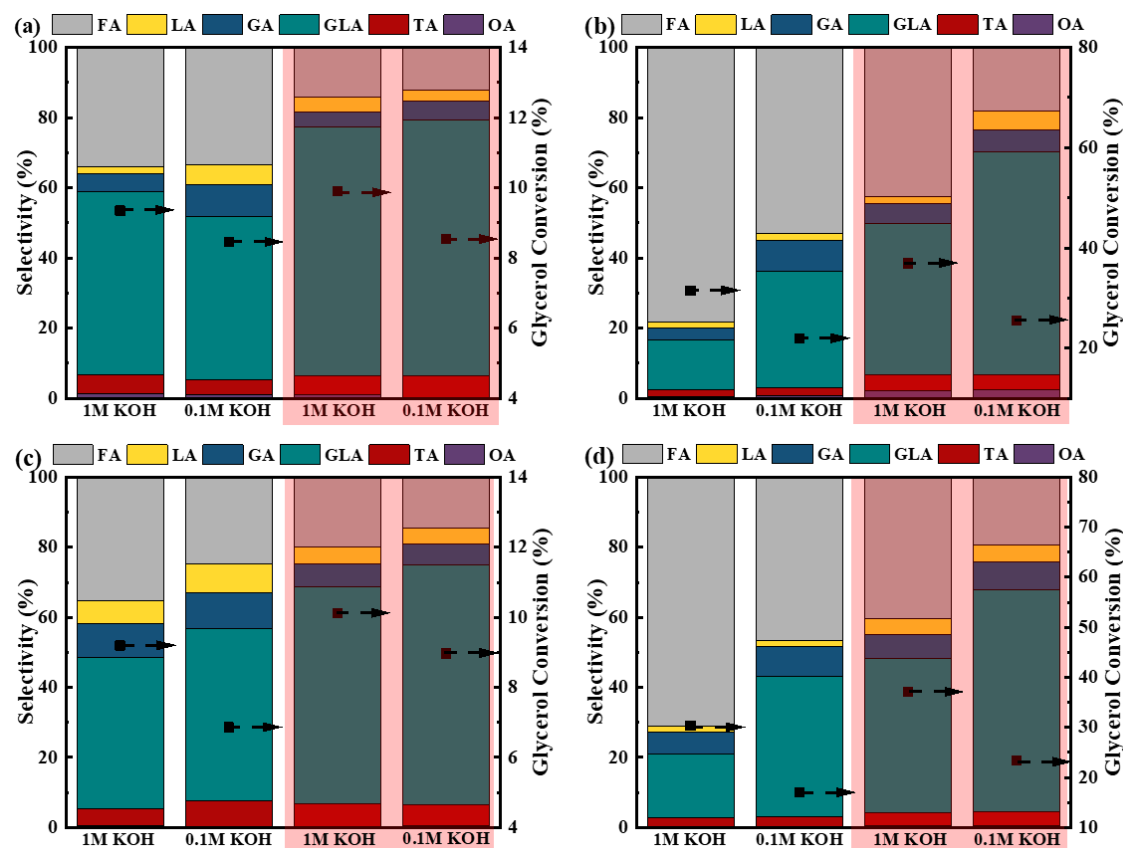


Figure 7.10. Product distributions and glycerol conversion at 1.4 V over the (a,b) Ni₈₀Pd₂₀ and (c,d) Ni₉₀Au₁₀ in a 0.1/1 M KOH+0.1 M glycerol. The left-hand figures illustrate product distributions after 30 min, while the right-hand illustrates products after 6 hrs. The red shaded border represents temperature at 50 °C.

In summary, addition of small amounts of Pd and Au impacts the selectivity by hindering the GLA oxidation to FA compared to the monometallic Ni, leading to higher selectivity to C₃ products at different applied potentials and temperatures. The ability of bimetallic to achieve higher selectivity to C₃ products was justified by either their smaller particle size or these auxiliary metals act as a co-catalyst in order to defend Ni from over-oxidation. In addition, lower KOH concentration further enhances the hindering of C-C bond cleavage, leading to higher C₃ products after 6 hours of continuous electrolysis. It is worth to mention that remarkable selectivity and activity of as-prepared catalyst can be possibly ascribed to the core-shell-like structure. For the Au@Ni and Pd@Ni catalysts, lattice parameter mismatch between the surrounded shell and the core, resulting in a strong strain in the crystal lattice over the atomic layers around the interface, thereby

altering d-band center of the metals. The relative d-band center is closely associated to the molecule's adsorption, thus varying the product selectivity and catalytic activity.⁵⁹ In contrast, the shell thickness for most of core-shell structures would strongly influence the catalytic activity via the tuned electronic effects.⁶⁰ The M@Ni (M = Pd or Au) NPs is comprised of a Pd or Au core and an outer Ni shell. Based on the electronic effects, the addition of auxiliary metal could induce the up-shift of d-band center of Ni, which would strengthen the OH adsorption onto the catalyst surface and then induce the GEOR intermediates removal.⁶¹ Ni nanoparticles adhering to the M@Ni surfaces can also employ as the catalytic active sites, and thus enhancing the active site density of these materials.

7.4 Conclusion

In this work, $\text{Ni}_x\text{Pd}_{1-x}$ ($x = 100, 98, 95$ and 90 at.%) and $\text{Ni}_x\text{Au}_{1-x}$ ($x = 100, 95, 90$ and 80 at.%) nanoparticles were fabricated for glycerol electrooxidation (GEOR) in 1 M KOH. Based on our physiochemical characterization, Ni-rich bimetallic possess a core-shell structure, which is highly beneficial for GEOR. Among different atomic ratios, $\text{Ni}_{80}\text{Pd}_{20}$ and $\text{Ni}_{90}\text{Au}_{10}$ nanoparticles display the highest current densities of 543 and 504 $\text{A.g}^{-1}_{\text{Ni}}$, which are ~ 4.5 and 4.2 times of spherical Ni, respectively. The addition of auxiliary metals (<20 at.%) tuned the electronic properties of Ni to shift the onset potential negatively, by as much as ~ 100 to 50 mV for GEOR. HPLC analyses reveal that Ni@Pd and Ni@Au tend to yield more C_3 products at any applied potentials and temperatures. For instance, a remarkable glycerate selectivity of $\sim 73.1\%$ and 65.7% for $\text{Ni}_{80}\text{Pd}_{20}$ and $\text{Ni}_{90}\text{Au}_{10}$ catalysts at 1.3 V and 50 °C, respectively. Notably, at high-applied potential (1.55 V) the spherical Ni is prone to generate 93.1% of formate via the C-C bonds breakage after 6 hours of electrolysis. Overall, the core-shell structure attributed significantly to generate higher current density with better selectivity to C_3 products in the electrolysis system. Theoretical calculations show that Pd@Ni NP is the most stable system compared to Au@Ni and monometallic Ni systems. In addition, on the Au@Ni nanoparticles the atomic radii mismatch produces an important strain between its layers. Also, the excess energy indicates that the mixed shell systems are energetically more stable. According with these results Au segregation could be a plausible phenomenon. Furthermore, WF, electronegativity, Bader charges and electronic structure analysis are all consistent with the idea of the Pd@Ni system could be more reactive than Au@Ni and monometallic Ni systems. Our DFT calculations matched the experimental results and

assisted us with a better understanding of some of the microscopic phenomena involved with the reactivity of bimetallic NPs.

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Supplementary Information E: Chapter 7

1. Computational modeling and calculations

All the calculations were performed using Density Functional Theory (DFT) as implemented by Vienna Ab-initio Simulation Package (VASP).¹⁻³ The projector augmented wave (PAW) pseudopotential method was used to account for the electron-ion core interaction⁴, we used the PBE functional in generalized gradient approximation (GGA) for the exchange-correlation term.⁵ The periodic boundary conditions were implemented with at least 10 Å vacuum in all directions to preclude interaction between a cluster and its images. The boxes were nanoparticles 15x15x15 and 20x20x20 Å for smaller and bigger system, respectively. The gamma point mesh was used for the reciprocal space integration for all the calculated systems. For the plane-wave basis set, a cut off energy of 700 eV was considered. All the structures have been optimized until the forces acting in each atom are less than 10^{-4} eV/Å. Spin polarized calculations were considered with the initial magnetic moment for each atom starting at NIONS*1.0. Bader analysis as implemented by *Tang et al.* was used to calculate electronic charges on atoms.^{6,7}

One of the most interesting aspects of cluster structure is the manifestation of non-crystallographic symmetries, which arise from the absence of translational periodicity. In particular, many clusters are found to have fivefold axes of symmetry, including two of the three main types of ordered structure adopted by simple atomic clusters. Decahedra have a single fivefold axis of symmetry and are based on pentagonal bipyramids, while icosahedra have six fivefold axes of symmetry. For modeling our system two different core elements (Pd, Au), three cluster sizes (small clusters of about 0.6 nm, with 13; nanometric clusters with 54- and 55-atoms), were considered. Two structure shapes icosahedral for the 13- and 55-atoms and decahedral for the 54-atoms nanoparticles (NP) (Figure E1). In addition, all properties calculated for the bimetallic clusters were directly compared with the ones of pure NP.

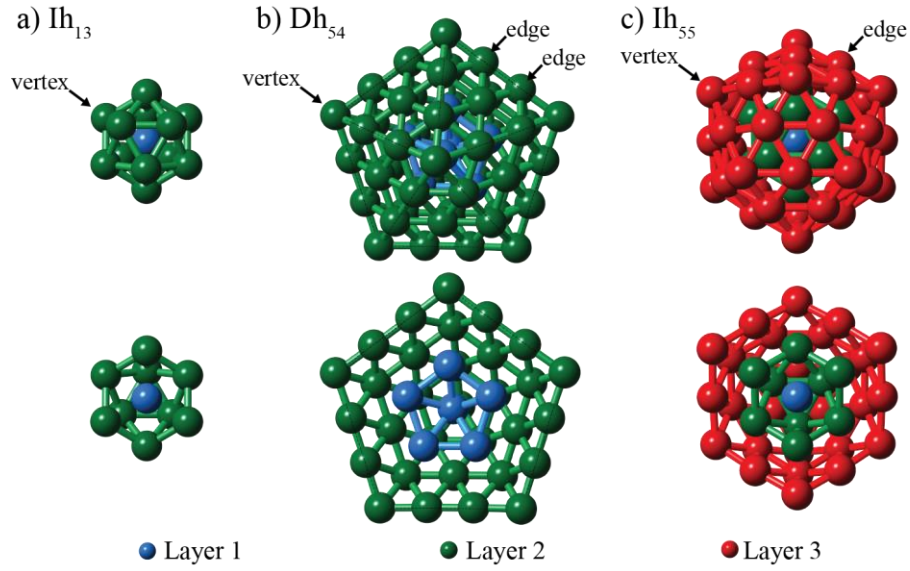


Figure E1. Schemes of the theoretical modeling of the nanoparticles. Different layers are identifying from inner to outer as layer 1, 2 and 3 by the colors blue, green and red, respectively. a) Ih_{13} with 2 layers, b) Dh_{54} with 2 layers, and c) Ih_{55} with 3 layers.

To determine the energetically most favorable configuration, are several ways to calculate the excess energy. Since metals with larger cohesive energy tend to give pure clusters with higher excess energy, E_{excess} , may be a somewhat biased index. For this reason, it may be preferable to use E_{excess}^* , defined as follows

$$E_{\text{excess}}^* = E_{M_m@Ni_n} - \left(\frac{m}{m+n}\right) E_{M_{(m+n)}} - \left(\frac{n}{m+n}\right) E_{Ni_{(m+n)}} \quad (E1)$$

where $E_{M_m@Ni_n}$, $E_{M_{(m+n)}}$ and $E_{Ni_{(m+n)}}$ are the total energies of the $M_m@Ni_n$ NP and the $M_{(m+n)}$ and $Ni_{(m+n)}$ pure systems with the same size ($m + n$ atoms) and geometry structures, respectively. And normalizing, arrive to

$$\Delta^* = E_{\text{excess}}^* / ((n + m)^{2/3}) \quad (E2)$$

The energetically favorable configuration, in general, is indicated by a negative value. Also, for the 13-atoms system we calculate the binding energy (E_b):

$$E_b = \frac{(E_{M_m@Ni_n} - n \epsilon_M - m \epsilon_{Ni})}{n + m} \quad (E3)$$

where the ϵ_M and ϵ_{Ni} are the energy of the isolated atom species ($M = Pd, Au$), respectively.

For considering the geometrical distortion we have calculated the layer strain. The average strain at each atomic layer in each nanoparticle ($e_{layer\#}^{M_m@Ni_n}$, with $\# = 1, 2, 3$) was expressed as a percentage of the total deformation as follow:

$$e_{layer\#}^{M_m@Ni_n} = 100 * \left(\frac{L_{layer\#}^{M_m@Ni_n} - L_{layer\#}^{pure}}{L_{layer\#}^{pure}} \right) \quad (E4)$$

where the average deformation of bonds in bimetallic NP layer ($L_{layer\#}^{M_m@Ni_n}$) was compared to the same layer from monometallic systems with the same atom species than the particular layer ($L_{layer\#}^{pure}$).

Regarding the electronic structure and reactivity, the d-band center (ϵ_d) was calculate used the Hammer-Nørskov method⁸⁻¹¹:

$$\epsilon_d = \frac{\int_{-\infty}^{\infty} E \rho(E - E_F) dE}{\int_{-\infty}^{\infty} \rho(E - E_F) dE} \quad (E5)$$

with $\rho(E - E_F)$ is the DOS projected on the d-states of the metal and E_F is the Fermi energy.

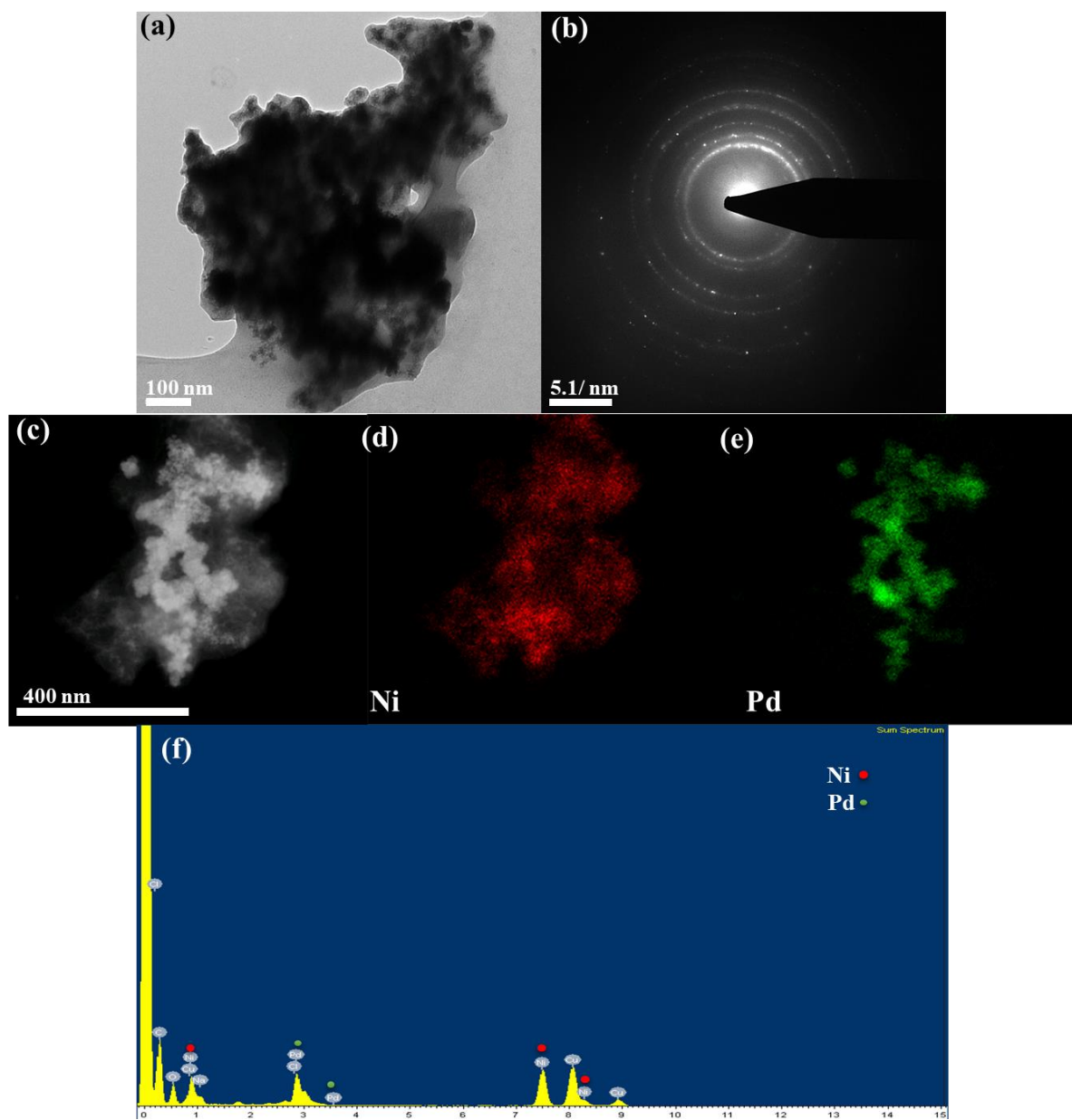


Figure E2. (a)TEM image of $\text{Ni}_{80}\text{Pd}_{20}$ nanostructures, (b) SAED patterns and (c) Dark Field-STEM image, EDS elemental mapping of (d) Ni and (e) Pd. (f) EDS spectrum of $\text{Ni}_{80}\text{Pd}_{20}$ catalyst.

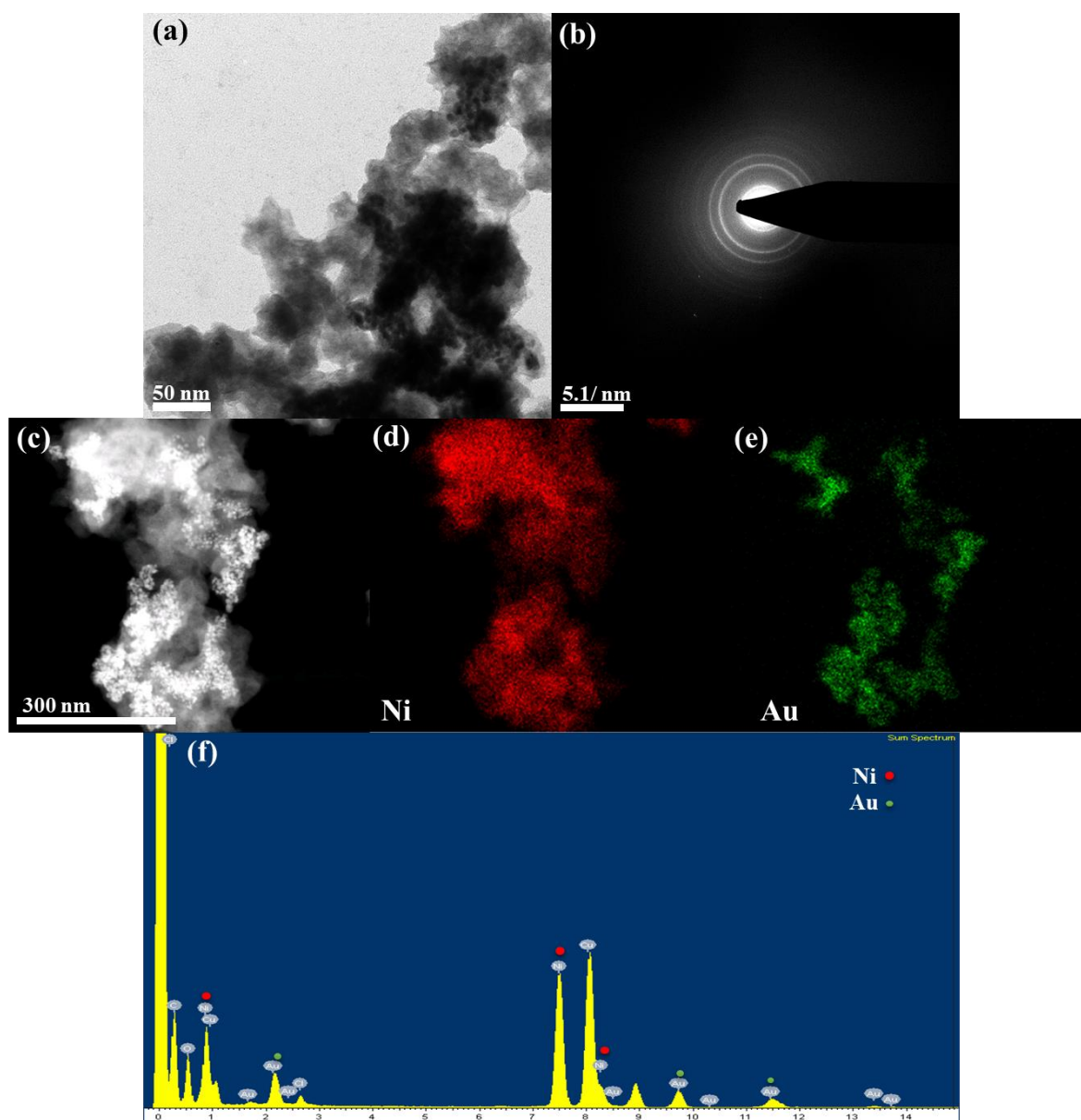


Figure E3. (a)TEM image of $\text{Ni}_{90}\text{Au}_{10}$ nanostructures, (b) SAED patterns and (c) Dark Field-STEM image, EDS elemental mapping of (d) Ni and (e) Au. (f) EDS spectrum of $\text{Ni}_{95}\text{Au}_5$ catalyst.

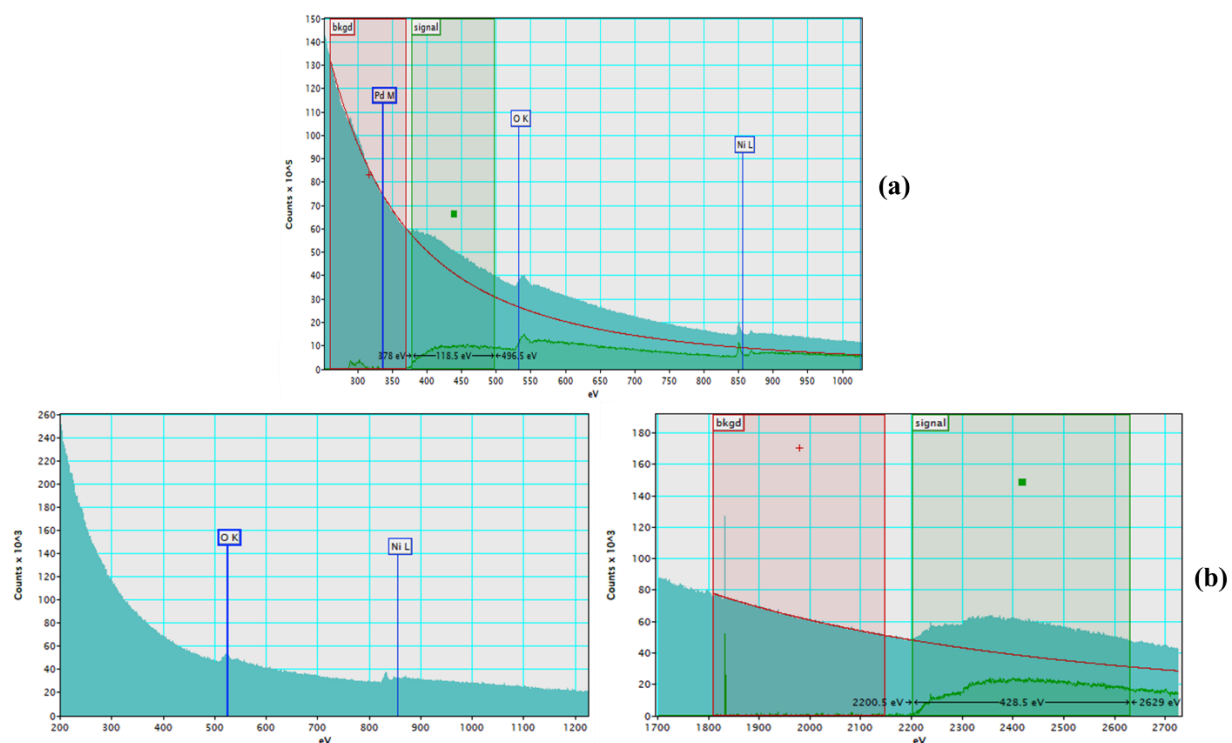


Figure E4. EELS spectra obtained at high spatial resolution of (a) $\text{Ni}_{90}\text{Pd}_{10}$ and b) $\text{Ni}_{90}\text{Au}_{10}$.

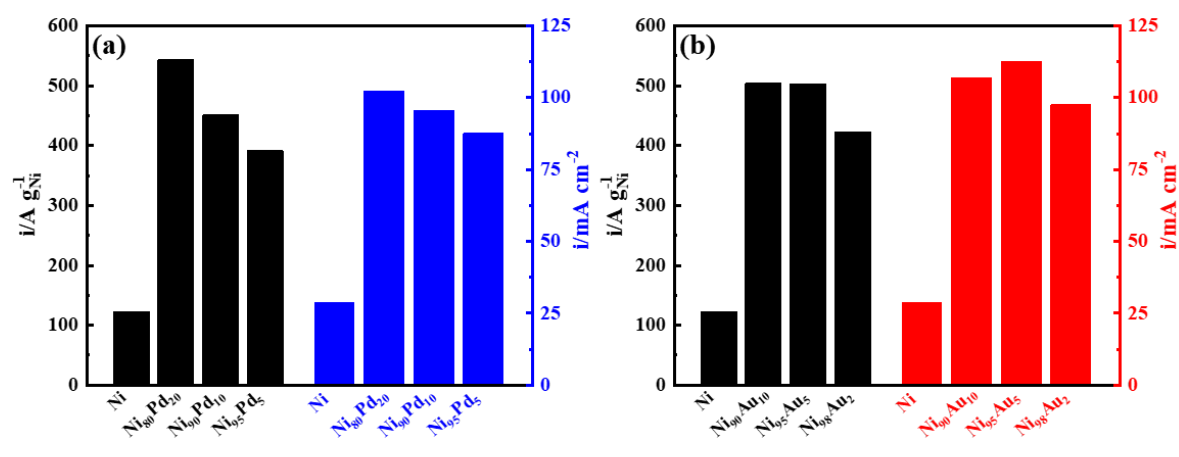


Figure E5. Comparison of current density after normalization to the Ni mass and the geometric surface area of the GC (0.196 cm^2) for (a) $\text{Ni}_{1-x}\text{Pd}_x$ and b) $\text{Ni}_{1-x}\text{Au}_x$.

2. Theoretical calculations

3.2.1 Work function

The work function (WF) was computed as the energetic difference between the vacuum level potential (ϕV) and the Fermi levels (E_F)¹²:

$$WF = \phi V - E_F \quad (E6)$$

Especially for the metal systems, the WF and E_F values provided information about the ability of the metal to gain or lose electrons.

Table E 7. 1. Work function and Fermi Levels from the different considering NP systems.

	SYSTEM	WF (eV)	E_Fermi (eV)
Ih₁₃	Au ₁₃	3.97	-3.67
	Pd ₁₃	4.71	-4.41
	Ni ₁₃	3.75	-3.56
	Au ₁ @Ni ₁₂	3.78	-3.56
	Au ₁ @Au ₁ Ni ₁₁	3.92	-3.69
	Au ₁ @Ni ₁ Au ₁₁	5.08	-4.75
	Ni ₁ @Au ₁ Ni ₁₁	3.81	-3.61
	Ni ₁ @Au ₁₂	4.95	-4.56
	Pd ₁ @Ni ₁₂	3.63	-3.42
	Pd ₁ @Pd ₁ Ni ₁₁	3.43	-3.20
	Pd ₁ @Ni ₁ Pd ₁₁	4.56	-4.25
	Ni ₁ @Pd ₁₂	4.64	-4.26
	Ni ₁ @Pd ₁ Ni ₁₁	3.72	-3.50
	Au ₅₅	5.07	-3.82
	Pd ₅₅	4.88	-3.84
Ih₅₅	Ni ₅₅	4.17	-3.37
	Au ₁ @Ni ₅₄	4.05	-3.29
	Ni ₁ @Au ₁ Ni ₁₁ @Ni ₄₂	2.96	-3.20
	Ni ₁ @Ni ₁₂ @Au ₁ Ni ₄₁	3.34	-3.45
	Au ₁₃ @Ni ₄₂	4.04	-3.17
	Pd ₁ @Ni ₅₄	4.01	-3.28
	Ni ₁ @Pd ₁ Ni ₁₁ @Ni ₄₂	3.04	-3.28
	Ni ₁ @Ni ₁₂ @Pd ₁ Ni ₄₁	4.11	-3.34
	Pd ₁₃ @Ni ₄₂	3.93	-3.12
Dh₅₄	Au ₅₄	5.06	-4.31
	Pd ₅₄	5.09	-4.34
	Ni ₅₄	3.98	-3.49
	Au ₇ @Ni ₄₇	4.06	-3.54
	Pd ₇ @Ni ₄₇	4.07	-3.57

3.2.2 13-atom Icosahedral systems

For testing our theoretical methodology, we study the geometry, stability, electronic structure and properties of 13 atoms icosahedral pure NP. For the Ni₁₃, we found that the Ni-Ni distances are 2.50 Å, 2.40 Å in the shell and core-shell, respectively. Also, the calculated E_b value is 3.30 eV. These results are in good agreement with that reported by Wang *et al.*¹³ For Pd₁₃ the inter-atomic distances between the core and its neighboring is 2.75 Å, while the surface Pd-Pd distance is 2.86 Å. The system total energy is -49.623 eV and the E_b is 2.35 eV. In the case of Au₁₃ NP the system total energy value is -26.556 eV ($E_b = 3.25$ eV) and the inter-atomic core-shell and surfaces distances are 2.78 Å and 2.92 Å, respectively. These results are in good agreement with the values reported by Wang *et al.*¹⁴, they found system total energies of -49.482 eV (-27.304 eV), with inter-atomic core-shell of 2.77 Å (2.77 Å) and Pd-Pd (Au-Au) surface distance of 2.77 Å (2.91 Å) for Pd₁₃ (Au₁₃) cluster. The binding energies agree with that reporter by Chou *et al.*¹⁵ and Hussein *et al.*¹⁶ When the Au₁@Ni₁₂ and the Pd₁@Ni₁₂ bimetallic systems are considered the binding energy decrease for first and slightly increase for the second making the last more stable. It must be noted that a more positive binding energy stronger is the NP cohesivity.

Considering the net charges, the Pd₁₃ NP have +0.16e⁻ in the core and -0.16e⁻ in the shell, for the Ni₁₃ system are +0.08e⁻ in the core and -0.08e⁻ in the shell, while in the Au₁₃ cluster they are +0.24e⁻ and -0.24e⁻ for the core, respectively. Regarding the electronic structure, the d-band PDOS curves are show in Figure E6. It can be seen that in all systems the spin up and spin down contributions are shifted and asymmetrical which is consistent with magnetic systems. In the case of the bimetallic NP both have lower magnetic moments that the Ni but higher that in the case of Pd and Au monometallic systems with values of 16.0, 8.0, 5.0, 10.5 and 15.6 μ_B for Ni₁₃, Pd₁₃, Au₁₃, Au₁@Ni₁₂ and Pd₁@Ni₁₂, respectively. The ϵ_d follow the trend Au₁₃ > Pd₁@Ni₁₂ > Au₁@Ni₁₂ > Ni₁₃ > Pd₁₃. These results agree with theoretical and experimental result reported in the literature.^{13,14,17} This analysis supports the results presented for the 54- and 55-atoms systems and the validity of the used methodology.

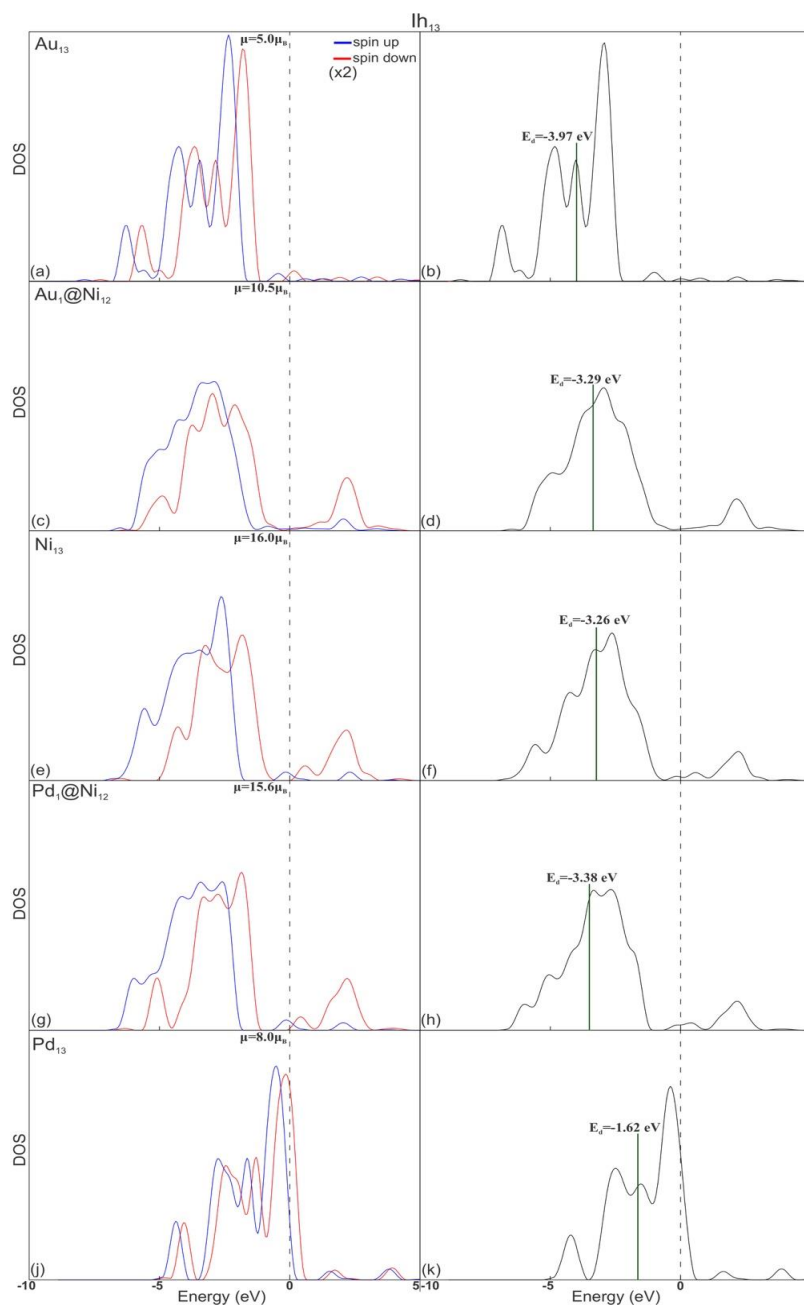


Figure E6. Curves for the d-band PDOS for the 13-atoms icosahedral systems. The blue and red curves indicate the spin up and spin down contribution, respectively. The black is the total d-band curves.

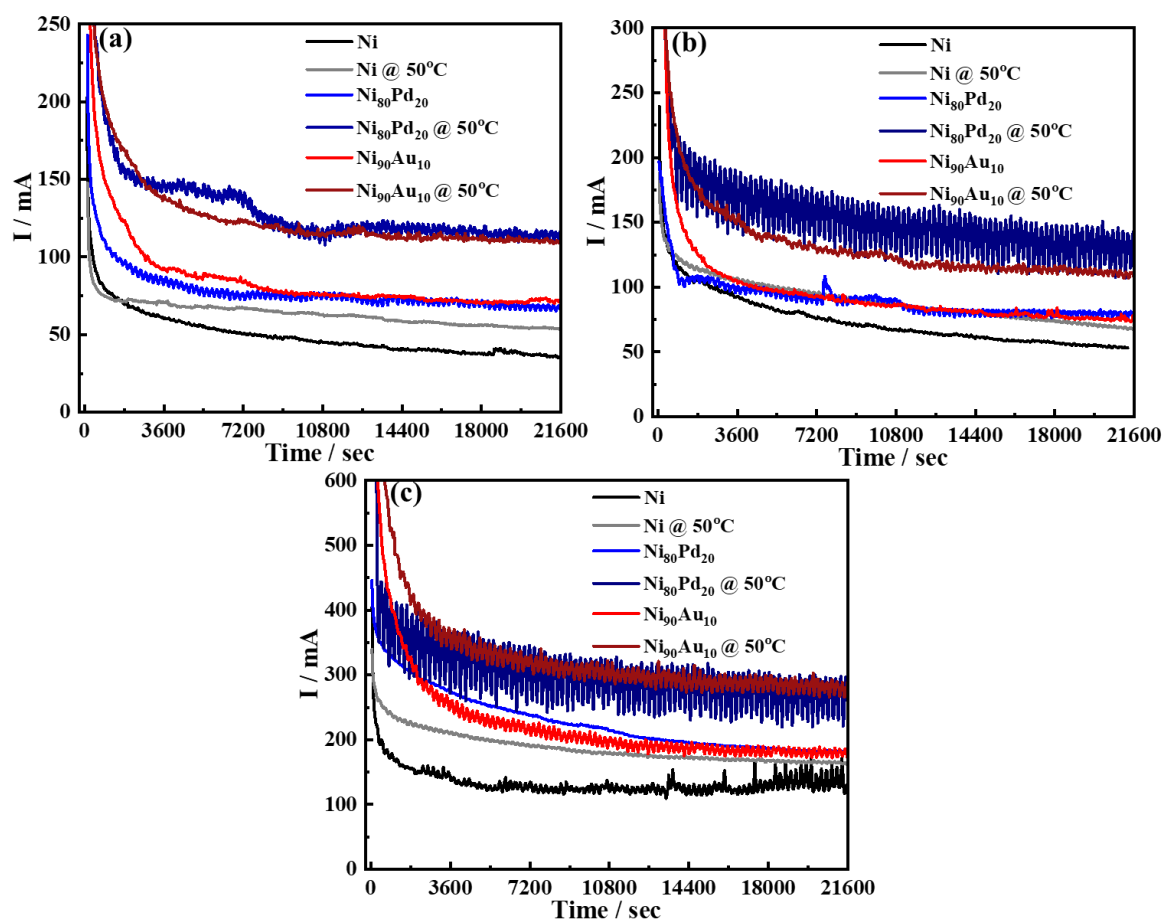


Figure E7. CA curves in the 25 cm^2 electrolysis cell at (a) 1.3 V , (b) 1.4 V and (c) 1.55 V for GEOR on $\text{Ni}_{1-x}\text{M}_x$ ($\text{M} = \text{Pd}$ and Au) catalysts in $1.0\text{ M KOH} + 0.1\text{ M glycerol}$ electrolyte at room temperature and 50°C .

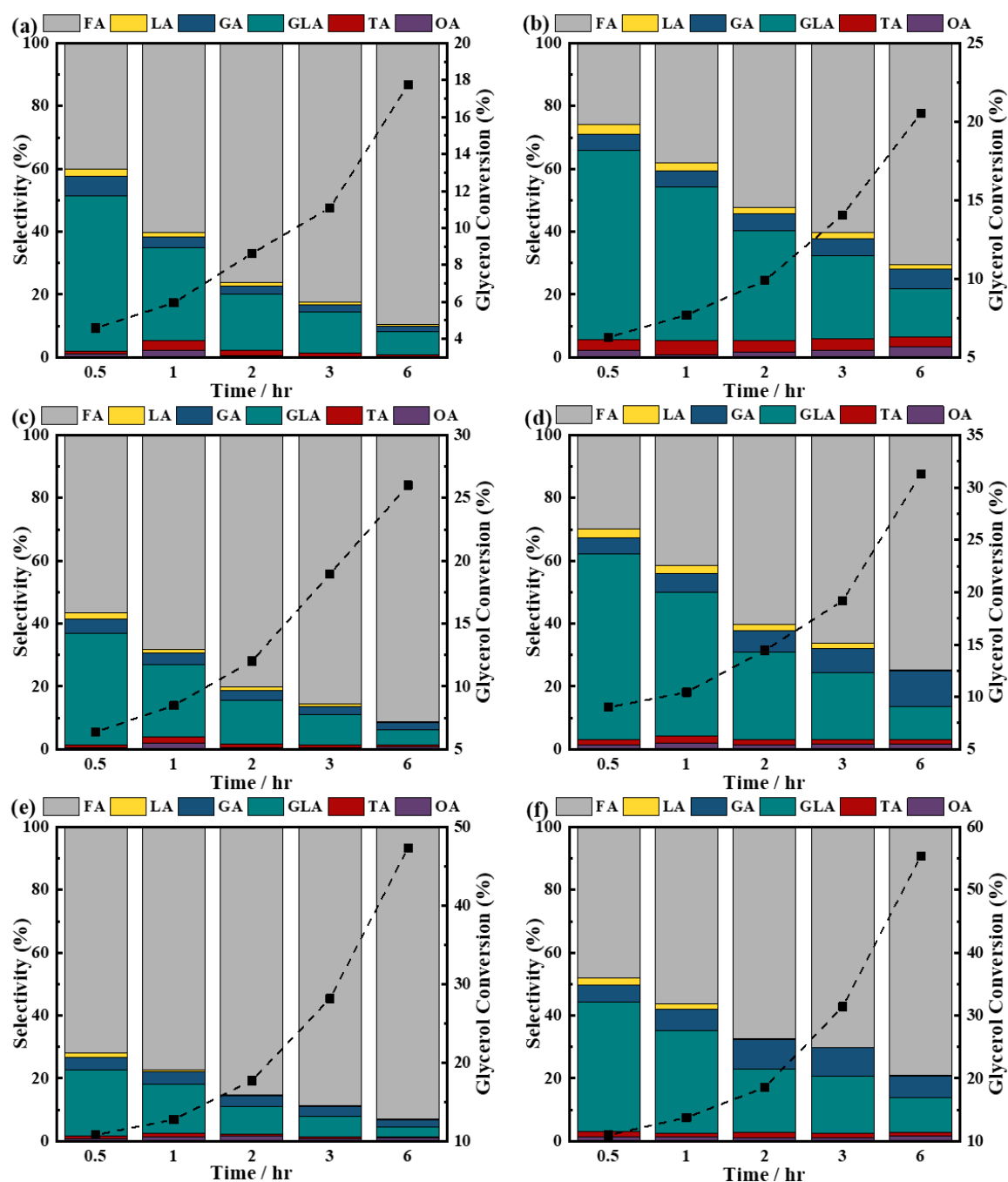


Figure E8. Product distributions and glycerol conversion (dashed line) on Ni at different applied potentials for different reaction time (a,b) 1.3 V, (c,d) 1.4 V and (e,f) 1.55 V, in a 1M KOH+0.1 M glycerol. The left-hand figures illustrate product distributions at room temperature, while the right-hand illustrates products at 50 °C. Gray: formate; Yellow: lactate; Navy: glycolate; Dark Cyan: glycerate; Wine: tartronate and Violet: oxalate.

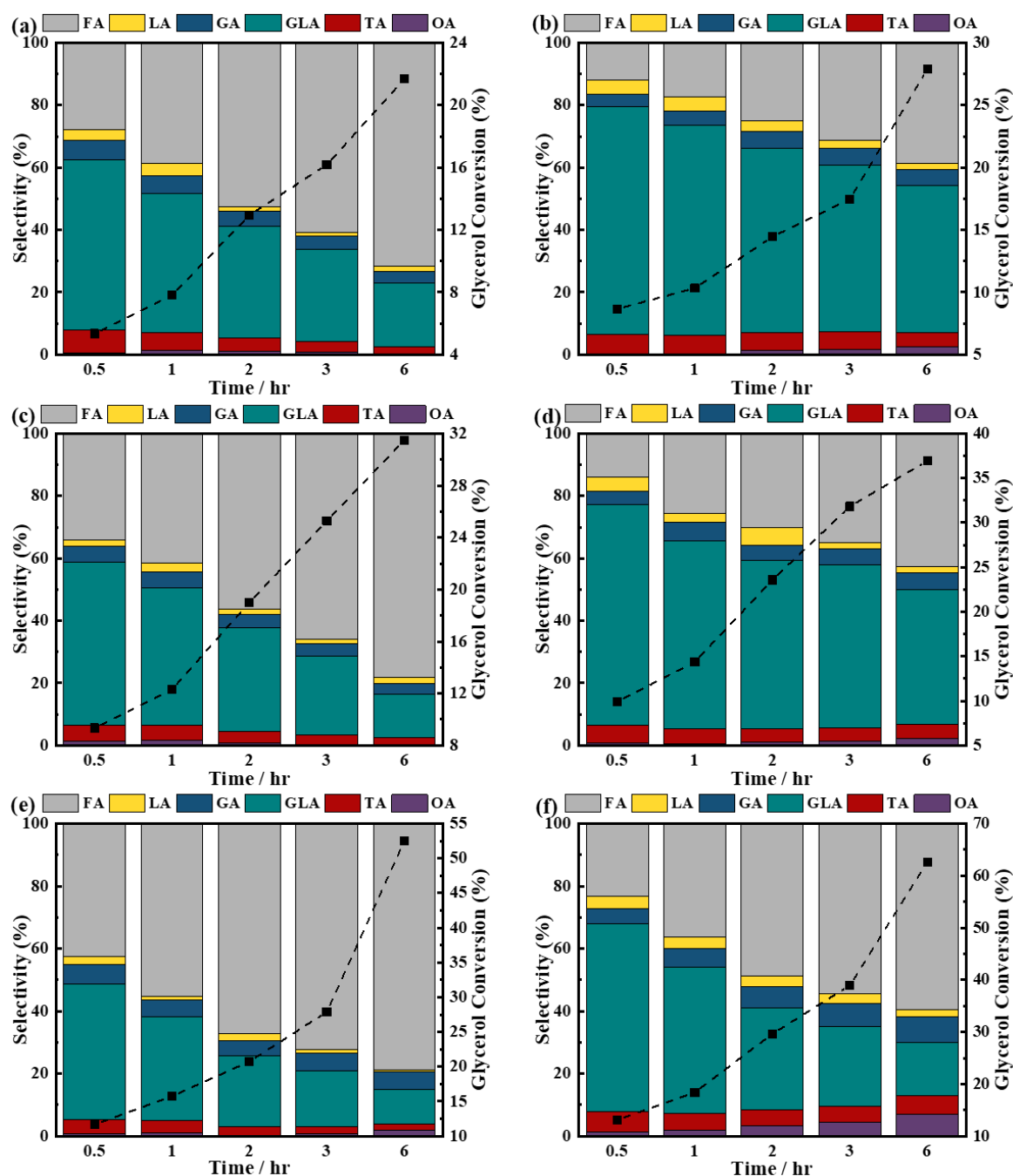


Figure E9. Product distributions and glycerol conversion (dashed line) on Ni₈₀Pd₂₀ at different applied potentials for different reaction time (a,b) 1.3 V, (c,d) 1.4 V and (e,f) 1.55 V, in a 1M KOH+0.1 M glycerol. The left-hand figures illustrate product distributions at room temperature, while the right-hand illustrates products at 50 °C. Gray: formate; Yellow: lactate; Navy: glycolate; Dark Cyan: glycerate; Wine: tartronate and Violet: oxalate.

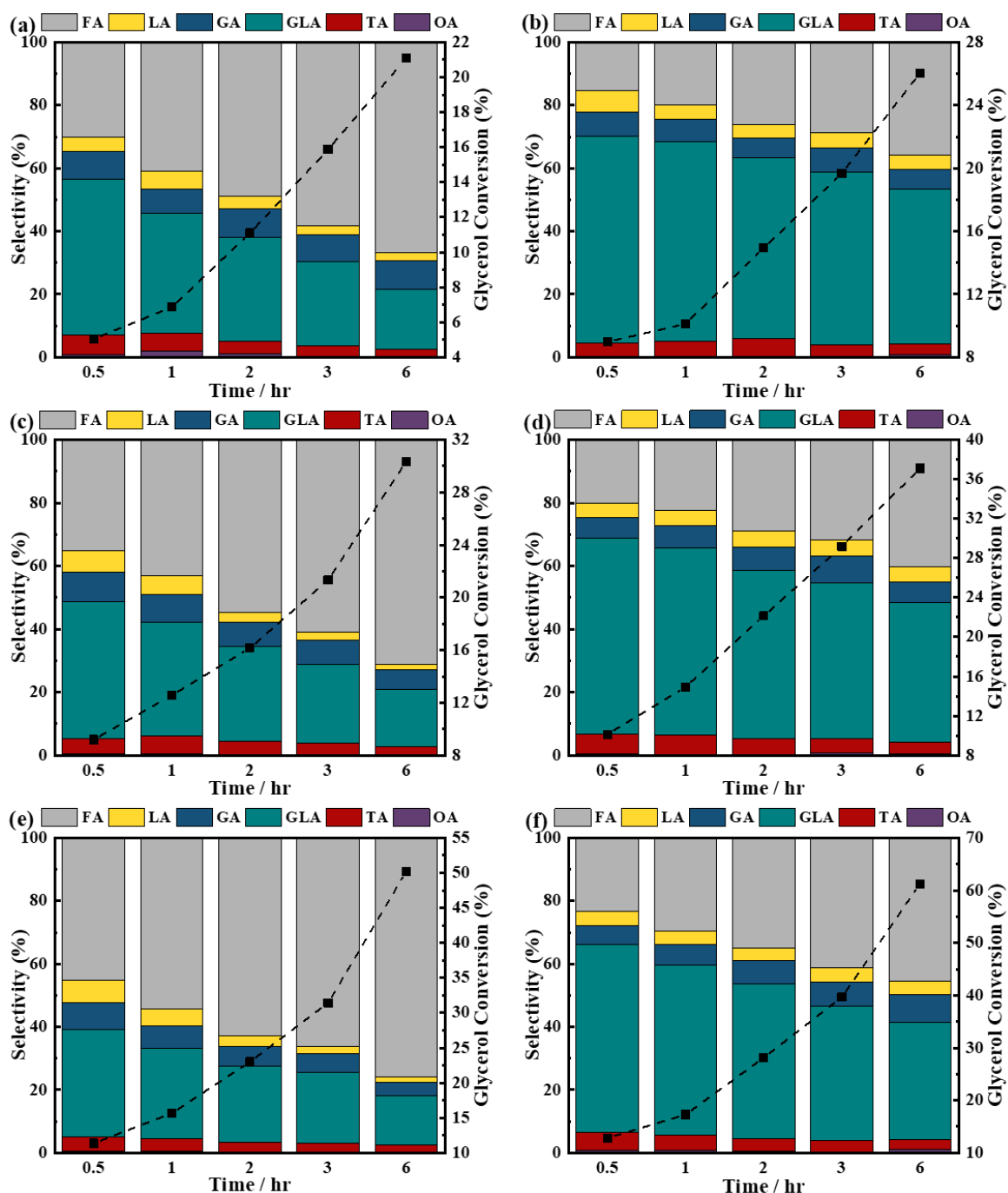


Figure E10. Product distributions and glycerol conversion (dashed line) on $\text{Ni}_{90}\text{Au}_{10}$ at different applied potentials for different reaction time (a,b) 1.3 V, (c,d) 1.4 V and (e,f) 1.55 V, in a 1M KOH+0.1 M glycerol. The left-hand figures illustrate product distributions at room temperature, while the right-hand illustrates products at 50 °C. Gray: formate; Yellow: lactate; Navy: glycolate; Dark Cyan: glycerate; Wine: tartronate and Violet: oxalate.

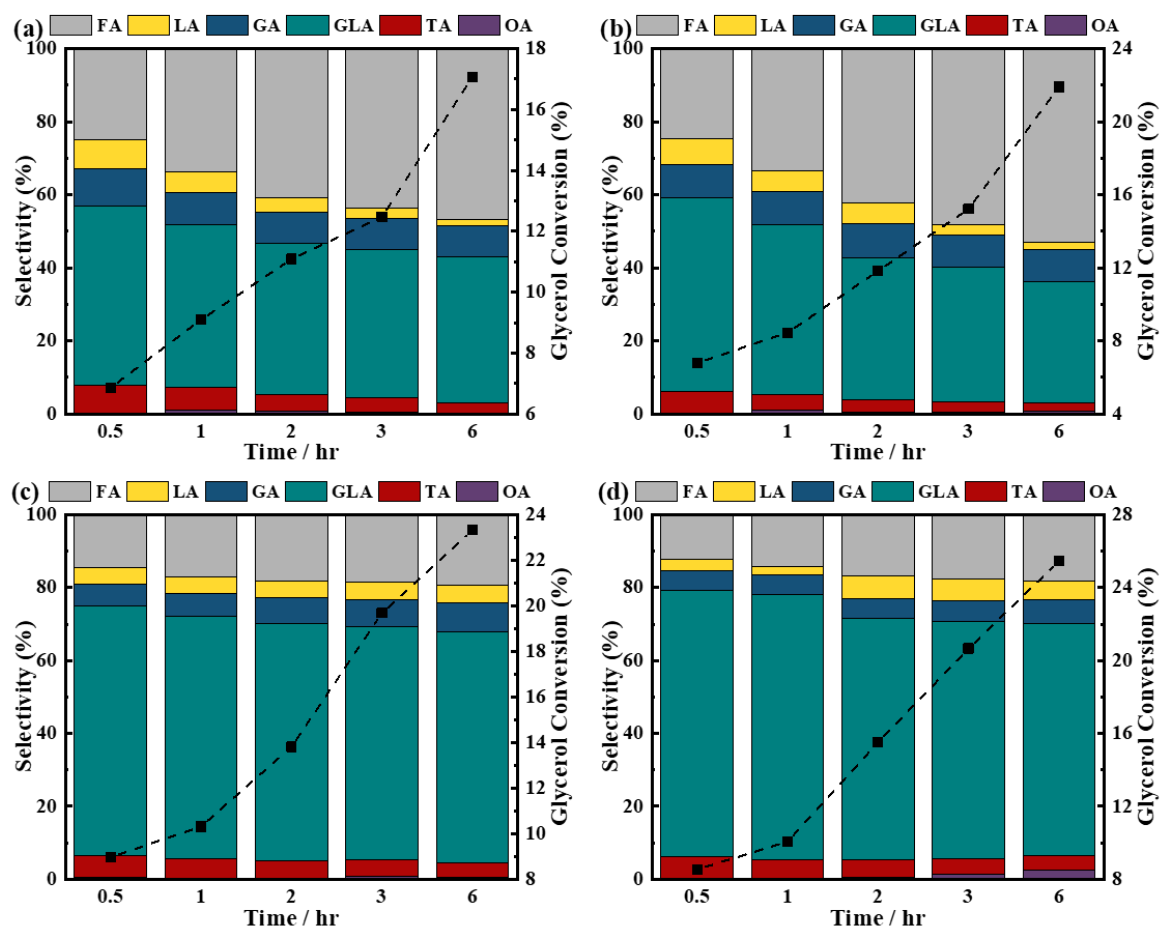


Figure E11. Product distributions and glycerol conversion (dashed line) at 1.4 V for different reaction time on (a,c) Ni₉₀Au₁₀ and (b,d) Ni₈₀Pd₂₀ in a 0.1M KOH+0.1M glycerol. The upper figures illustrate product distributions at room temperature, while the below illustrates products at 50 °C. Gray: formate; Yellow: lactate; Navy: glycolate; Dark Cyan: glycerate; Wine: tartronate and Violet: oxalate.

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Chapter 8

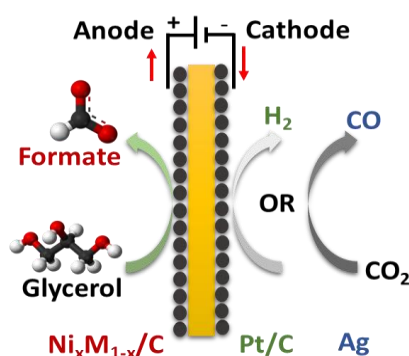
8 Selective Electrooxidation of Glycerol to Formic acid over Carbon Supported $\text{Ni}_{1-x}\text{M}_x$ ($\text{M} = \text{Bi}$, Pd and Au) Nano-catalysts and Co-Electrolysis of CO_2

Based on the paper:

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Abstract

The composition effect of carbon supported $\text{Ni}_x\text{M}_{1-x}$ ($\text{M} = \text{Bi}$, Pd and Au) nanomaterials towards glycerol electrooxidation (GEOR) was evaluated in alkaline media. Ni-rich catalysts with different atomic ratios (M atomic ratio $\leq 20\%$) were synthesized by the heatless co-reduction method and characterized by various physicochemical and electrochemical techniques. All structures of the $\text{Ni}_x\text{M}_{1-x}/\text{C}$ catalysts were composed of a rich-phase of $\text{Ni}(\text{OH})_2$, as evidenced by TDA-TGA and XPS. Among the different nanomaterials, the $\text{Ni}_{0.9}\text{Au}_{0.1}/\text{C}$ catalyst provided the lowest onset potential (+0.12 V vs. Hg/HgO) and the highest peak current density. In-situ infrared spectroscopy experiments combined with electrochemical measurements exhibited the formation of formate for all catalysts, thus indicating the breakage of C-C bonds of glycerol. GEOR led to 100 % selectivity for formate after 1 hr electrolysis and 100 % conversion of glycerol after 24 hr at +1.55 V. Furthermore, when testing these inexpensive catalysts in tandem with cathodic CO_2 electro-reduction, the anodic $\text{Ni}_{0.9}\text{Au}_{0.1}/\text{C}$ catalyst displayed the highest partial current density for CO and the lowest onset.



8.1 Introduction

Continuous efforts have been devoted to developing efficient electrochemical conversion technologies to generate energy and/or value-added products from oxygenated biomass such as glucose, furfural, xylose and glycerol.¹⁻⁴ Particularly, glycerol (by-product of biodiesel production) is one of the top 12 platform compounds and has great potential to be transformed into more economical products such as glyceric,

tartronic, lactic and formic acids.⁵ Among various technologies being studied for glycerol valorization, electrochemical technologies are more promising due to straightforward operation, are environmentally friendly and require low operating temperatures and pressures.⁶ Furthermore, the electrocatalytic oxidation processes of glycerol on the anode of either a fuel or electrolysis cell is tunable by means of electrode potential, surface crystallinity, electrocatalyst composition (i.e. nanoparticles with defined morphologies, and core-shell structures) and utilization of different support materials.⁷ Controlling these parameters could lead to a lower oxidation onset potential, a higher product selectivity at high conversion and in return a cheaper process is achieved.

Thermodynamic data indicates that the use of glycerol as anodic reactant in an electrolysis cell could be more energetically interesting than water electrolysis for hydrogen production.⁸ This is due to lower theoretical cell voltage for glycerol electrolysis ($U_{\text{cell}}^0 = 0.003 \text{ V}$, $n = 14$ for the complete oxidation of glycerol into CO_2) compared to water electrolysis ($U_{\text{cell}}^0 = +1.229 \text{ V}$, $n = 2$), where n is the number of electrons generated per molecule oxidized.⁹ However, the main limitation in using glycerol as a hydrogen source is the slow kinetics of its oxidation reaction. For this purpose, alkaline media was favoured over acidic media, leading to faster electrochemical kinetics and allowing using free or low loaded Pt-group metal catalysts for both reactions: glycerol electrooxidation at the anode and H_2 evolution at the cathode.¹⁰⁻¹² Another interesting approach is the co-electrolysis of glycerol and CO_2 as a pathway to value-added chemicals. Currently, CO_2 electro-reduction processes comprise of the anodic oxygen evolution reaction (OER) coupled to the cathodic CO_2 reduction. Thermodynamic analysis indicates that OER requires $\sim 90\%$ of the electricity consumption because of high anodic potential (cell voltage of $\sim -1.6 \text{ V}$) on Pt black electrode.¹³ However, altering anodic OER to glycerol electro-oxidation reaction (GEOR) results in lowering the CO_2 electroreduction cell voltage by $\sim -0.85 \text{ V}$ with 37-53% reduction in electricity requirements, thus, improving its feasibility.

Regardless of the significant advances made during the last two decades in the fuel cell and electrolysis cell technology, the anodic current performance for glycerol electro-reforming is not yet close to attaining the widespread commercialization targets based on the United States Department of Energy (DOE).^{14,15} Currently, many efforts have been devoted to developing non-Pt group metal catalysts to minimize the cost and

enhance the performance of electrochemical technologies. Among various electrode materials, nickel (Ni) is considered as one of the most promising non-precious electrocatalytic material and has been utilized in several electrochemical applications such as alkaline batteries, sensors, alcohol oxidation and fuel cells.¹⁶⁻²¹ This attraction is due to nickel's low preparation cost, long-term stability, resistance to CO poisoning and high surface oxidation performance by the formation of high valence oxyhydroxide species (β -NiOOH) in alkaline medium.²²⁻²⁵ Nonetheless, the poor electrical conduction of these Ni^{3+} species and agglomeration of small Ni nanoparticles (NPs) seriously limit their catalytic performance.²⁶ To overcome these issues, Ni NPs can be immobilized and dispersed on a two-dimensional solid support, typically high specific surface area electron conductive carbon materials.²⁷ The electrocatalytic performance of the resulting nanocomposites can be enhanced significantly due to high conductive matrices, fast electron transfer kinetics and high surface area with abundant active sites.²⁸⁻³⁰

In this context, developing and finding highly stable and active electrocatalysts is of great significance for promoting GEOR in the electrolysis cells operating at low temperature. Other promising approaches for Ni catalysts have been suggested, such as compositing or alloying with other catalytic elements. The modifying effect of noble metals by nickel can provide a lot of information for understanding catalytic kinetics for GEOR and designing more stable and active catalysts. For instance, Au/Ni on polystyrene spheres³¹, $\text{Pt}_2\text{Ni}_1/\text{C}$ and $\text{Pd}_6\text{Ni}_4/\text{C}$ materials³² led to higher catalytic activity and stability in comparison to the monometallic ones. This enhancement can be ascribed to electronic and geometric modifications.³³ Ni, an oxophilic metal like ruthenium (Ru), possesses the unique capability of generating efficient OH_{ads} at lower overpotential and thus facilitates oxidative desorption of the intermediates³⁴, corresponding to the so-called bifunctional mechanism of electrocatalysis.³⁵ Therefore, the transition metal (Ni) served as a promoter and was able to reduce the precious metal amounts without significantly affecting the catalytic performance. However, only few studies have been devoted to the electro-oxidation of biomass-derived glycerol using Ni-rich alloyed catalysts, the topic of this study.

Here we demonstrate, carbon supported $\text{Ni}_x\text{M}_{1-x}$ ($\text{M} = \text{Bi}, \text{Pd}$ and Au) nanoparticles (NPs) with different atomic ratios, prepared using straightforward sodium borohydride (NaBH_4) co-reduction method. Addition of small quantities of second metal

(≤ 20 at.%) has shown positive effects on catalytic performance with a lower onset potential and long durability of 24 hrs. Detailed analyses of product distribution revealed that $\text{Ni}_x\text{M}_{1-x}/\text{C}$ own high capacities to cleave the C-C bond of glycerol, generating 100% selectivity towards formate with 100% conversion of glycerol at + 1.55V. Lastly, co-electrolysis of CO_2 and glycerol process was introduced, showing that $\text{Ni}_{0.9}\text{Au}_{0.1}/\text{C}$ catalyst attained the highest partial current density for CO of $\sim 6.0 \text{ mA.cm}^{-2}$ and lowest onset cell voltage of -1.0 V . To our knowledge, no work has been reported in the literature on co-electrolysis of glycerol and CO_2 using Ni-rich anode catalysts for such process.

8.2 Experimental

8.2.1 Preparation of $\text{Ni}_x\text{M}_{1-x}$ (M= Pd, Au and Bi) nanoparticles

All carbon supported Ni, $\text{Ni}_x\text{Pd}_{1-x}$ (atomic ratio $x = 0.95, 0.90, 0.80$), $\text{Ni}_x\text{Au}_{1-x}$ and $\text{Ni}_x\text{Bi}_{1-x}$ (atomic ratio $x = 0.98, 0.95, 0.90$) NPs were prepared by sodium borohydride (NaBH_4) co-reduction method at room temperature from metal chloride salt without any capping agent. The detailed procedure of this method was reported elsewhere for unsupported Ni.³⁶ After 30 min of metal reduction, a given amount of carbon powder (Vulcan XC72, Cabot Corp.) was introduced to the solution to attain 30 wt. % of metal loading. The colloidal mixture was filtered and rinsed 3 times with acetone. The catalytic residue was dried in an oven at 313 K for 15 hours.

8.2.2 Physicochemical characterizations

All detailed procedures of different physicochemical techniques (XRD, TEM, SAED, HAADF, EDS and EELS) have been reported earlier in our previous publication.³⁷ Thermogravimetric Analysis (TGA/DTA, TA Instrument model SDT Q 600 apparatus) were performed to determine the metal loadings. The catalyst powders were gradually heated in alumina crucible from 25°C to 1050°C with an air flow of 100 mL min^{-1} and heating rate of 10 K min^{-1} . An empty alumina crucible was used as reference. XPS spectra were collected using a Kratos Axis ULTRA X-ray photoelectron spectrometer with monochromatic Al K-alpha excitation. The Binding Energy (BE) scale was assigned by adjusting the C1s peak at 284.6 eV .

8.2.3 Electrochemical measurements

The electrochemical setup comprised of a conventional three-electrode thermostated cell fitted with a mercury/mercury oxide (Hg/HgO) reference electrode, a glassy carbon (GC) disk (0.071 cm²) and a glassy carbon plate (4 cm² surface area) acted as working electrode and counter electrode, respectively. The linear sweep voltammetry (LSV) and cyclic voltammetry (CV) measurements were carried out using a Voltalab PGZ402 potentiostat (Radiometer analytical) in a N₂-purged 1.0 M KOH (99.99%, Sigma-Aldrich) and 0.1 M glycerol (99.98%, Sigma-Aldrich) electrolyte at 293 K. Prior to electrochemical measurements, a catalytic ink was prepared as following: 17.7 mg of Ni_xM_{1-x}/C (M = Pd, Au and Bi) materials were added to aqueous suspension of 2.117 mL of ultrapure water (Milli-Q[®] Millipore, 18.2 MΩ cm at 293 K), 0.674 ml of isopropanol (CHROMASOLV[™] LC-MS, Fluka Analytical) and 354 μL of commercial solution of Nafion (5 wt. % in aliphatic alcohols, Sigma-Aldrich). The prepared ink was homogenized for 2 min and 3 μL was deposited onto the glassy carbon disk.

8.2.4 In-situ fourier transform infrared spectroscopy (FTIRS) measurements

In-situ FTIRS measurements were carried out on a Bruker IFS 66v/S FTIR spectrometer with a reflected beam at a 65° incident angle on the electrode surface. The chamber was under vacuum in order to eliminate the CO₂ and atmospheric water interferences from the beam path. The detector was HgCdTe type, cooled beforehand by liquid nitrogen. All the measurements were performed in a special tailored spectroelectrochemical cell fitted with CaF₂ prism at the bottom. The spectrum was acquired by averaging 512 interferograms with 4 cm⁻¹ resolution. Sample Spectra were recorded every 50 seconds during LSV carried out in a 0.1 or 1.0 M KOH and 0.1 M glycerol solution from -0.900 to +0.775 V vs Hg/HgO at a scan rate of 1 mV s⁻¹. Data were processed as follows ^{1,8}:

$$\frac{\Delta R}{R} = \frac{R_E - R_{E,ref}}{R_{E,ref}} \quad (8.1)$$

where R_E is the reflectivity recorded at the electrode potential E during the positive potential scan and $R_{E,ref}$ is the reflectivity used as reference recorded at -0.900 V vs

Hg/HgO. Negative and positive going bands represent respectively the increase and decrease of species at the electrode surface.

8.2.5 Continuous electrolysis measurements

Continuous electrolysis tests were performed at 293 K with a 1.0 M KOH and 0.1 M glycerol aqueous solution in a 25 cm² electrolysis cell. The anode and the cathode were comprised of 2 mg_{metal} cm⁻² of carbon supported Ni-based catalysts Ni_xM_{1-x}/C (M = Pd, Au and Bi) and Pt/C, respectively and the Nafion (as binder) loading of the electrode was 0.8 mg cm⁻² in deionized water and isopropanol. Both compartments were separated by a simple filter paper (WhatmanTM) and mechanically compressed in the cell. DC power supply (E3614A from Agilent) and Digital Multimeters (34405A from Agilent) were used to applied and measure the cell voltage and to record the current crossing the cell, respectively. A 30 ml solution (1.0 M KOH + 0.1 M glycerol) was fed continuously on both compartments at 30 mL min⁻¹. The current was recorded for 24 hrs at two different cell voltages of +1.30 and +1.55 V. HPLC (Varian Prostar) equipped with a column (Transgenomc ICSep ICE-COREGEL 107H) was utilized to analyze the products at each hour for 6 hours with UV detector set at $\lambda = 210$ nm. The chromatography was performed with 7 mM H₂SO₄ aqueous solution with 0.6 mL min⁻¹ flow rate. The last solutions at 24 hrs were neutralized by HCl, freeze-dried and put in Deuterium oxide (D₂O 99.9 % purity, Sigma Aldrich) for analysis in ¹H NMR (Bruker Ultrashield 400 plus with a Bruker B-ACS 60 automatic sample changer and a Bruker AD-XT pump).

8.2.6 Electrode preparation for co-electrolysis of CO₂ and glycerol

Commercially available silver (<100 nm, Sigma-Aldrich, product number: 576832) was used as the cathode catalysts to study CO₂ electroreduction to CO. The as-prepared nickel bi-metallics, as well as platinum (<100 nm, Alfa Aesar, product number: 43838) and gold (<100 nm, Sigma-Aldrich, product number: 636347) controls, were used as anode catalyst for GEOR. To prepare Ag and Ni bimetallic electrodes, about 10 mg of the catalyst powder was weighed out in a glass vial. 500 μ L and 9 mL of deionized water (DI, Barnstead E-pure) were added to the Ag and Ni alloys, respectively. Then, 26 μ L of Nafion ionomer (5wt%, Fuel Cell Earth) was added to the vial followed by 1 mL and nine mL of isopropyl alcohol (IPA, Fisher Chemical) for Ag and Ni alloys, respectively. For the Pt and Au catalysts, about 3 mg of catalyst powder was weighed out followed by the addition of 300 μ L of DI water, 7.8 μ L of Nafion, and 700 μ L IPA. The mixture was

then sonicated using a probe sonicator to form a cohesive catalyst ink. The ink was then airbrushed onto a $5 \times 1 \text{ cm}^2$ gas diffusion electrode (Sigracet 35BC, Fuel Cell Store), corresponding to 2 electrodes, using an airbrushing setup described previously.³⁸ Close to 50% of the original catalysts is lost during airbrushing, resulting in a final loading of $1.0 \pm 0.1 \text{ mg cm}^{-2}$ for the Ag and Ni bimetallic electrodes and $0.3 \pm 0.03 \text{ mg cm}^{-2}$ for the Pt and Au.

8.2.7 Co-electrolysis of CO₂ and glycerol in a flow electrolyzer

The airbrushed electrodes (preparation of electrode is in ESI) were tested in a flow electrolyzer, as previously reported.¹³ CO₂ (Airgas) was constantly fed to the back side of the Ag NPs cathode at a flowrate of 17 sccm using a flow controller (Smart-Trak 2, Sierra Instruments), whereas the GEOR was performed on Ni_xM_{1-x}/C at the anode. Ag reduces CO₂ mainly to CO and H₂ with traces of formate.³⁹ Both catholyte (2.0 M KOH, Fisher Chemical) and anolyte (2.0 M KOH + 2.0 M glycerol, Fisher Chemical) were constantly flowed at 0.5 mL min^{-1} via syringe pump (PHD 2000, Harvard Apparatus) to electrolyte chambers separated by an anion exchange membrane (FAA-3-PK-75, Fumatech). The electrolyzer was operated potentiostatically; the cell voltages (-1.50 , -1.40 , -1.30 , -1.20 , -1.10 , -1.00 , -0.90 , -0.80 and -0.75 V) were applied and the corresponding currents measured using an Autolab PGSTAT-30, EcoChemie potentiostat. Multimeters (Crenova MS8233D) were used to measure cathode and anode potentials against Ag/AgCl reference electrodes (3 mol kg^{-1} , RE-5B BASi). At each cell voltage, the system was left to equilibrate for 200 seconds before taking injections via gas chromatograph (Thermo Finnigan Trace GC) equipped with a thermal conductivity detector to measure any gaseous products. A pressure regulator (Cole Parmer, 00268TC) connected to a vacuum pump was placed downstream of the GC and set to 14.20 psi to help facilitate gaseous product transfer from the cathode surface to the effluent gas stream. Liquid samples were taken from the anolyte to be analyzed for liquid products using ¹H NMR.

8.3 Results and discussion

8.3.1 Physicochemical characterization of Ni_xM_{1-x}/C materials

Physicochemical characterizations were performed to obtain information on the composition and structure of Ni_xM_{1-x}/C materials.

XRD patterns of as-prepared Ni/C and $\text{Ni}_x\text{M}_{1-x}/\text{C}$ NPs ($\text{M} = \text{Pd}, \text{Au}$ and Bi) of different ratios are presented in (Figure 8.1a and Figure F.1 a-c in SI). Six intense peaks were observed. These sharp peaks indicate that pure NaCl crystallized in the cubic system with the $\text{Fm}\bar{3}\text{m}$ symmetry space group as stated in the (JCPDS 05-0628 card).⁴⁰ The formation of NaCl is explained by the presence of chlorides anions from the metal salt used as precursors and of sodium cations brought by addition of sodium borohydride for the co-reduction reaction. While common peak was detected at $\sim 25^\circ$, which refers to turbostratic graphite (002) plane of the Vulcan carbon support.⁴¹ However, no structural information of Ni or $\text{Ni}(\text{OH})_2$ was detected, which could be due to the NaCl interference. The Ni/C sample was rinsed with ultrapure water and the related XRD pattern is given in inset of Figure 8.1a inset. After rinsing, the broadening diffraction peaks of low intensity illustrates an amorphous structure of Ni/C. It was also noticed in Figure F1a,b in SI that $\text{Ni}_x\text{Pd}_{1-x}/\text{C}$ and $\text{Ni}_x\text{Au}_{1-x}/\text{C}$ exhibited diffraction peaks located at the characteristic positions for a face centered cubic (fcc) structure, typical of metallic Pd (111) and Au (111). The XRD patterns of $\text{Ni}_x\text{Bi}_{1-x}/\text{C}$ agree with (PDF-Nr.: 03-065-2366) data, confirming two reflection peaks of Bi_2O_3 (002) and (220) in the rhombohedral system (Figure F1c in SI).⁴²

Figure 8.1b and Figure F2a-c in SI show the TGA/DTA plots for the as-prepared Ni-based materials. The relative mass percentage is plotted as function of temperature, which detects a significant mass loss at five temperature intervals. The first transition below 200°C corresponds to the elimination of adsorbed water on the catalyst powder. The second transition translates the metal oxides (NiO) formation in the range of $200\text{--}340^\circ\text{C}$ and is ascribed to the dehydration of $\text{Ni}(\text{OH})_2$. Following this, the carbon support is combusted in the range of $340\text{--}800^\circ\text{C}$ and then the vaporization of NaCl molten salts occurs at 800.5°C .⁴³ The remaining material at the end of calcination (1050°C) for all the catalysts are in the range from ~ 24 and $35\text{ wt.}\%$, which is in fair accordance with the initial target value of $30\text{ wt.}\%$ metal loading.

Typical TEM micrographs (Figure 8.1c and Figure F3-F11a in SI) of all $\text{Ni}_x\text{M}_{1-x}/\text{C}$ catalysts reveal the structural morphology of agglomerated NPs on carbon support with a network of small branches. However, due to the low contrast between Ni nanostructure and the carbon support, it is quite challenging to estimate the average particle size of the catalyst. In certain spots the grain size is $\leq 3\text{ nm}$, which is significantly lower value than

that obtained in our previous work on unsupported Ni-based materials.³⁷ Additionally, selected area electron diffraction (SAED) analysis reveals asset of full rings, indicating that Ni/C has no crystallization degree (Figure 8.1d) which agrees with our XRD data in Figure 8.1a.

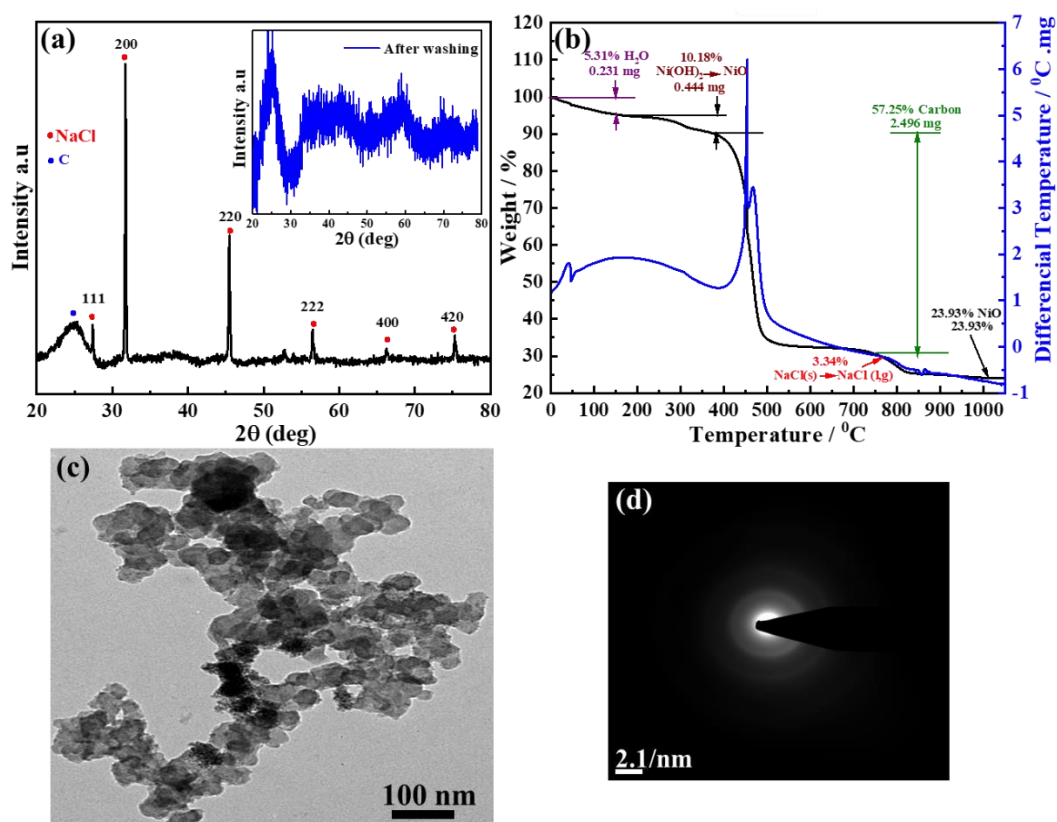


Figure 8.1. (a) XRD pattern of Ni/C, (b) TGA/DTA measurements of Ni/C (metal loading: 30 wt%) in temperature range 25-1050 °C, (c) TEM image and (d) Amorphous SAED patterns of Ni/C.

To further characterize the $\text{Ni}_x\text{M}_{1-x}/\text{C}$ materials with transition and post-transition metal ions, HAADF-STEM, EDS, EDS mapping and STEM-EELS analysis were performed. In Figure 8.2 and Figure F3-F11 b-g in SI, EDS mapping images confirm the presence of Ni (shown in red), O (shown in yellow), C (shown in blue) and that the second metal, either Pd, Au or Bi (shown in green), is well dispersed in the selected area of $\text{Ni}_x\text{M}_{1-x}/\text{C}$ catalysts. The EDS spectra are also in accordance with the elemental composition of $\text{Ni}_x\text{M}_{1-x}/\text{C}$, as confirmed by the presence of the characteristic peaks of oxygen, palladium, gold, bismuth and nickel. Furthermore, the chemical microstructure of the surfaces of the Ni-rich nanoparticles were also examined using STEM-EELS analysis.

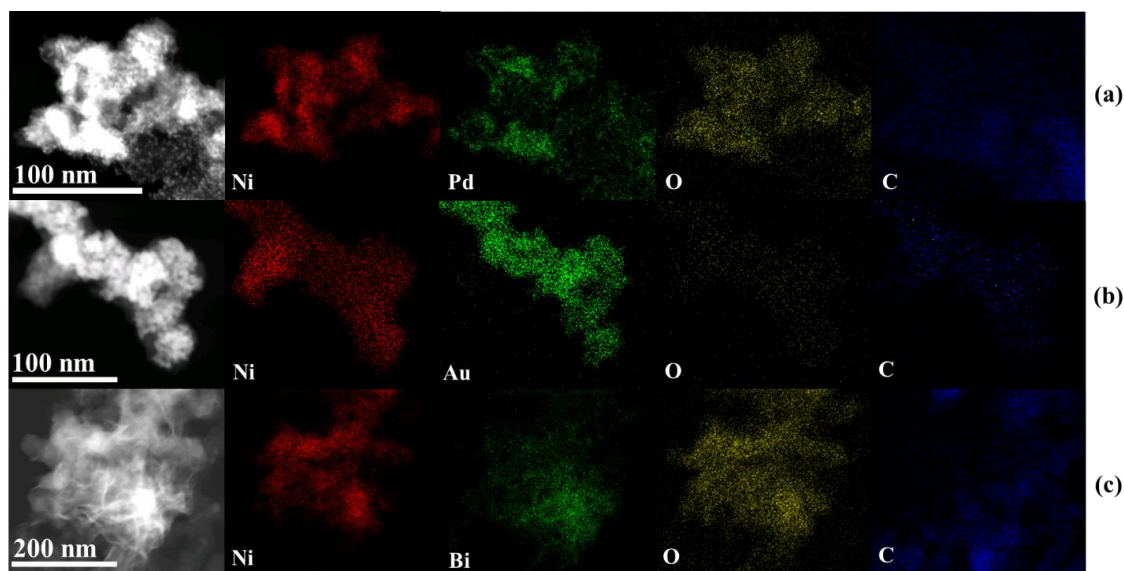


Figure 8.2. Dark Field-STEM image, EDS mapping of Ni, Pd, Au, O and C of carbon supported Ni-based catalysts (a) $\text{Ni}_{0.8}\text{Pd}_{0.2}/\text{C}$, (b) $\text{Ni}_{0.9}\text{Au}_{0.1}/\text{C}$ and (c) $\text{Ni}_{0.9}\text{Bi}_{0.1}/\text{C}$.

Figure 8.3 illustrates the HAADF-STEM images for $\text{Ni}_{0.8}\text{Pd}_{0.2}/\text{C}$, $\text{Ni}_{0.9}\text{Au}_{0.1}/\text{C}$ and $\text{Ni}_{0.9}\text{Bi}_{0.1}/\text{C}$ catalysts. Figure 8.3 also shows the elemental distribution of Ni $L_{2,3}$, Pd- $M_{4,5}$, Au- $M_{4,5}$ and Bi- $M_{4,5}$ within the particle, which were extracted from different signals of ~ 855 , 400, 2200 and 2600 eV, respectively (Figure F12 in SI). The Ni (red) versus Pd, Au and Bi (green) composite images indicate that the Pd, Au and Bi core is partly surrounded by a pure Ni shell, indicating the possibility of a core-shell structure in some areas. However, $\text{Ni}_{0.9}\text{Bi}_{0.1}/\text{C}$ (Figure 8.3c) adopted a nanoflake-like morphology varying remarkably from that seen for $\text{Ni}_{0.8}\text{Pd}_{0.2}/\text{C}$ and $\text{Ni}_{0.9}\text{Au}_{0.1}/\text{C}$ NPs.

Figure 8.4 a-d depicts the XPS spectra of the Ni 2p, Pd 3d, Au 4f and Bi 4f core level regions, respectively. The Ni/C XPS spectrum on the binding energy range corresponding to Ni 2p_{3/2} and Ni 2p_{1/2} shows two main peaks at 856.2 and 874.1 eV, respectively, and two satellite peaks located at 861.9 and 880.1 eV, respectively (Figure 8.4a). The spin orbital splitting of the two main peaks is 17.9 eV, which is the characteristics of a $\text{Ni}(\text{OH})_2$ phase with no metallic Ni.^{44,46} In the $\text{Ni}_x\text{M}_{1-x}/\text{C}$ (M = Pd, Au and Bi) XPS spectra, one can see four peaks corresponding to Ni 2p, exhibiting a slight shift compared to Ni/C (Table F1 in SI).

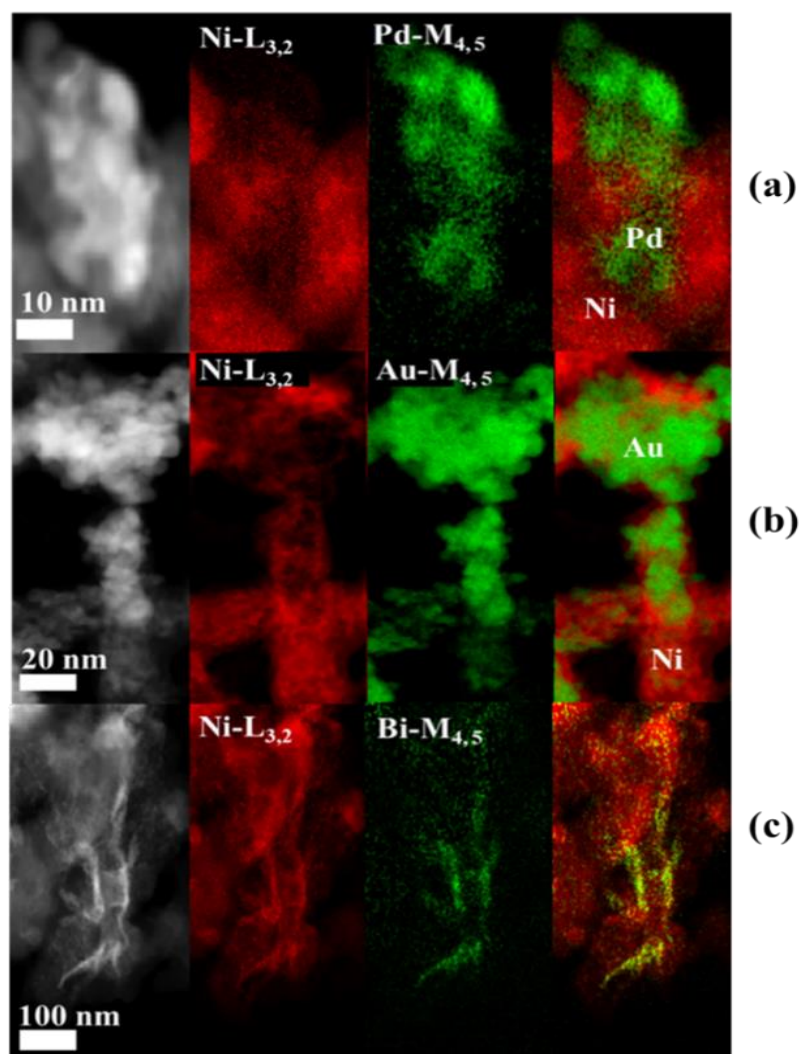


Figure 8.3. HAADF-STEM images and EELS Map of Ni-L_{2,3}, Pd-M_{4,5}, Au-M_{4,5} and Bi-M_{4,5} of carbon supported Ni-based catalysts (metal loading: 30 wt%) (a) Ni_{0.8}Pd_{0.2}/C, (b) Ni_{0.9}Au_{0.1}/C and (c) Ni_{0.9}Bi_{0.1}/C.

In Figure 8.4b, the Pd 3d region is comprised with a doublet peaks centered at 337.8 and 343.4 eV (spin-orbital splitting of 5.6 eV), in good correlation with the reported values for PdO₂.^{46,47} Moreover, Au 4f spectrum appears at lower range between 80-90 eV with two doublets Au 4f_{7/2} (84.2 eV) and Au 4f_{5/2} (87.9 eV) in Figure 8.4c. The position of the peaks indicates the formation of a pure metal gold (Au (0)) with the 3.7 eV binding energy distance.^{46,48} In Figure 8.4d, the two strong XPS peaks detected at binding energies of 159.7 and 165.0 eV were attributed to Bi 4f_{7/2} and Bi 4f_{5/2} of Bi³⁺ in Bi₂O₃ with 0.7 eV higher energy positions than pure Bi₂O₃.^{49,50} This shift could be ascribed to the changes in the chemical environment caused by Ni addition.

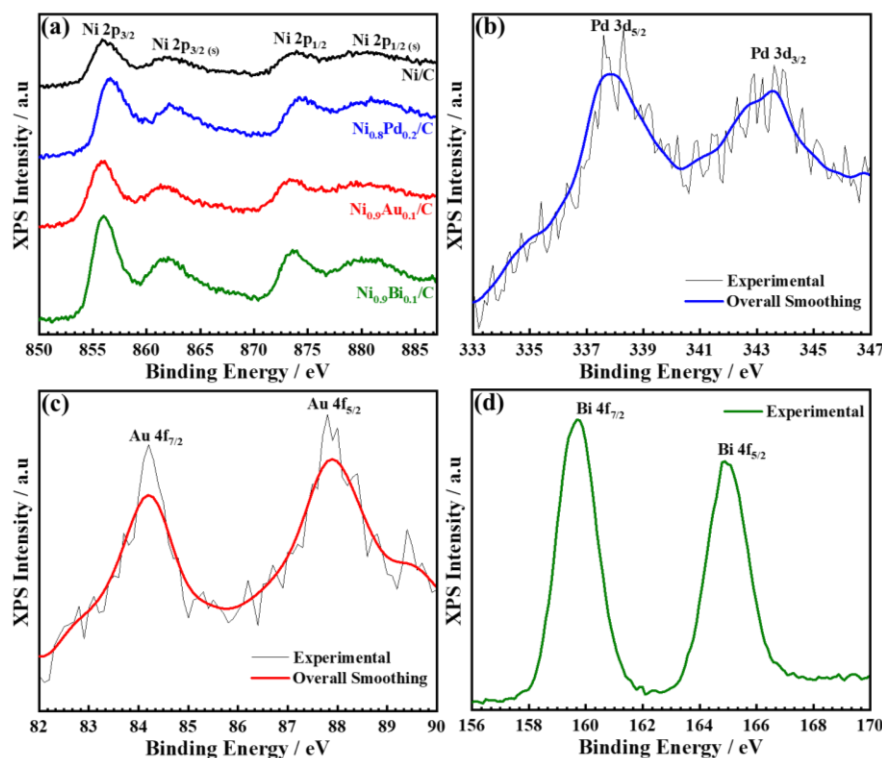


Figure 8.4. XPS peaks of $\text{Ni}_x\text{M}_{1-x}/\text{C}$ ($\text{M} = \text{Pd}, \text{Au}$ and Bi) (a) Ni 2p, (b) Pd 3d, (c) Au 4f and (d) Bi 4f.

8.3.2 Evaluation of the catalytic activity

Cyclic voltammograms (CV) recorded for $\text{Ni}_x\text{M}_{1-x}/\text{C}$ materials ($\text{M} = \text{Pd}, \text{Au}$ and Bi) at 0.05 V s^{-1} in 1.0 M KOH aqueous electrolyte are illustrated in Figure 8.5a and Figure F13 in SI. The $\text{Ni}^{\text{II}}/\text{Ni}^{\text{III}}$ redox process of the mono-metallic material is well established in our previous studies.^{20,37,51} The reversible oxidation of $\beta\text{-Ni}(\text{OH})_2$ to $\beta\text{-NiOOH}$ takes place between $+0.49$ and $+0.60 \text{ V}$ vs. Hg/HgO in the positive-going scan, and the reduction of $\beta\text{-NiOOH}$ species to $\beta\text{-Ni}(\text{OH})_2$ occurs between $+0.50$ and $+0.20$ in the negative-going scan. For potential higher than $+0.60 \text{ V}$ in the positive-going scan, the increase of current density is related to the oxygen evolution reaction. At last, a reduction process in the -0.15 to -0.35 V vs. Hg/HgO , identified by the navy rectangle in Figure 8.5a, is the reduction of either another nickel oxide species or of oxygen generated during the oxygen evolution reaction (OER).⁵²

In the case of data normalization for $\text{Ni}_x\text{M}_{1-x}/\text{C}$ materials, it is complex to evaluate the electro-active surface areas (ECSA) with the use of a bi-metallic as the estimation involves many uncertainties.⁵³ Therefore, the currents were normalized with geometric surface area of the GC disk (0.071 cm^2). When comparing the CVs in Figure 5, the

different $\text{Ni}_x\text{M}_{1-x}/\text{C}$ catalysts clearly exhibit separate potential regions for the surface reactions of their respective co-catalysts (Pd, Au and Bi). For $\text{Ni}_{80}\text{Pd}_{20}/\text{C}$, the small cathodic peak appears at -0.36 V vs. Hg/HgO is attributed to the reduction of Pd oxides (PdO).^{1,20} The cathodic peak close to $+0.14\text{ V}$ vs. Hg/HgO for $\text{Ni}_{90}\text{Au}_{10}/\text{C}$ is associated to the reduction of quasi-2D oxide state of Au (AuO or $\text{Au}(\text{OH})_2$).^{1,54} Whereas for $\text{Ni}_{90}\text{Bi}_{10}/\text{C}$, an anodic peak appears at lower potential ($\sim -0.52\text{ V}$ vs. Hg/HgO), which is corresponding to a thin layer formation of $\text{Bi}(\text{OH})_3$ sites at the electrode surface.⁵⁵

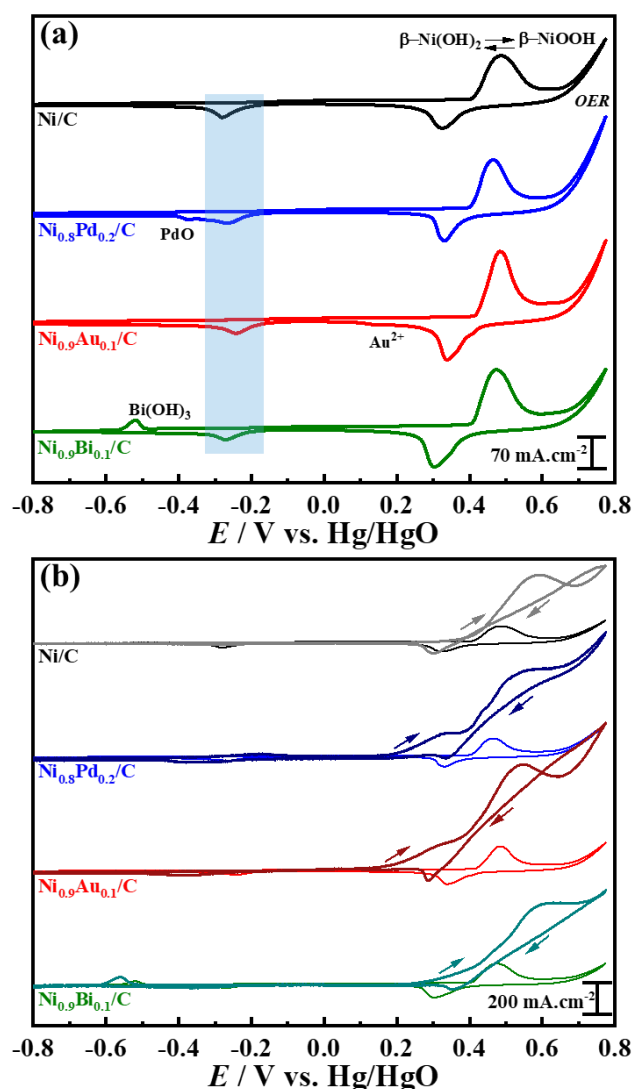


Figure 8.5. Cyclic voltammograms of $\text{Ni}_x\text{M}_{1-x}/\text{C}$ ($\text{M} = \text{Pd}, \text{Au}$ and Bi) catalysts in N_2 -purged (a) 1.0 M KOH and (b) $1.0\text{ M KOH} + 0.10\text{ M glycerol}$ electrolyte (bold line) at 0.05 V s^{-1} scan rate and 293 K (5^{th} stable cycle).

By comparing CVs in the presence and the absence of glycerol, we observe that the onset potential of GEOR is shifted toward lower potential by as much as ~ 180 to 370 mV less than the potential for the $\text{Ni}^{\text{II}} \rightarrow \text{Ni}^{\text{III}}$ transition (Figure 8.5b and F14 in SI) This

phenomenon is attributed to the dependency of GEOR with the preliminary steps of the transformation of β -Ni(OH)₂ into β -NiOOH. Similar observation was already detected by Oliveria *et al.* and Houache *et al.*^{22-24,20} The LSVs of GEOR in 1.0 M KOH + 0.1 M glycerol were recorded at 0.05 and 0.001 V s⁻¹, respectively on the different Ni-rich catalysts (Figure 8.6 and Figure F15 in SI). Ni/C catalyst presents an overpotential for GEOR close to 0.31 V vs. Hg/HgO, which is approximately 100, 180 and 140 mV lower than our previous studies on unsupported Ni³⁷ and bulk Ni, before and after treatment in ascorbic acid, respectively.²⁰

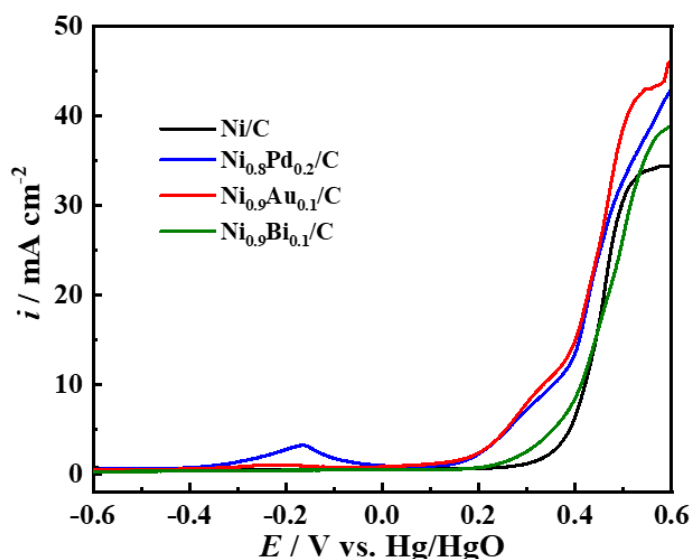


Figure 8.6. LSVs of Ni_xM_{1-x}/C (M = Pd, Au and Bi) catalysts in N₂-purged 1.0 M KOH + 0.1 M glycerol electrolyte at 0.001 V s⁻¹ scan rate and 293 K.

In comparison, bi-metallic Ni_xM_{1-x}/C materials present a shift of the onset potential towards lower values for glycerol electro-oxidation than that of mono-metallic. Among different materials, the Ni_{0.9}Au_{0.1}/C electrocatalyst displayed the highest current density, reaching 46 mA cm⁻² with a concurrent onset potential at ~ +0.12 V vs. Hg/HgO. In contrast, the Ni_{0.8}Pd_{0.2}/C catalyst has slightly higher overpotential potential ($E_{\text{onset}} = \sim +0.16$ V vs. Hg/HgO) compared to Ni_xAu_{1-x}/C (Figure F15a). An additional oxidation peak appears at ca. ~ -0.35 V vs. Hg/HgO ascribed to GEOR on Pd sites, indicating that palladium by itself has significantly lower onset potentials compared to nickel.²⁰ Figure F15b illustrates that only higher Pd content of 20 at. % was able to observe this oxidation peak which could be due to two possible reasons: (i) the presence of a rich Ni causes some surface segregation of the Pd active sites as shown in EELS mapping (Figure 8.3a) and (ii) excess formation of Ni²⁺ increases the concentration of OH_{ads} and/or OH⁻, which

in turn could hamper glycerol transportation to the Pd active sites.⁵³ Moreover, the onset potential of GEOR on the Ni_{0.98}Bi_{0.02}/C and Ni_{0.95}Bi_{0.05}/C materials was approximately the same as that on Ni/C, with the maximum current density slightly higher in Ni_{0.95}Bi_{0.05}/C (Figure F15c in SI). However, at high bismuth content of 10 at. % the overpotential dropped by 0.08 V compared to Ni/C.

In summary, small addition (≤ 20 at.%) of Pd, Au or Bi atoms to Ni nanoparticles clearly indicate that GEOR on the bimetallic catalysts improve the activity and significantly shifts the onset potential to lower values. This enhancement could be attributed to the changes in the electronic interactions between the active sites and the reactant on the catalysts and/or to the bifunctional mechanism.

8.3.3 *In-situ* infrared spectroscopy measurements

The *in situ*-spectroelectrochemical measurements have been carried out to shed light on the GEOR process taking place at the electrolyte/electrode interface on 10 different Ni-rich catalysts. Infrared spectra were recorded as a function of the electrode potential in a N₂-purged 1.0 M and 0.1 M KOH electrolyte at 293 K and 0.001 V s⁻¹ for the electro-oxidation of 0.1 M glycerol as shown in Figure 8.7-8.8 and Figure F16-F17 in SI. Spectra recorded for GEOR in high KOH concentration (1.0 M) lead to the formation of three main absorption peaks in the so-called infrared fingerprint region of the organic molecules between 1100 and 1600 cm⁻¹, labelled as band A to C on each figure (Figure 8.7 and Figure F16 in SI). These three peaks occur instantaneously at around 1350, 1385 and 1581 cm⁻¹ (bands A, B and C in Figure 8.7 and Figure F16 in SI). The absorption band at ~1350 cm⁻¹ corresponds to symmetric (O-C-O) stretching of formate.⁵⁶ The band located at ~1385 cm⁻¹ is clearly associated to symmetric (O-C-O) stretching of formate and glycerate.^{37,56} Besides, the absorption peak detected at 1581 cm⁻¹ is assigned to a different asymmetric COO⁻ group of carboxylate species²²⁻²⁴ with a shoulder at ~1670 cm⁻¹. These three absorption peaks appear on all the materials with different intensities, demonstrating that the main reaction products don't alter depending on the catalyst composition and applied potential considered in this study. In the context of variation of absorption band intensities, functional groups are consumed or formed at different rates. An upward absorption peaks at ~ 1050 and 1113 cm⁻¹ assigned to ν (C-O) stretching of CH₂-OH functions corresponds to glycerol consumption.⁵⁷

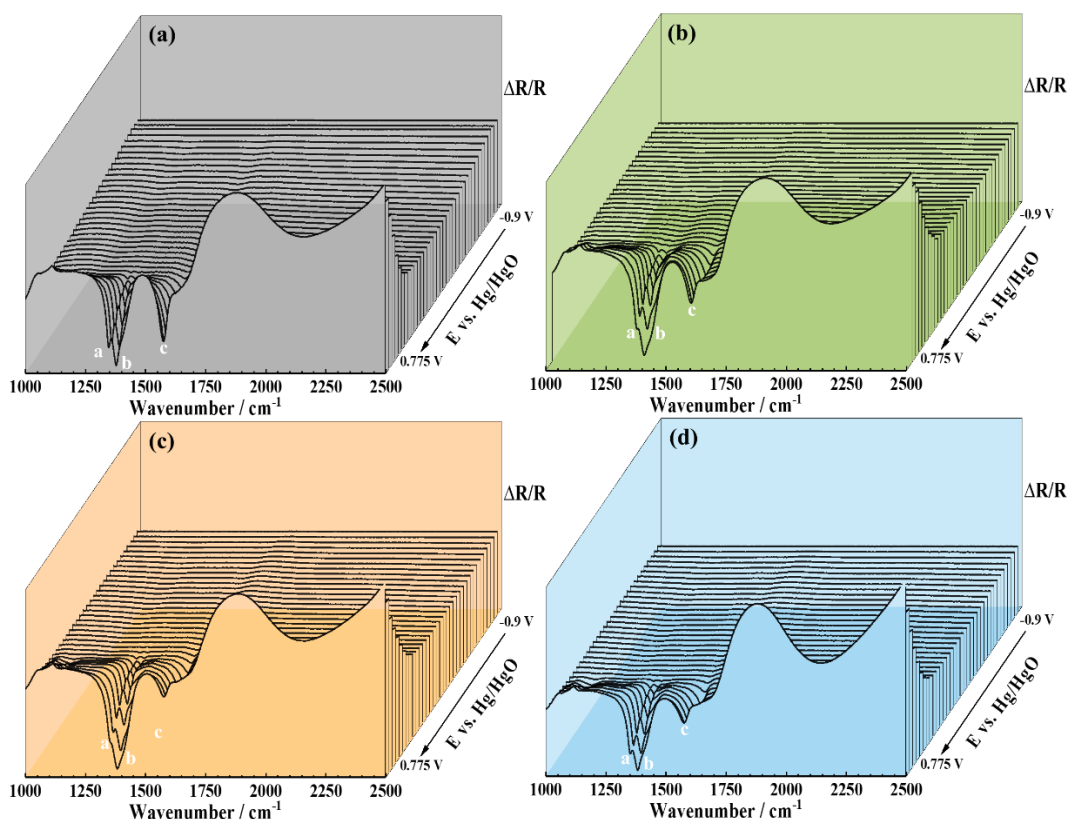


Figure 8.7. Infrared spectra recorded during GEOR on (a) Ni/C, (b) Ni_{0.8}Pd_{0.2}/C, (c) Ni_{0.9}Au_{0.1}/C and (d) Ni_{0.9}Bi_{0.1}/C catalysts in 1.0 M KOH + 0.1 M glycerol electrolyte at 293 K. Scan rate: 0.001 V s⁻¹, resolution 4 cm⁻¹.

Similar remarks for lower concentration KOH (0.1 M) can be made from the infrared spectra recorded for glycerol electro-oxidation on the different Ni-rich catalysts (Figure 8.8 and Figure F17 in SI). The absorption peaks are positioned at the same wavenumber values as for higher KOH concentration (1 M KOH), indicating a similar formation of the functional species stated above. An intense peak appears at 2343 cm⁻¹ on Ni/C for $E > +0.53$ V vs. Hg/HgO (band D in Figure 8.8a), which has lower intensity on Ni_xAu_{1-x}/C materials at $E = 0.775$ V vs. Hg/HgO (Figure 8.8c and Figure F17c-d in SI). This absorption peak corresponds to CO₂ formation.^{22,23}

In those cases, it is worth to note the presence of an absorption band between 1400 and 1450 cm⁻¹, which could be attributed to the formation of carbonates. However, the CO₂ absorption band is not visible with Ni_xPd_{1-x}/C (Figure 8.8b and Figure F17a-b in SI) and Ni_xBi_{1-x}/C (Figure 8.8d and Figure F17e-f in SI) materials, as well as the absorption bands between 1400 and 1450 cm⁻¹. The same observation can be made for all catalysts tested in 1.0 M KOH: the increase of the KOH concentration avoids the formation of carbonate and CO₂ and favor the formation of formate. The CO₂ visibility is mainly due

to the change of interfacial pH to acid due to the consumption of hydroxyl in a thin layer close to electrode and CaF_2 prism.^{20,22-24}

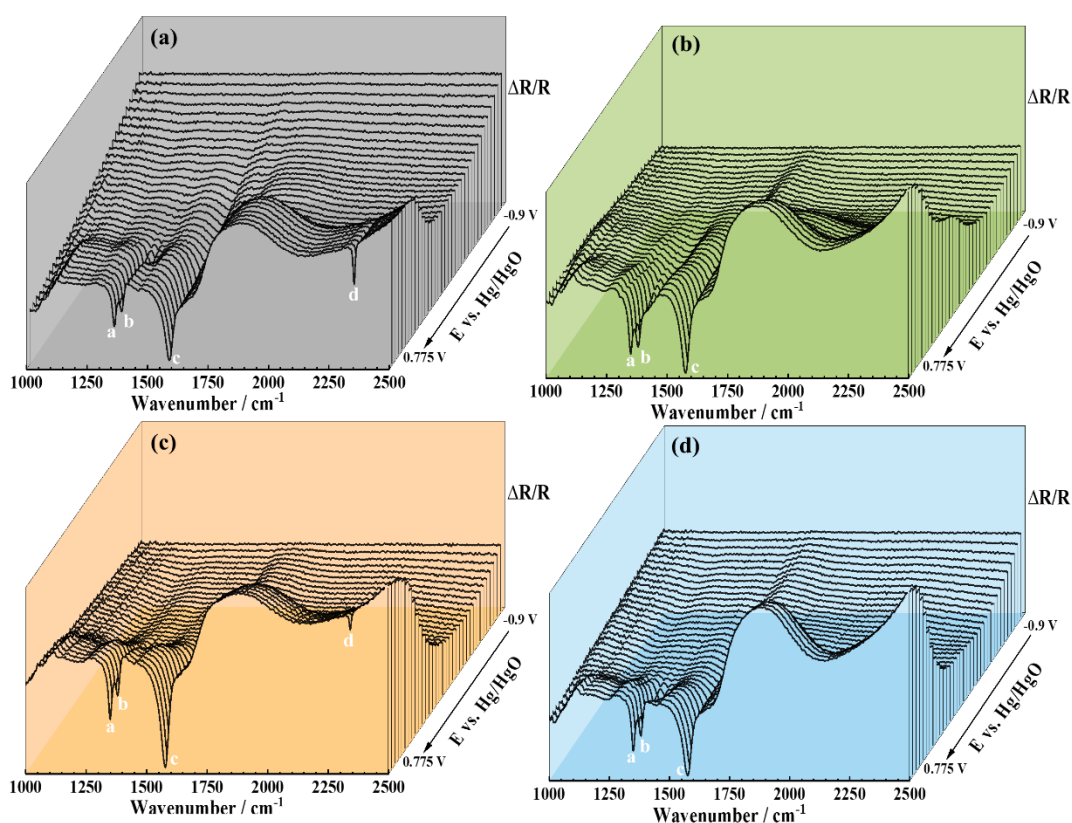


Figure 8.8. Infrared spectra recorded during GEOR on (a) Ni/C, (b) $\text{Ni}_{0.8}\text{Pd}_{0.2}/\text{C}$, (c) $\text{Ni}_{0.9}\text{Au}_{0.1}/\text{C}$ and (d) $\text{Ni}_{0.9}\text{Bi}_{0.1}/\text{C}$ catalysts in 0.1 M KOH + 0.1 M glycerol electrolyte at 293 K. Scan rate: 0.001 V s^{-1} , resolution 4 cm^{-1} .

From both these studies, all $\text{Ni}_x\text{M}_{1-x}/\text{C}$ catalysts are very promising in terms of activity and selectivity towards formate formation at mild electrode potentials and high KOH concentration. For this reason, Ni/C, $\text{Ni}_{0.8}\text{Pd}_{0.2}/\text{C}$, $\text{Ni}_{0.9}\text{Au}_{0.1}/\text{C}$ and $\text{Ni}_{0.9}\text{Bi}_{0.1}/\text{C}$ catalysts were selected to perform continuous scale-up electrolysis measurements for 24 hrs to accumulate reaction products and determine the selectivity of glycerol electro-oxidation in 1.0 M KOH.

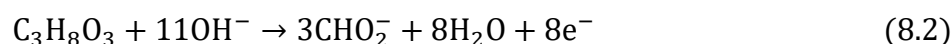
8.3.4 Electrolysis measurements

The mechanistic analysis was accomplished to determine the reaction products by HPLC and NMR after applying CA measurements in a 25 cm^2 (geometric area) continuous electrolysis cell for 24 hrs at two constant cell voltages of +1.30 V and +1.55 V selected from the *in situ* infrared study. For GEOR at the anodic compartment, the

current dropped monotonically over the 24 hr - electrolysis time range as shown in (Figure F18 in SI).

The analyses by HPLC of the reaction mixture were performed every hour for 6 hrs using an aliquot of 0.6 ml of solution. The data (Figure. F19a-d in SI) show the evolution of the chromatograms with the time of glycerol electrolysis on Ni/C, Ni_{0.8}Pd_{0.2}/C, Ni_{0.9}Au_{0.1}/C and Ni_{0.9}Bi_{0.1}/C catalysts. In all figures, the main peak is detected at retention time of ~ 10.46 min for GEOR, clearly corresponding to formic acid which is confirmed by the reference chromatogram (Figure F20a in SI). Hence, at +1.30 V two additional small peaks appear at retention time of ~ 8.31 and 9.45 min. The first peak (at ~ 8.31 min) appears after one-hour electrolysis and remains stagnant for a longer period; this could be due to the injection peak or the formation of glyceric acid in a negligible quantity at the very early stage of electrolysis measurements. The second peak (~ 9.45 min) increases gradually with time and is mainly pronounced for the Ni_{0.9}Au_{0.1}/C catalyst. We propose that it could be the formation of lactic acid in small traces, since this compound is well known to be selective towards GEOR on gold materials.⁵⁸ These two peaks were confirmed by the reference chromatogram as shown in (Figure F20b and c in SI). While at higher cell voltage ($U_{\text{cell}} = +1.55$ V), only the formate peak was evident.

Figure 8.9a-h compare the experimental concentration of formate ($C_{\text{formate,exp}}$) carried out by HPLC experiments with the theoretical concentration of formate ($C_{\text{formate,theo}}$) determined by the Faraday's law via eight-electron process, assuming only the formation of formate as shown in reaction (8.2):



Finding the resulting Faradic efficiency for formate formation can be given using equation (8.3)¹:

$$\eta_F = \frac{C_{\text{formate,exp}}}{C_{\text{formate,theo}}} \quad (8.3)$$

First, in the case of Ni/C and Ni_{0.9}Bi_{0.1}, a very good agreement between the experimental concentration of formate determined by HPLC and the theoretical one for a 100% selectivity is obtained for both cell voltages, the difference lying certainly in the standard deviations of the experiment. This observation indicates a very selective

production of formate with these catalysts. The curves at low cell voltage ($U_{\text{cell}} = +1.30$ V) for $\text{Ni}_{0.8}\text{Pd}_{0.2}/\text{C}$ and $\text{Ni}_{0.9}\text{Au}_{0.1}/\text{C}$ in Figure 8.9c and e, respectively, do not overlap, demonstrating that other products are generated. It can be reasonably proposed that the supplementary product corresponds to that detected at 9.45 min by HPL. It seems that this product acts as intermediate which is not stable in GEOR and tends to be further oxidized to formate at high cell voltage (+1.55 V), as both curves become closer each other (Figure 8.9d and f).

Due to these limit scenarios, it was possible to calculate the limit concentration of glycerol ($C^{\text{8e}^-}_{\text{Glycerol}}(t)$) and its conversion ($X^{\text{8e}^-}_{\text{Glycerol}}(t)$) at different reaction times assuming 100% selectivity to formate, according to the following equations:

$$C_{\text{Glycerol}}(t) = 0.1 - \frac{C_{\text{formate,exp}}(t)}{3} \quad (8.4)$$

$$X_{\text{Glycerol}}(t) = \frac{0.1 - C_{\text{Glycerol}}(t)}{0.1} \quad (8.5)$$

All obtained results are summarized in (Table SI 8.2 in SI). For 6 hr electrolysis of glycerol on Ni/C, the conversion rates increase significantly by applying higher applied potentials, i.e. 11.7 % and 32.7 % for $U_{\text{cell}} = +1.30$ V and +1.55 V, respectively. Compared to Ni/C, the bi-metallic catalysts show a better tendency for glycerol conversion throughout the electrolysis duration. $\text{Ni}_{0.8}\text{Pd}_{0.2}/\text{C}$ and $\text{Ni}_{0.9}\text{Au}_{0.1}/\text{C}$ have the highest value after 6 h electrolysis with glycerol conversion of 73.1 % and 63.1 %, respectively. In the case of $\text{Ni}_{0.9}\text{Bi}_{0.1}/\text{C}$ catalyst, the results are still impressionable, with 46.4 % conversion and 100 % selectivity towards formate.

At the end of the electrolysis measurements an additional identification technique (^1H NMR) was performed to identify the product distribution after 24 hr of CA in 0.1 M glycerol solution (Fig. 8.10a and b). The ^1H NMR spectra of the initial solution (1.0 M KOH + 0.1 M glycerol) before electrolysis measurement (Fig. F20a and b in SI) exhibit with typical signals for glycerol with several peaks in the 3.4-3.7 ppm range and of a standard solution (1.0 M KOH + 0.1 M formate) with a single formate peak at ~ 8.4 ppm, respectively. After 24 hr electrolysis at a cell voltage of +1.30 V, the signal of glycerol has been reduced for all catalysts as shown in Fig.8.10a.

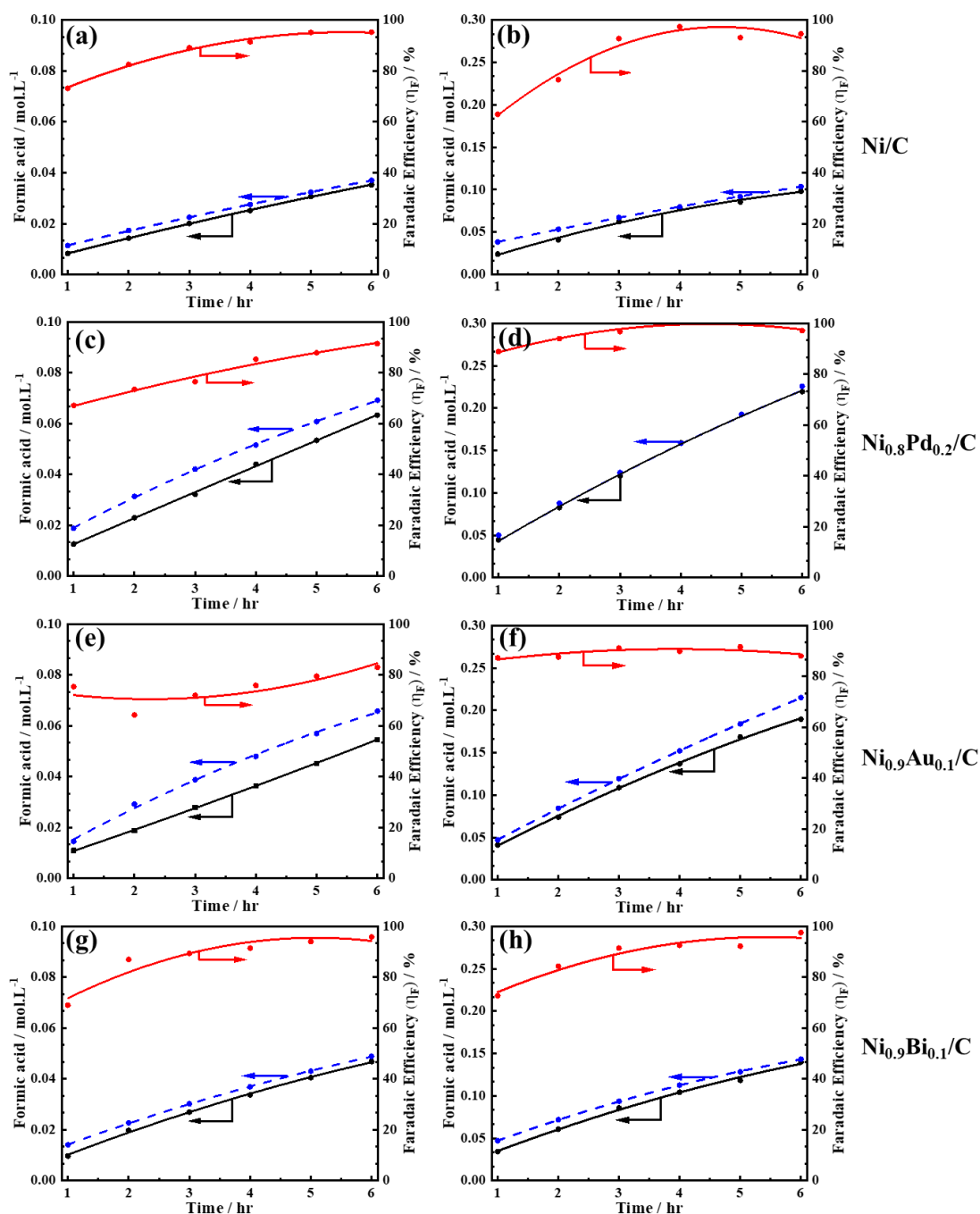


Figure 8.9. Comparison of the experimental concentration of formate determined by HPLC (black line) with the theoretical one for a 100% selectivity (blue dotted line) and Faradaic efficiency for formate production (red line) as a function of electrolysis time on (a,b) Ni/C, (c,d) Ni_{0.8}Pd_{0.2}/C, (e,f) Ni_{0.9}Au_{0.1}/C, and (g,h) Ni_{0.9}Bi_{0.1}/C at +1.30 V (on the left-hand side) and +1.55 V (on the right-hand side).

While at higher voltage ($U_{\text{cell}} = +1.55$ V), the glycerol peaks disappear completely, indicating 100% conversion (Fig. 8.10b). Furthermore, in ¹H NMR spectra formate has been detected as the major product ($\delta \approx 8.4$ ppm), which indicates that C-C bond of glycerol was broken. In addition, it is noteworthy to mention that the intensity of the

formate signal at +1.55 V decreases for all $\text{Ni}_{1-x}\text{M}_x/\text{C}$ compared to that at +1.30 V. This translates likely in the higher ability of modified Ni catalysts for the formation of CO_3^{2-} .

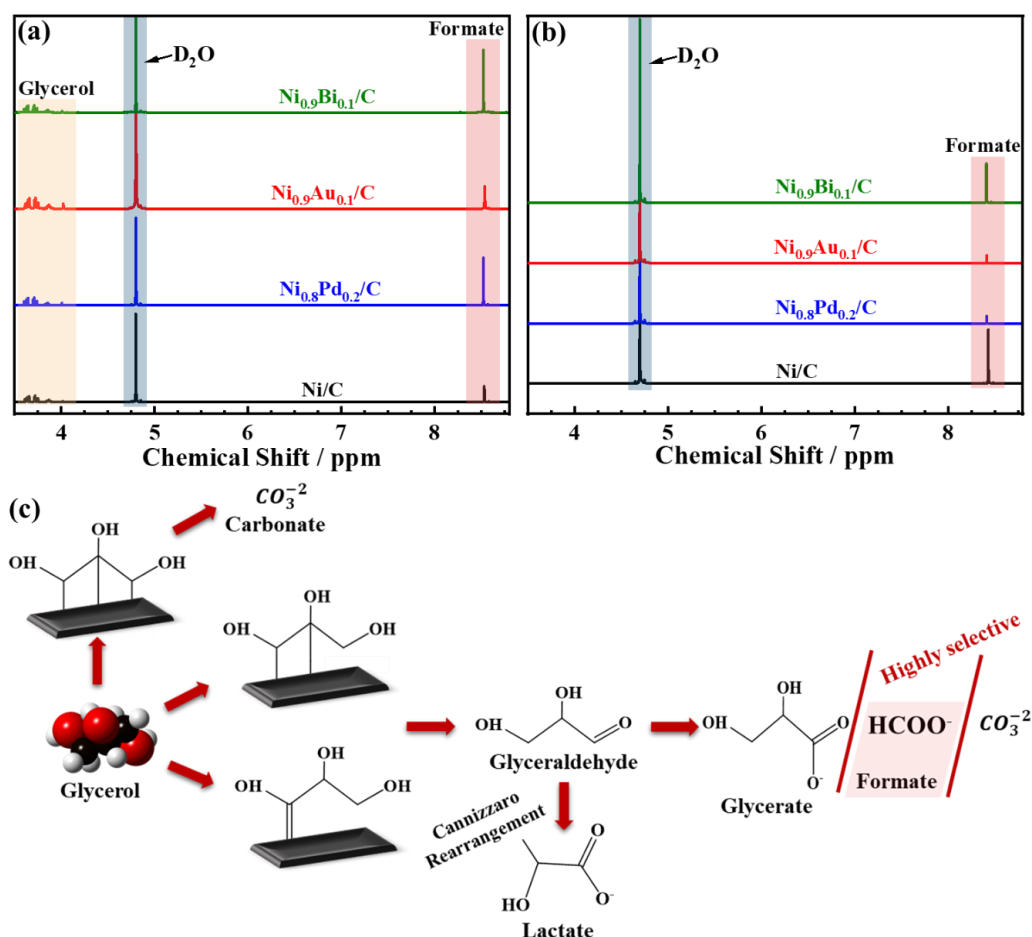


Figure 8.10. ^1H NMR spectra of 1.0 M KOH + 0.1 M glycerol solution after neutralization with HCl, lyophilization and dissolution into D_2O . The spectra correspond to different Ni-based catalysts at the cell voltages of (a) +1.30 V and (b) +1.55 V after 24 hrs of electrolysis. (c) Suggested reaction pathways for GEOR over $\text{Ni}_x\text{M}_{1-x}/\text{C}$ ($\text{M} = \text{Pd}, \text{Au}$ and Bi) catalysts.

In summary, all qualification and quantification analyses are in good correlation, indicating the formation of formate as one of the major products on the anode carbon supported Ni-M shell-core structures with cathodic hydrogen production, we suggested the reaction mechanism in Figure 8.10c. The counter electrode reaction on Pt/C hydrogen at a cell voltage as low as +1.30 V, which corresponds to the low energy consumption of $\sim 35 \text{ kWh kg}^{-1}$.⁵⁹

8.3.5 Co-electrolysis of CO₂ and glycerol in a flow electrolyzer

A possible approach to achieve cost-effective electro-oxidation of glycerol using Ni-rich bi-metallic catalysts is to execute this reaction parallel with CO₂ electroreduction using Ag NPs as cathode catalyst. Running this co-electrolysis process in a flow electrolyzer revealed that all Ni bimetallic catalysts are active towards GEOR as shown in Figure 8.11 and Figure F22-F24 in SI. Out of all the Ni_xAu_{1-x}/C catalysts, the Ni_{0.9}Au_{0.1}/C catalyst achieved the highest partial CO current density of ~6.0 mA.cm⁻² at -1.5 V as shown in (Figure F23). For the Ni_xPd_{1-x}/C and Ni_xBi_{1-x}/C samples, the best performers were Ni_{0.95}Pd_{0.05}/C and Ni_{0.95}Bi_{0.05}/C, showing partial CO current densities of about 3.3 and 1.7 mA.cm⁻², respectively, at 1.5 V (Figure F22 and F24 in SI). Adding Au and Pd to Ni enhances the activity; however, Bi behaves similarly to Ni as both the Ni_xBi_{1-x}/C and Ni/C anodes depicted the lowest activities. Compared to the carbon-supported Ni_{0.95}Bi_{0.05} and Ni, both Ni_{0.9}Au_{0.1}/C and Ni_{0.95}Pd_{0.05}/C anodes exhibit lower onset cell voltages for the CO₂ electroreduction. The onset cell potential value for Ni/C and Ni_{0.95}Bi_{0.05}/C is around -1.30 V, while using Ni_{0.9}Au_{0.1}/C and Ni_{0.95}Pd_{0.05}/C dropped the cell voltage significantly by 0.3 V ($U_{\text{cell,onset}} = -1.0$ V) and 0.2 V ($U_{\text{cell,onset}} = -1.1$ V), respectively, as illustrated in Figure 8.11b. We also noticed in Figure 8.11a that both reference Pt and Au mono-metallics catalysts at the anode outperform all of the Ni-rich bimetallic catalysts, leading to better overall activity (62 and 25 mA.cm⁻² @ -1.5 V, respectively) with lower onset cell potentials ($E_{\text{onset}} = -0.75$ and -0.9 V, respectively) for CO₂ electroreduction. Furthermore, ¹H NMR analysis of the anolyte indicates the formation of both formate and lactate in this co-electrolysis experiment as illustrated in (Figure F25 in SI).

If we were to attempt a durability study with these catalysts, we would continuously apply 1.5 V and monitor any the total current and CO Faradaic efficiency for changes. However, since the total current for all Ni_xAu_{1-x}/C experiments at this cell potential was <10 mA cm⁻², the durability test would not provide much insight on catalyst stability because it is a relatively low current compared to the capabilities of the flow cell and industrially relevant current densities (≥ 200 mA cm⁻²).⁶⁰⁻⁶² Increasing the cell potential would indeed provide higher current densities but would also begin to introduce OER and therefore negate the study of GEOR for these catalysts.

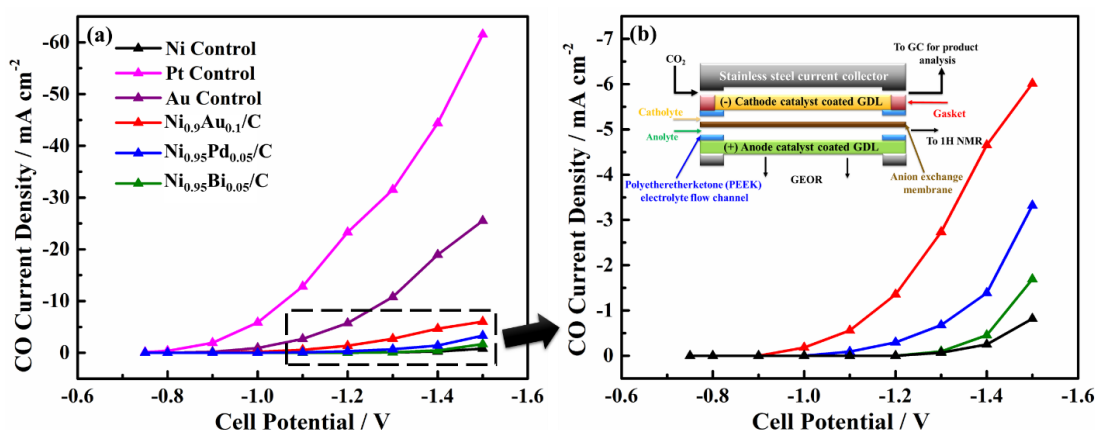


Figure 8.11. (a) The co-electrolysis performance of the most active carbon supported NiAu, NiPd, and NiBi nano-catalysts as well as the Pt, Au, and Ni/C controls. The graph plots the partial CO current density with respect to applied cell potential; the graph on the right (b) magnifies the data from Ni-based anodes with a schematic representation of the setup.

With these active anodes, the entire flow electrolyzer requires less cell voltage (total energy) to reduce CO₂ to CO, an observation we also noted in our previous work when using Pt at the anode.¹³ Reducing the total energy helps to make all electroreduction products more feasible by widening the operating cell potential range.⁶¹ Lowering the energy requirement of co-electrolysis also reduces carbon emissions considering the supplying electrical grid is only partially renewable.¹³ As stated earlier, Pt and Au are more active for CO₂ electroreduction, however these catalysts are precious metals and thus drive up the cost for the capital expenditure of this electrolysis setup. Specifically, the market prices of Pt, Au, and Ni are approximately 30, 52, and 0.016 USD gram⁻¹, respectively.⁶³⁻⁶⁵ Ultimately, being able to utilize Ni as the main component of the anode catalysts could reduce the catalyst price significantly (~2000-3000 lower). This saving reduces the cost of the setup and in turn decreases the minimum current density needed to make production of CO₂ electroreduction commodities (CO in our case) more feasible⁶¹.

8.4 Conclusion

Nanosized materials based on nickel-rich metals have been prepared by a heatless co-reduction method. The Ni_xM_{1-x}/C (M= Bi, Pd and Au) nanocatalysts with different atomic ratios (≤ 20%) have been characterized, indicating the possibility of a M-core Ni-shell structure which optimized the performance of these materials. The electrochemical measurements performed in 1.0 M KOH electrolyte permitted the surface

characterization of each electrode catalyst. As evidenced, the Pd, Au and Bi elements were present in their composition and they modified the electronic properties of Ni to shift the overpotential to lower values, by as much as 0.19 to 0.08 V for GEOR. *In-situ* infrared spectroscopy measurements showed that the major product was formate, which is attributed to symmetric and asymmetric carboxylate species. However, no significant changes in selectivity was observed for all $\text{Ni}_x\text{M}_{1-x}/\text{C}$. In addition to Ni/C, we chose the three best catalysts to run 24-hour continuous electrolysis in a 25 cm^2 cell at a potential of +1.30 and +1.55 V and the reaction products were analyzed by HPLC and ^1H NMR. After 1 hr electrolysis, both applied potentials led to 100% selectivity for formate production, which is in a good correlation with a qualitative analysis. At higher voltage ($U_{\text{cell}} = +1.55\text{ V}$), the glycerol peaks disappear completely, indicating 100% conversion after 24 hr electrolysis for all four catalysts. Moreover, co-generation of value-added products at the anode using cost-effective $\text{Ni}_x\text{M}_{1-x}/\text{C}$ in combination with CO_2 electro-reduction to CO at the cathode using Ag was tested. These flow electrolyzer experiments revealed that out of all $\text{Ni}_x\text{M}_{1-x}/\text{C}$ catalysts, the $\text{Ni}_{0.9}\text{Au}_{0.1}/\text{C}$ catalyst achieved the highest partial current density for CO of $\sim 6.0\text{ mA}\cdot\text{cm}^{-2}$ and lowest onset cell voltage of -1.0 V , which is in a good agreement with the electrochemical measurements. All these insights anticipate the possibility to control the selectivity and activity of these Ni-based electro-catalysts toward a given product.

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Supplementary Information F: Chapter 8

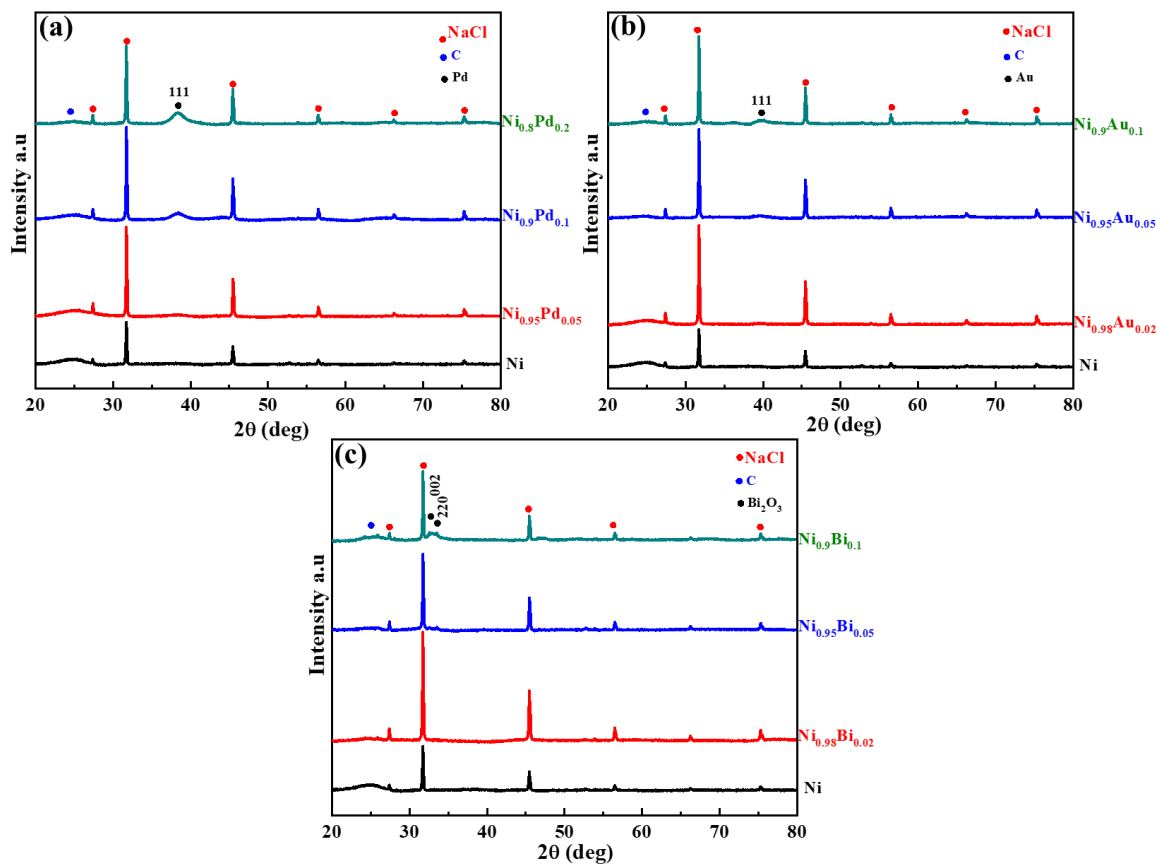


Figure F1. XRD pattern of carbon supported Ni-based catalysts (metal loading: 30 wt%).
 (a) $\text{Ni}_x\text{Pd}_{1-x}/\text{C}$, (b) $\text{Ni}_x\text{Au}_{1-x}/\text{C}$ and (c) $\text{Ni}_x\text{Bi}_{1-x}/\text{C}$.

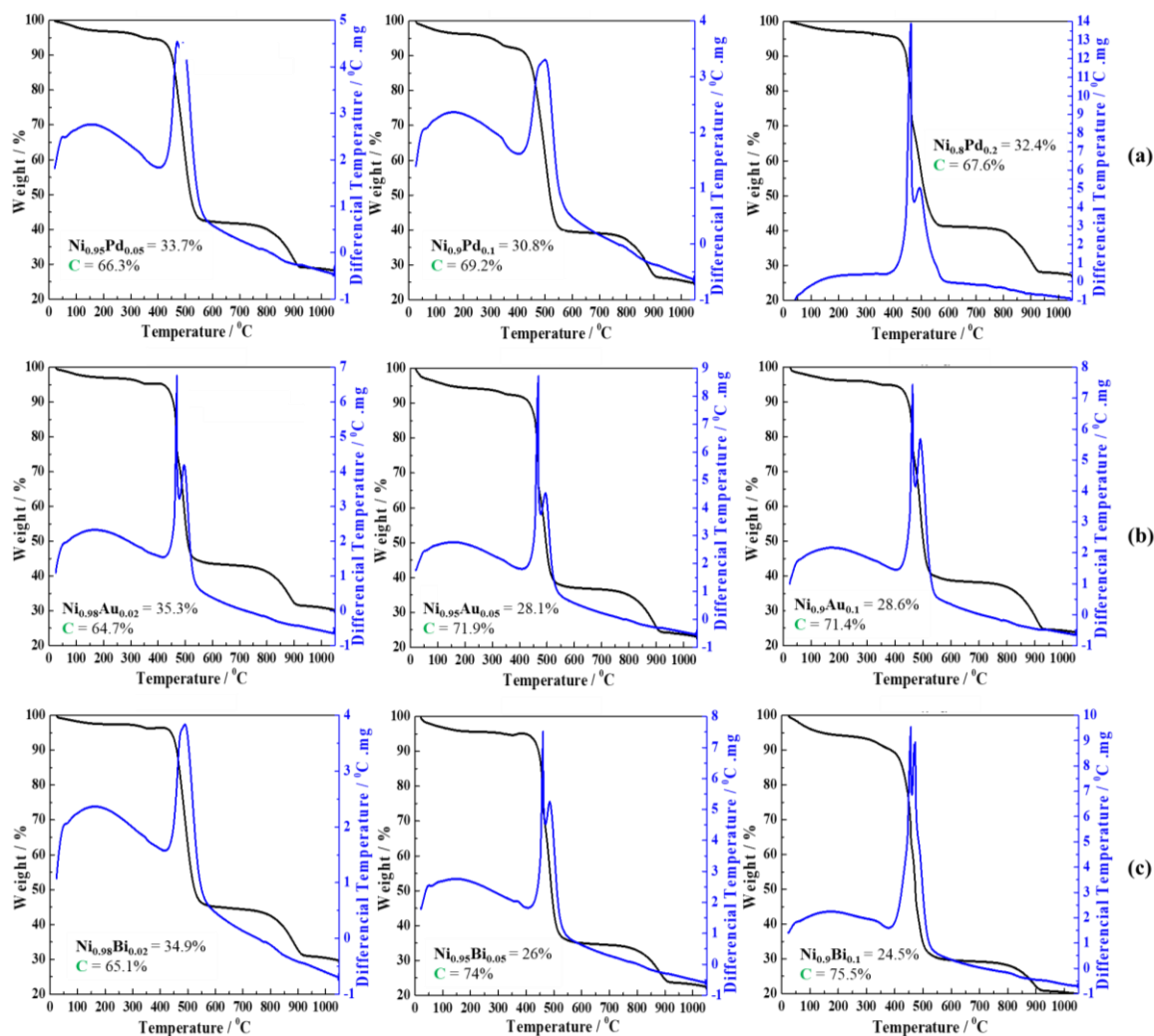


Figure F2. TGA/DTA measurements of carbon supported Ni-based catalysts (metal loading: 30 wt%) in temperature range 298-1323 K at a heating rate of 5 K min⁻¹. (a) Ni_xPd_{1-x}/C, (b) Ni_xAu_{1-x}/C and (c) Ni_xBi_{1-x}/C.

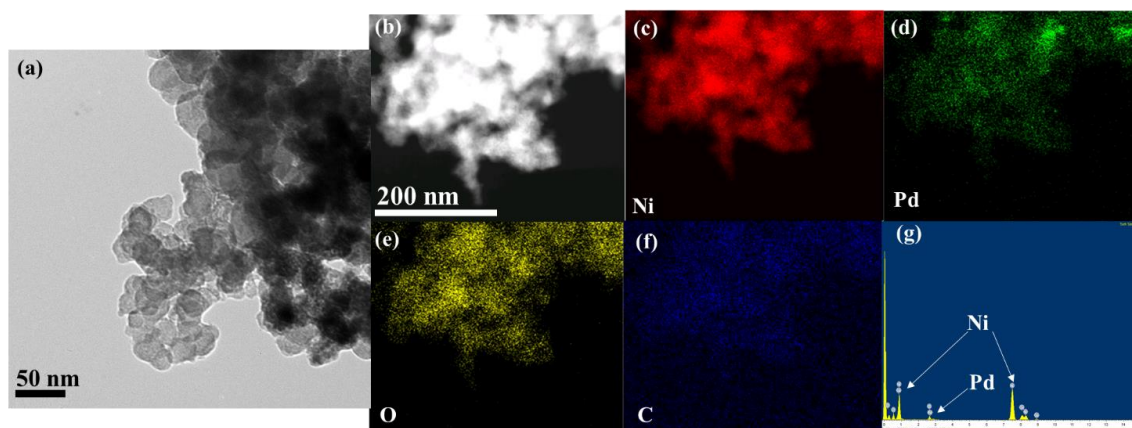


Figure F3. (a) TEM image of $\text{Ni}_{95}\text{Pd}_5/\text{C}$, (b) Dark Field-STEM image, EDS mapping of (c) Ni, (d) Pd, (e) O and (f) C. (g) EDS spectrum of $\text{Ni}_{0.95}\text{Pd}_{0.05}/\text{C}$.

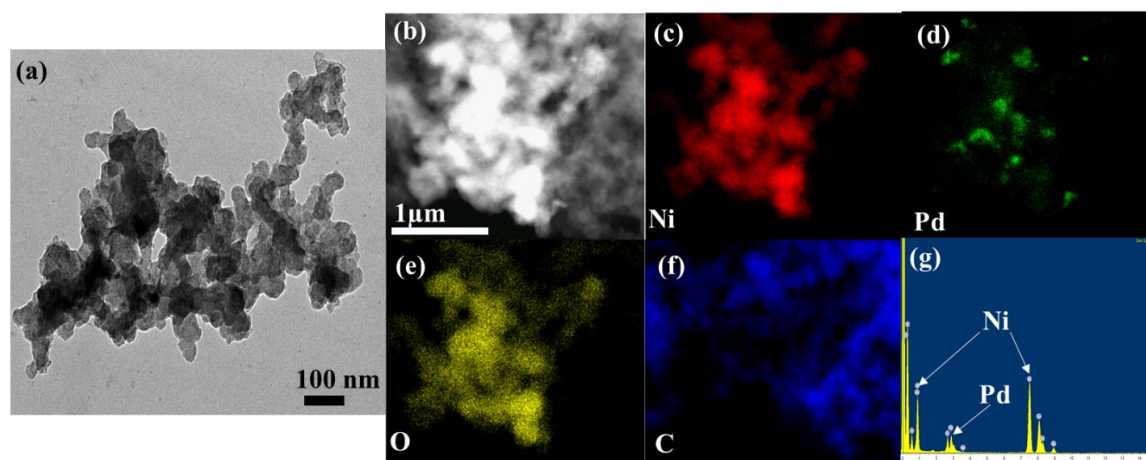


Figure F4. TEM image of $\text{Ni}_{90}\text{Pd}_{10}/\text{C}$, (b) Dark Field-STEM image, EDS mapping of (c) Ni, (d) Pd, (e) O and (f) C. (g) EDS spectrum of $\text{Ni}_{0.9}\text{Pd}_{0.1}/\text{C}$.

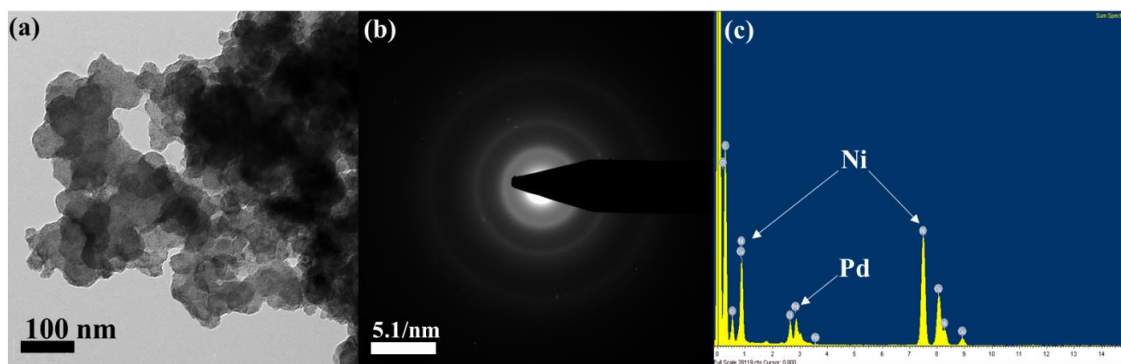


Figure F5. (a) TEM image, (b) SAED patterns and (c) EDS spectrum of $\text{Ni}_{0.8}\text{Pd}_{0.2}/\text{C}$.

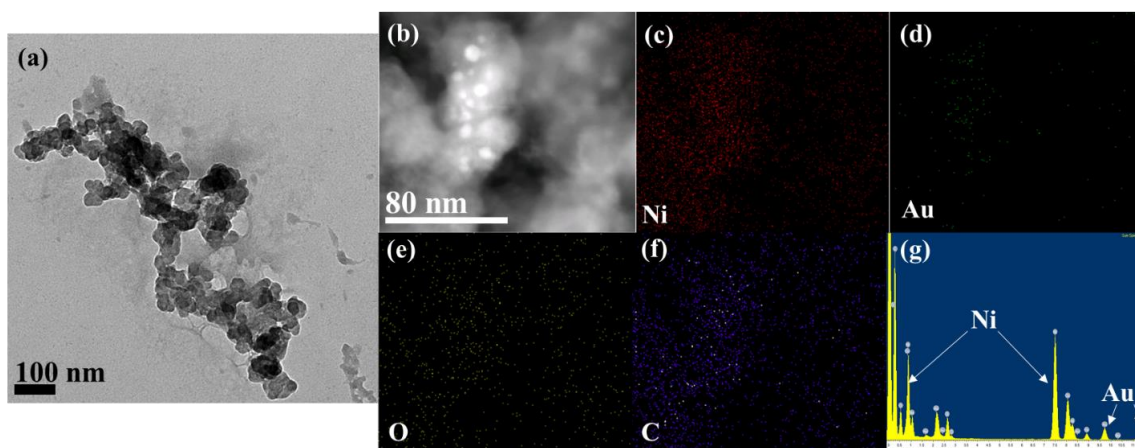


Figure F6. (a) TEM image of $\text{Ni}_{98}\text{Au}_2/\text{C}$, (b) Dark Field-STEM image, EDS mapping of (c) Ni, (d) Au, (e) O and (f) C. (g) EDS spectrum of $\text{Ni}_{0.98}\text{Au}_{0.02}/\text{C}$.

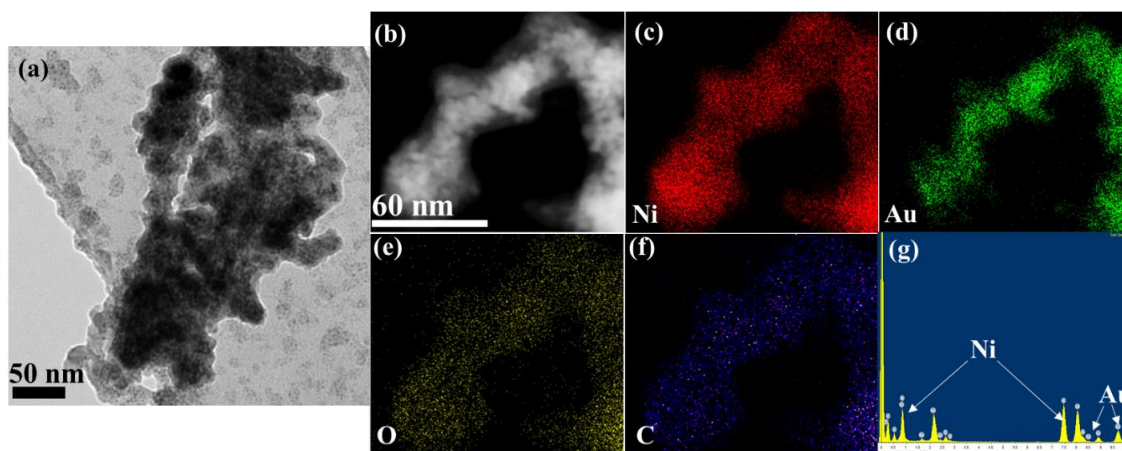


Figure F7. (a) TEM image of $\text{Ni}_{95}\text{Au}_5/\text{C}$, (b) Dark Field-STEM image, EDS mapping of (c) Ni, (d) Au, (e) O and (f) C. (g) EDS spectrum of $\text{Ni}_{0.95}\text{Au}_{0.05}/\text{C}$.

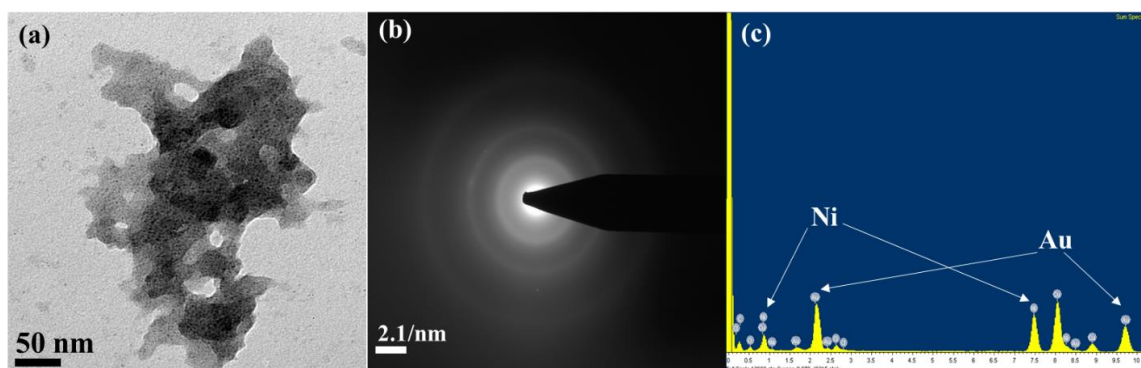


Figure F8. (a) TEM image, (b) SAED patterns and (c) EDS spectrum of $\text{Ni}_{0.9}\text{Au}_{0.1}/\text{C}$.

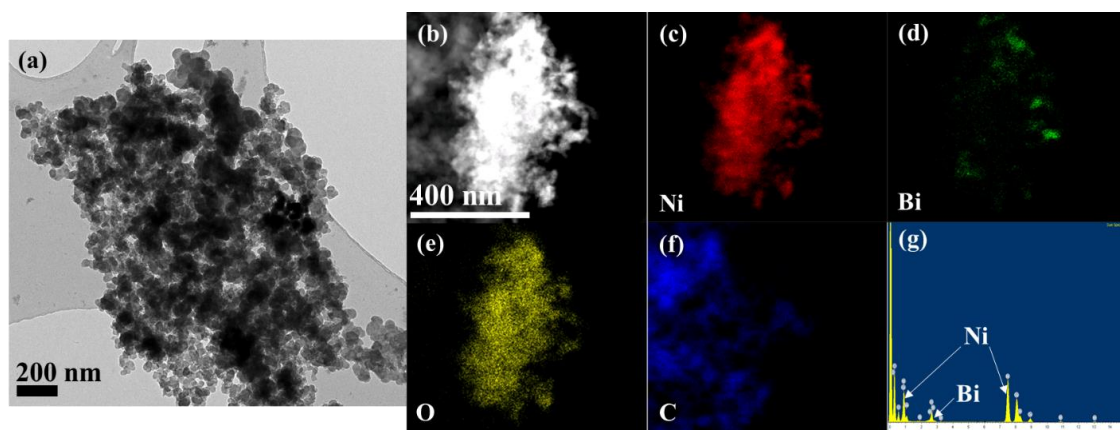


Figure F9. (a) TEM image of $\text{Ni}_{98}\text{Bi}_2/\text{C}$, (b) Dark Field-STEM image, EDS mapping of (c) Ni, (d) Bi, (e) O and (f) C. (g) EDS spectrum of $\text{Ni}_{0.98}\text{Bi}_{0.02}/\text{C}$.

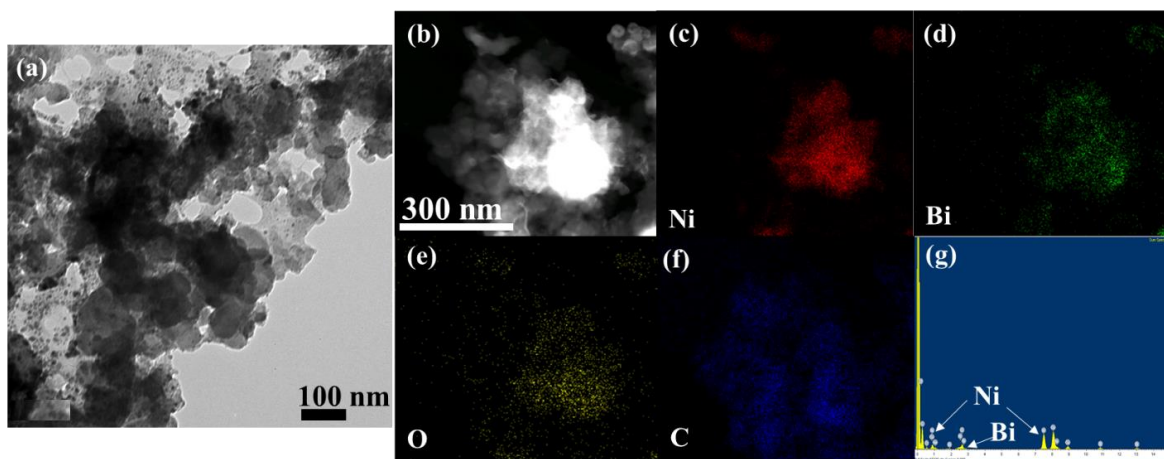


Figure F10. (a) TEM image of $\text{Ni}_{95}\text{Bi}_5/\text{C}$, (b) Dark Field-STEM image, EDS mapping of (c) Ni, (d) Bi, (e) O and (f) C. (g) EDS spectrum of $\text{Ni}_{0.95}\text{Bi}_{0.05}/\text{C}$.

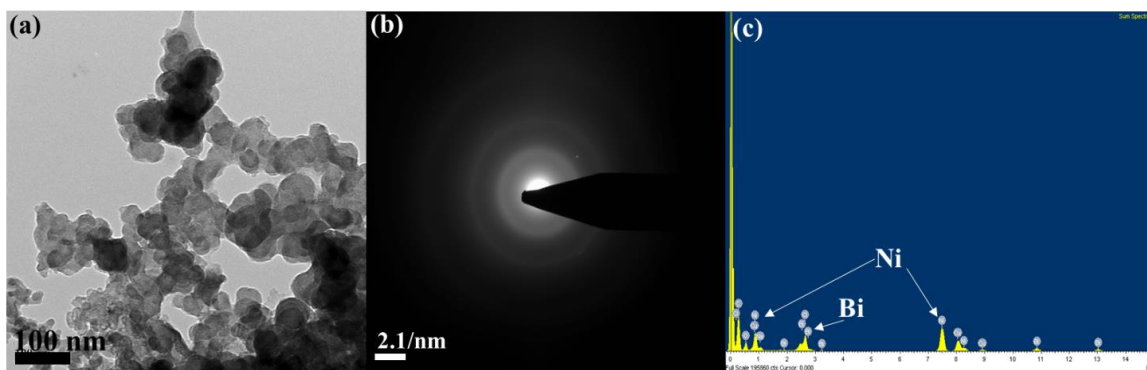


Figure F11. (a) TEM image, (b) SAED patterns and (c) EDS spectrum of $\text{Ni}_{0.9}\text{Bi}_{0.1}/\text{C}$.

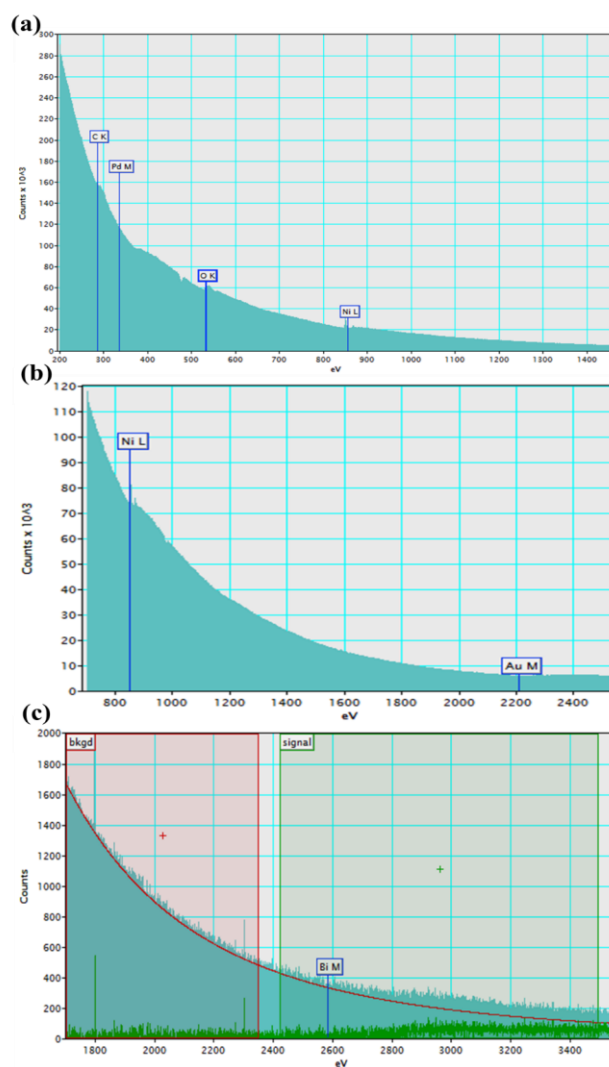
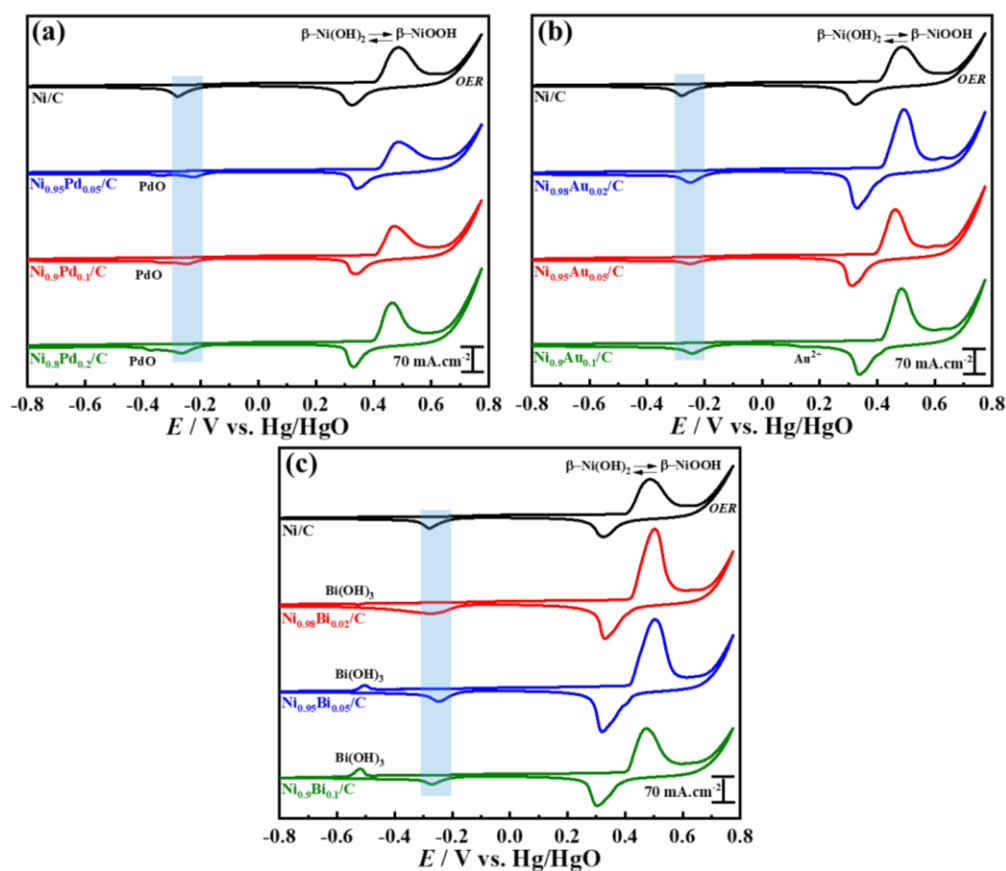


Figure F12. (a) EELS spectra obtained at high spatial resolution of a) $\text{Ni}_{0.8}\text{Pd}_{0.2}/\text{C}$ b) $\text{Ni}_{0.9}\text{Au}_{0.1}/\text{C}$ and c) $\text{Ni}_{0.9}\text{Bi}_{0.1}/\text{C}$.

Table F1. Summary of XPS spectra of Ni 2p of Ni_xM_{1-x}/C (M = Pd, Au and Bi) catalysts.

Materials	Binding Energy (eV)			
	Ni 2p _{3/2}	Ni 2p _{3/2} (s)	Ni 2p _{1/2}	Ni 2p _{1/2} (s)
Ni/C	856.2	861.9	874.1	880.1
Ni _{0.8} Pd _{0.2} /C	856.5	862.5	874.5	880.9
Ni _{0.9} Au _{0.1} /C	856	861.6	873.7	879.93
Ni _{0.9} Bi _{0.1} /C	856.1	861.9	873.9	880.2

**Figure F13.** Cyclic voltammograms of Ni_xM_{1-x}/C (M = Pd, Au and Bi) catalysts in N₂-purged 1.0 M KOH: (a) Ni_xPd_{1-x}/C, (b) Ni_xAu_{1-x}/C and (c) Ni_xBi_{1-x}/C at 0.05 V s⁻¹ scan rate and 293 K (5th stable cycle).

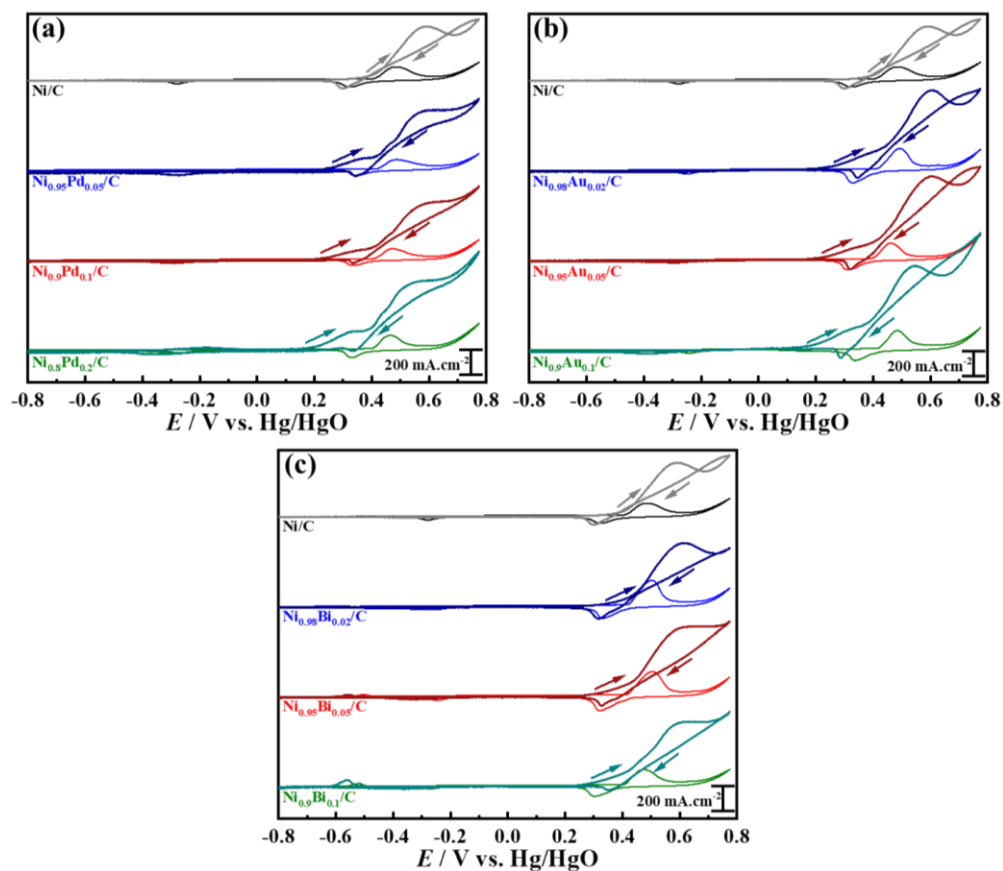


Figure F14. Cyclic voltammograms of $\text{Ni}_x\text{M}_{1-x}/\text{C}$ ($\text{M} = \text{Pd}, \text{Au}$ and Bi) catalysts in N_2 -purged 1.0 M KOH (thin line) and in 1.0 M KOH+ 0.1 M glycerol (bold line): (a) $\text{Ni}_x\text{Pd}_{1-x}/\text{C}$, (b) $\text{Ni}_x\text{Au}_{1-x}/\text{C}$ and (c) $\text{Ni}_x\text{Bi}_{1-x}/\text{C}$ at 0.05 V s^{-1} scan rate and 293 K (5th stable cycle).

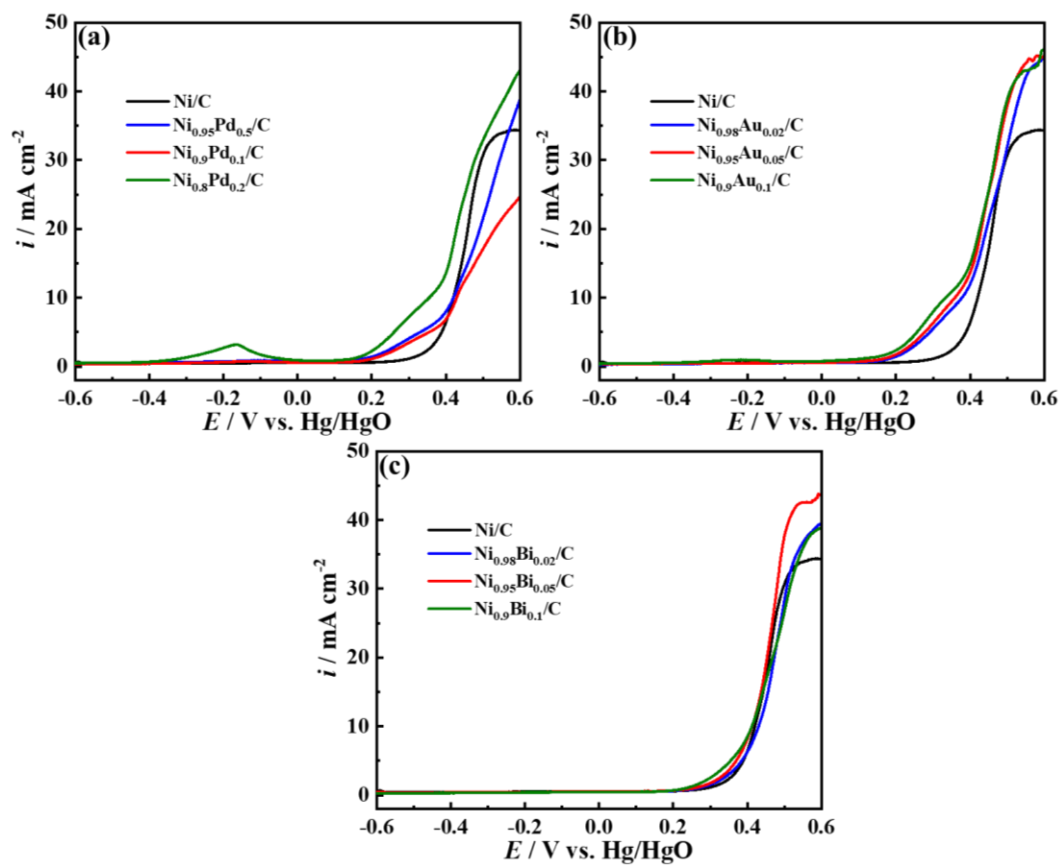


Figure F15. LSVs of $\text{Ni}_x\text{M}_{1-x}/\text{C}$ ($\text{M} = \text{Pd}, \text{Au}$ and Bi) catalysts in N_2 -purged 1.0 M KOH + 0.1 M glycerol electrolyte: (a) $\text{Ni}_x\text{Pd}_{1-x}/\text{C}$, (b) $\text{Ni}_x\text{Au}_{1-x}/\text{C}$ and (c) $\text{Ni}_x\text{Bi}_{1-x}/\text{C}$ at 0.001 V s^{-1} scan rate and 293 K.

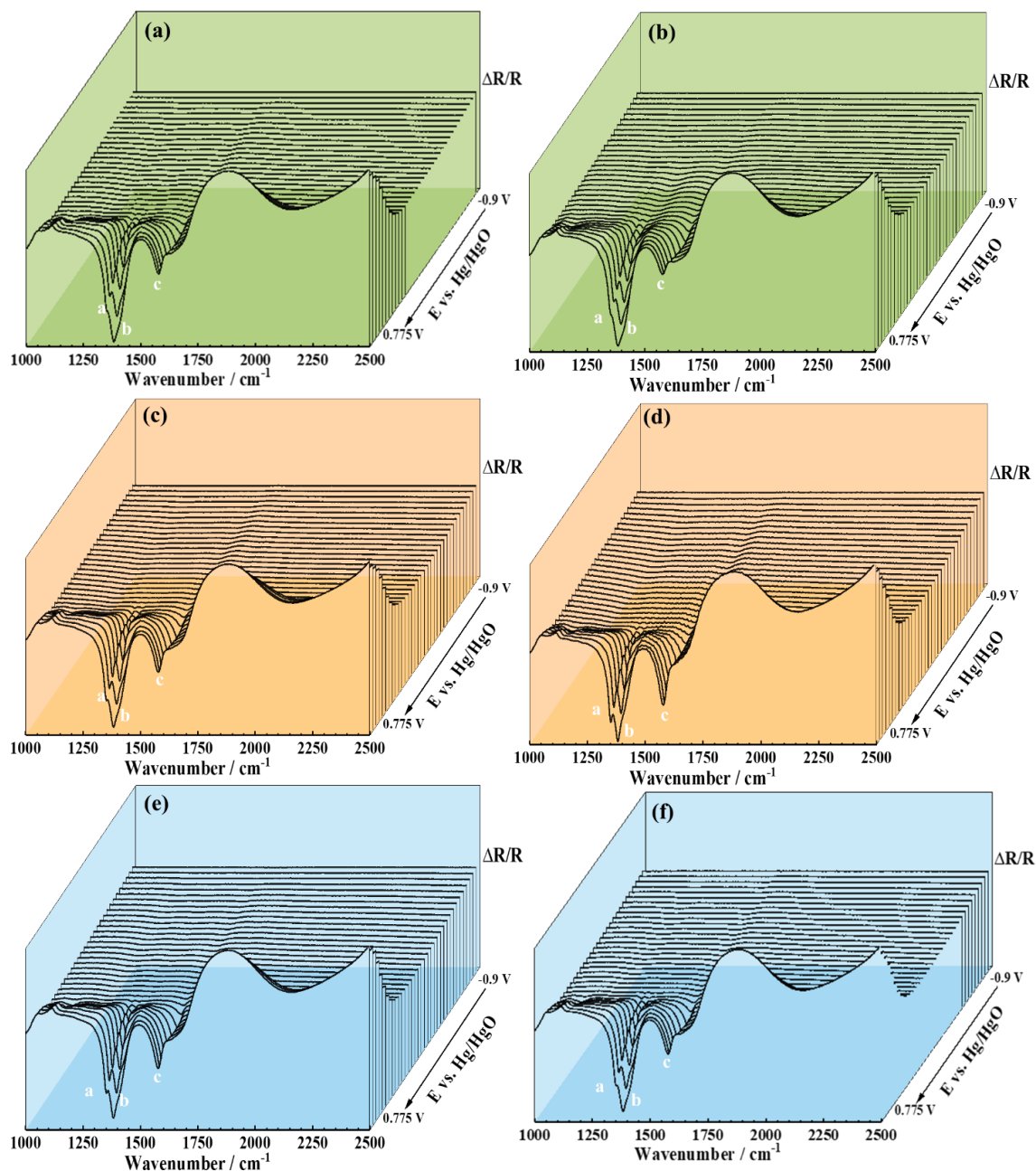


Figure F16. Infrared spectra recorded during GEOR on (a) Ni_{0.95}Pd_{0.05}/C, (b) Ni_{0.9}Pd_{0.1}/C, (c) Ni_{0.988}Au_{0.02}/C, (d) Ni_{0.95}Au_{0.05}/C, (e) Ni_{0.98}Bi_{0.02}/C and (f) Ni_{0.95}Bi_{0.05}/C catalysts in 1.0 M KOH + 0.1 M glycerol electrolyte at 293 K. Scan rate: 0.001 V s⁻¹, resolution 4 cm⁻¹.

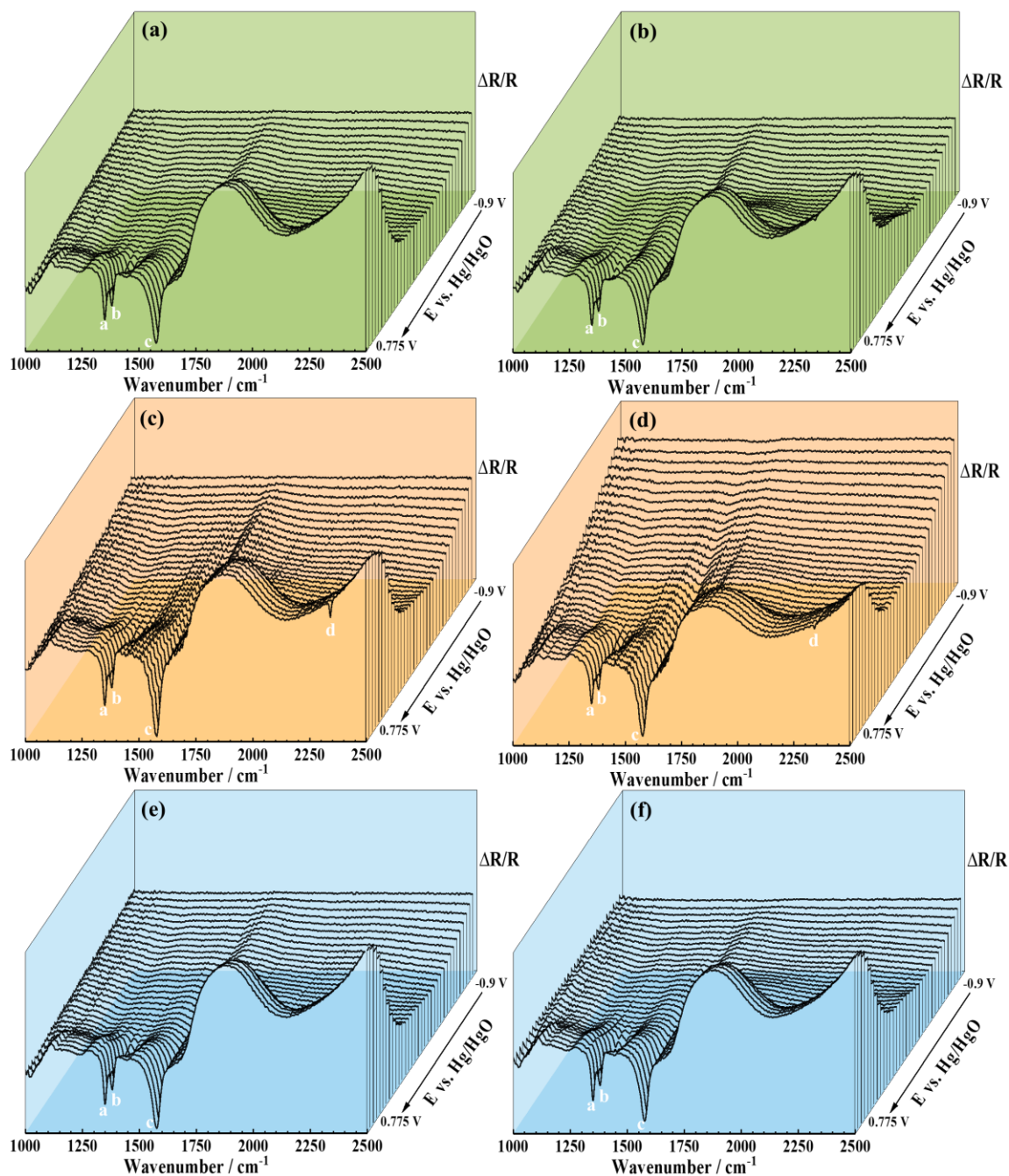


Figure F17. Infrared spectra recorded during GEOR on (a) $\text{Ni}_{0.95}\text{Pd}_{0.05}/\text{C}$, (b) $\text{Ni}_{0.9}\text{Pd}_{0.1}/\text{C}$, (c) $\text{Ni}_{0.988}\text{Au}_{0.02}/\text{C}$, (d) $\text{Ni}_{0.95}\text{Au}_{0.05}/\text{C}$, (e) $\text{Ni}_{0.98}\text{Bi}_{0.02}/\text{C}$ and (f) $\text{Ni}_{0.95}\text{Bi}_{0.05}/\text{C}$ catalysts in 0.1 M KOH + 0.1 M glycerol electrolyte at 293 K. Scan rate: 0.001 V s^{-1} , resolution 4 cm^{-1} .

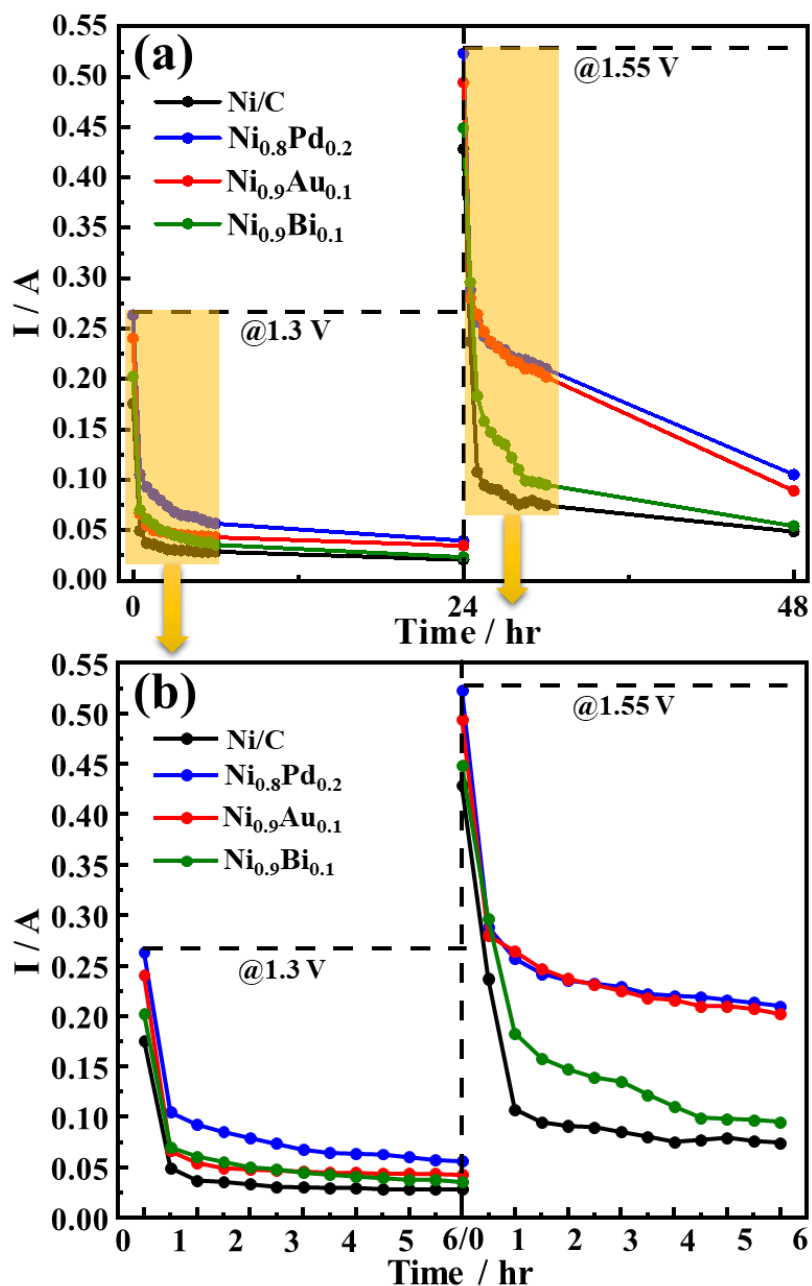


Figure F18. CA curves at +1.3 and +1.55 V in the 25 cm² electrolysis cell for glycerol electrooxidation on different carbon supported Ni-based catalysts in 1.0 M KOH + 0.1 M glycerol electrolyte at 293 K.

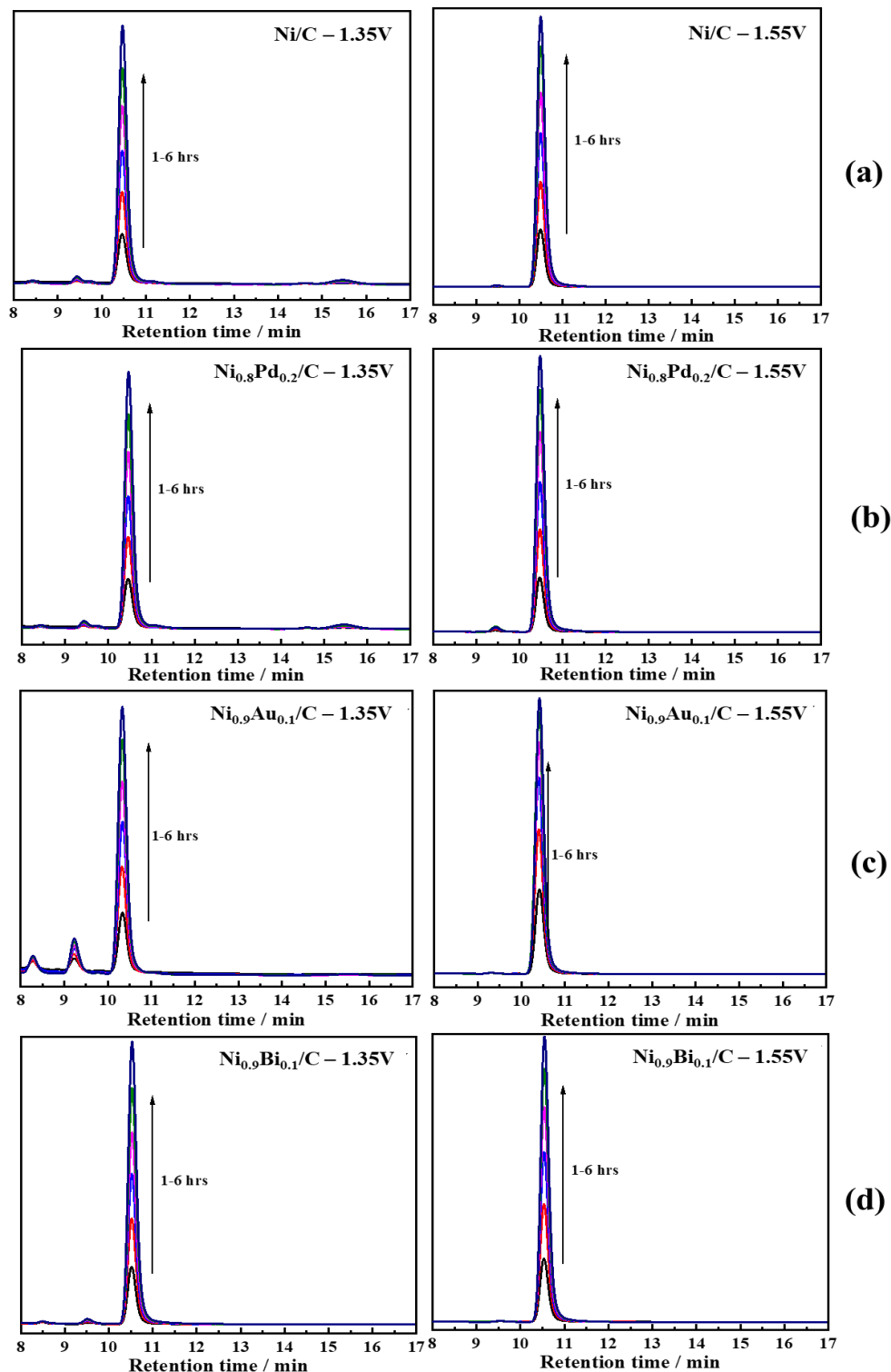


Figure F19. HPLC measurements recorded as function of time during electrolysis in 1.0 M KOH + 0.1 M glycerol solution at two different applied potentials. (a) Ni/C, (b) Ni_{0.8}Pd_{0.2}/C, (b) Ni_{0.9}Au_{0.1}/C and (c) Ni_{0.9}Bi_{0.1}/C.

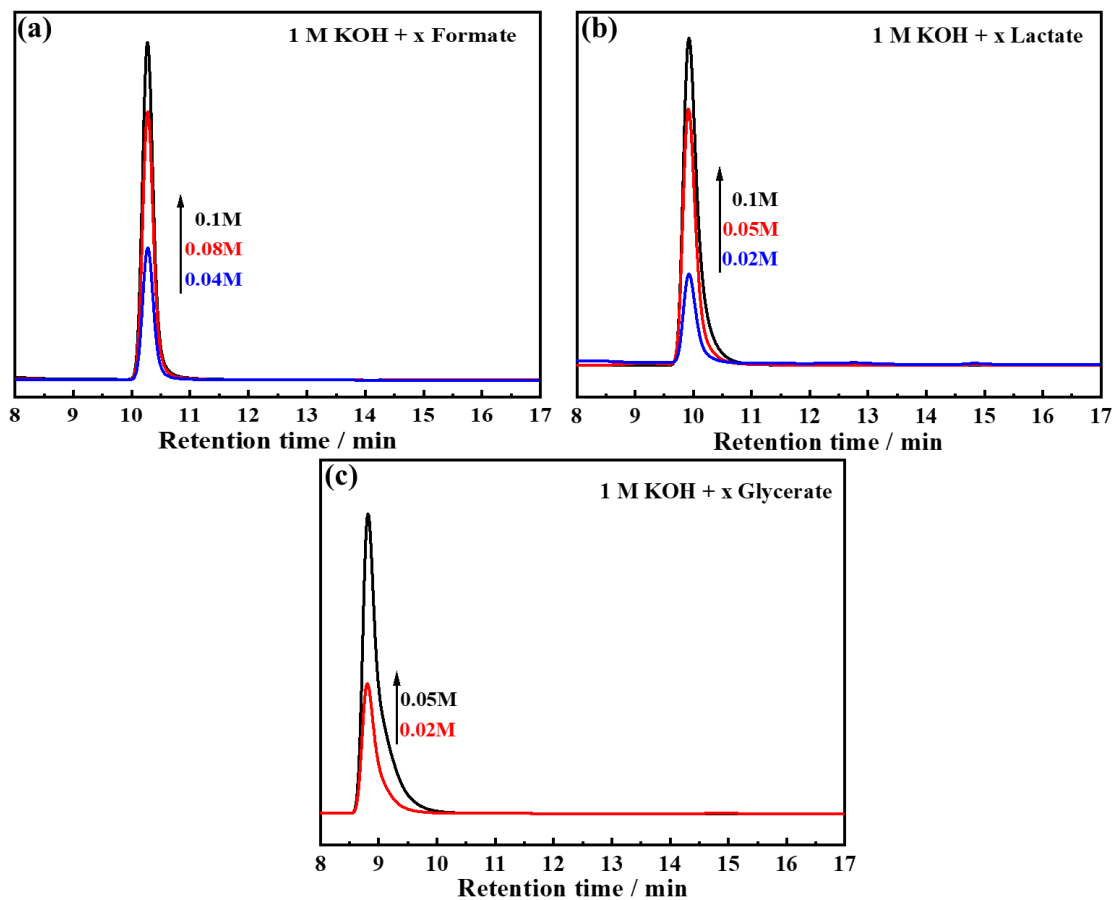


Figure F20. HPLC measurements for standard solution of formate, lactate and glycerate in 1.0 M KOH electrolyte.

Table F2. Calculations of the glycerol conversion and formate selectivity using electrolysis and HPLC data.

Ni/C												
Time (h)	Q _{Elec} (A.h)		C _{Formate,Exp} (mol. L ⁻¹)		C _{Formate,Theor} (mol. L ⁻¹)		η_F (%)		C _{Glycerol} (mol. L ⁻¹)		X _{Glycerol} (%)	
	1.3V	1.55V	1.3V	1.55V	1.3V	1.55V	1.3V	1.55V	1.3V	1.55V	1.3V	1.55V
1	0.0684	0.2474	0.0083	0.0242	0.0114	0.0385	73.1	62.9	0.0972	0.0919	2.8	8.1
2	0.104	0.3437	0.0143	0.0409	0.0173	0.0534	82.5	76.5	0.0952	0.0864	4.8	13.6
3	0.1352	0.4330	0.0200	0.0624	0.0225	0.0673	89	92.6	0.0933	0.0792	6.7	20.8
4	0.1651	0.5134	0.0251	0.0777	0.0275	0.0798	91.3	97.3	0.0916	0.0741	8.4	25.9
5	0.1939	0.5908	0.0307	0.0854	0.0323	0.0918	95	93	0.0898	0.0715	10.2	28.5
6	0.2223	0.6672	0.0352	0.0981	0.0370	0.1037	95.2	94.5	0.0883	0.0673	11.7	32.7
Ni _{0.8} Pd _{0.2} /C												
1	0.1294	0.3220	0.0127	0.0445	0.0189	0.0501	67.1	89	0.0958	0.0852	4.2	14.8
2	0.2152	0.5651	0.0230	0.0826	0.0314	0.0879	73.5	94	0.0923	0.0725	7.7	27.5
3	0.2889	0.7972	0.0322	0.1200	0.0421	0.1239	76.45	96.8	0.0893	0.0600	10.7	40
4	0.3542	1.0201	0.0441	0.1591	0.0516	0.1586	85.3	100	0.0853	0.0470	14.7	53.1
5	0.4171	1.2390	0.0534	0.1926	0.0608	0.1926	87.9	100	0.0822	0.0358	17.8	64.2
6	0.4751	1.4523	0.0634	0.2194	0.0692	0.2258	91.5	98	0.0789	0.0269	21.1	73.1
Ni _{0.9} Au _{0.1} /C												
1	0.0935	0.3133	0.0110	0.0412	0.0145	0.0471	75.4	87.3	0.0963	0.0863	3.7	13.7
2	0.1440	0.5616	0.0188	0.0741	0.0292	0.0845	64.3	87.7	0.0937	0.0753	6.3	24.7
3	0.1914	0.7931	0.0280	0.1089	0.0388	0.1193	72	91.2	0.0907	0.0637	9.3	36.3
4	0.2367	1.0123	0.0364	0.1369	0.0480	0.1523	75.9	89.9	0.0879	0.0544	12.1	45.6
5	0.2809	1.2231	0.0453	0.1687	0.0570	0.1840	79.5	91.7	0.0849	0.0438	15.1	56.2
6	0.3246	1.4299	0.0546	0.1894	0.0658	0.2151	83	88.1	0.0818	0.0369	18.2	63.1
Ni _{0.9} Bi _{0.1} /C												
1	0.0906	0.3027	0.0097	0.0342	0.0141	0.0471	69	72.7	0.0968	0.0886	3.2	11.4
2	0.1462	0.4630	0.0198	0.0607	0.0227	0.0720	87	84.3	0.0934	0.0798	6.6	20.2
3	0.1944	0.6027	0.0270	0.0857	0.0302	0.0937	89.4	91.5	0.0910	0.0714	9	28.6
4	0.2374	0.7248	0.0338	0.1043	0.0369	0.1127	91.5	92.6	0.0887	0.0652	11.3	34.8
5	0.2769	0.8255	0.0405	0.1184	0.0430	0.1283	94.1	92.2	0.0865	0.0605	13.5	39.5
6	0.3145	0.9223	0.0469	0.1399	0.0489	0.1434	95.8	97.6	0.0844	0.0534	15.6	46.6

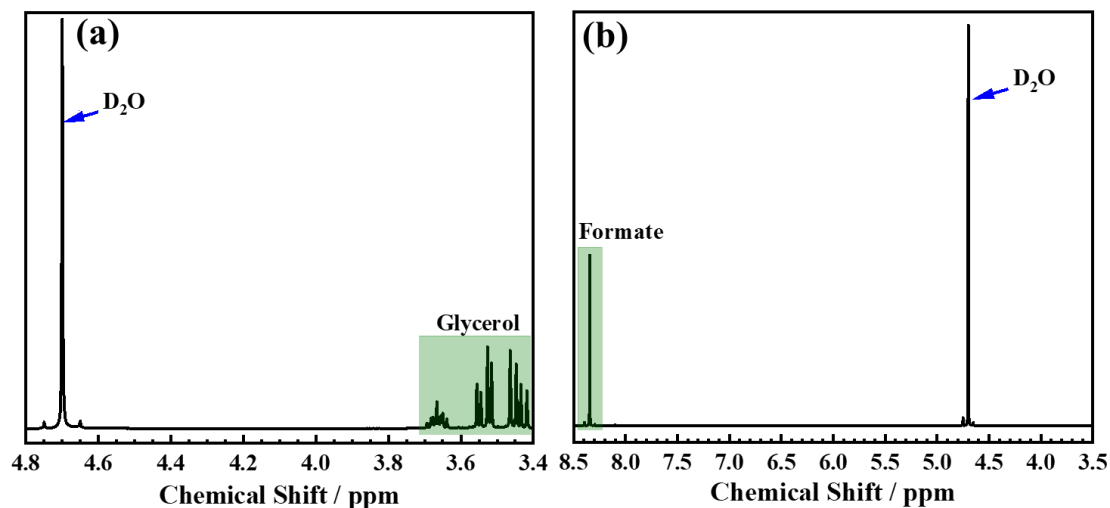


Figure F21. ^1H NMR spectra of (a) 1.0 M KOH + 0.1 M glycerol and (b) 1.0 M KOH + 0.1 M formate solutions after neutralization with HCl, lyophilization and dissolution into D_2O . The spectra correspond to initial solution before 24 hrs electrolysis.

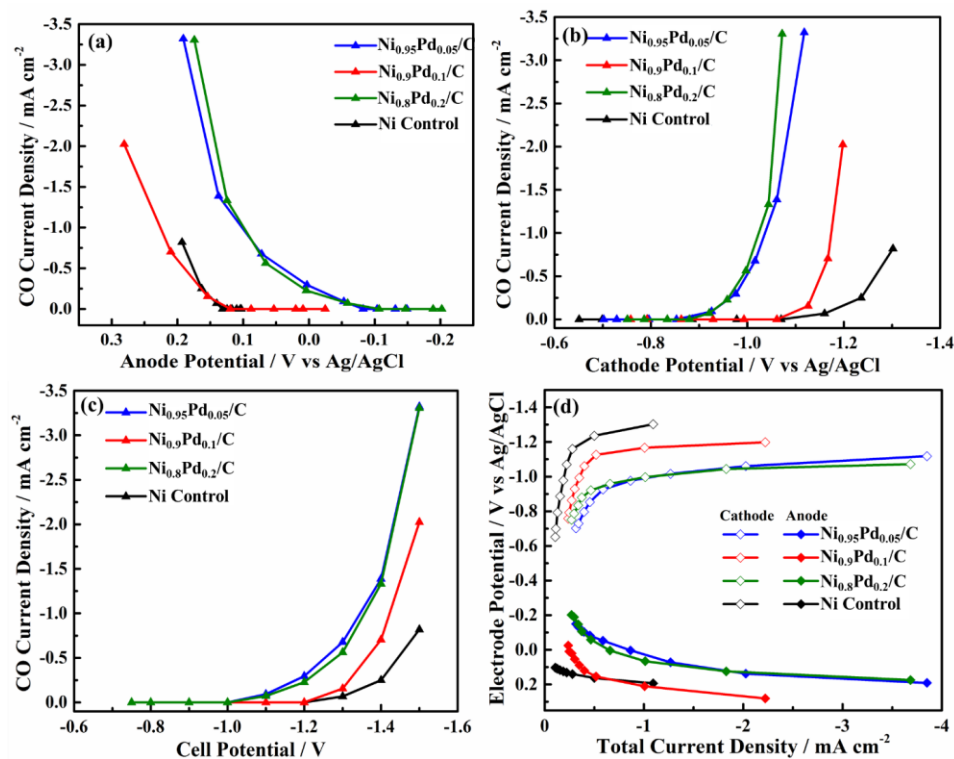


Figure F22. The co-electrolysis performance of $\text{Ni}_x\text{Pd}_{1-x}/\text{C}$ in 2.0 M KOH + 2.0 M glycerol electrolyte.

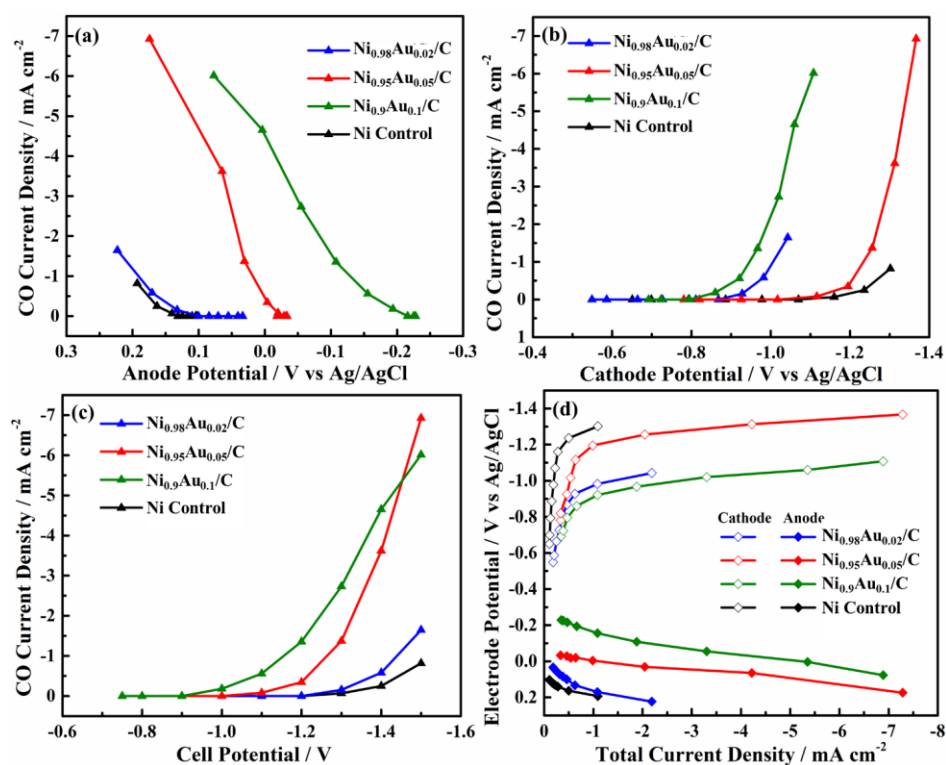


Figure F23. The co-electrolysis performance of $\text{Ni}_x\text{Au}_{1-x}/\text{C}$ in 2.0 M KOH + 2.0 M glycerol electrolyte.

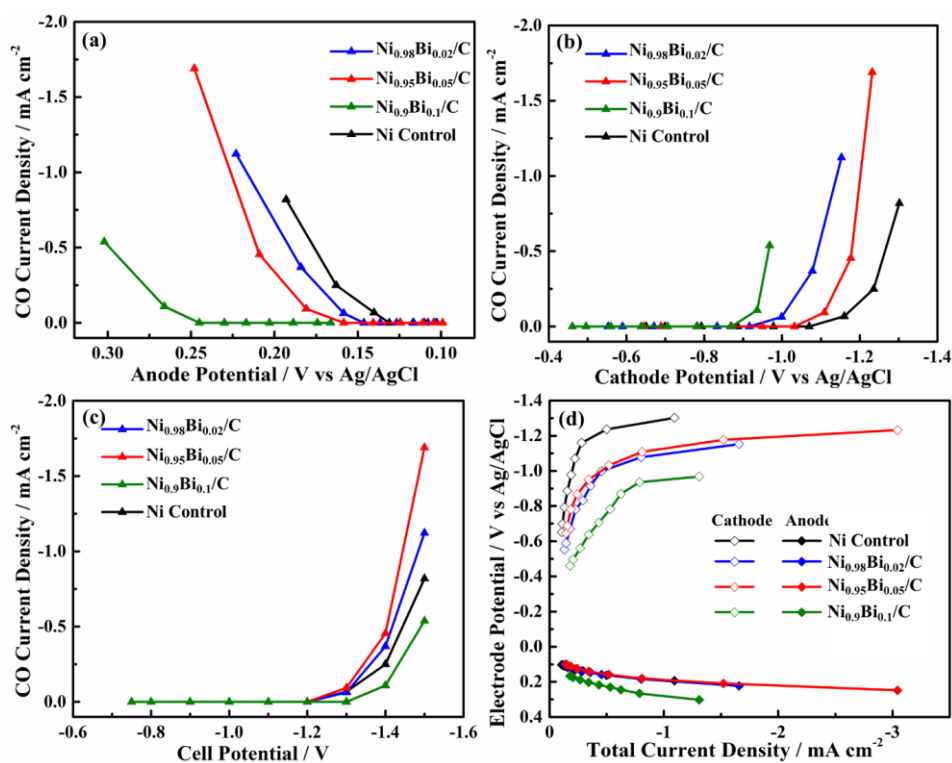


Figure F24. The co-electrolysis performance of $\text{Ni}_x\text{Bi}_{1-x}/\text{C}$ in 2.0 M KOH + 2.0 M glycerol electrolyte.

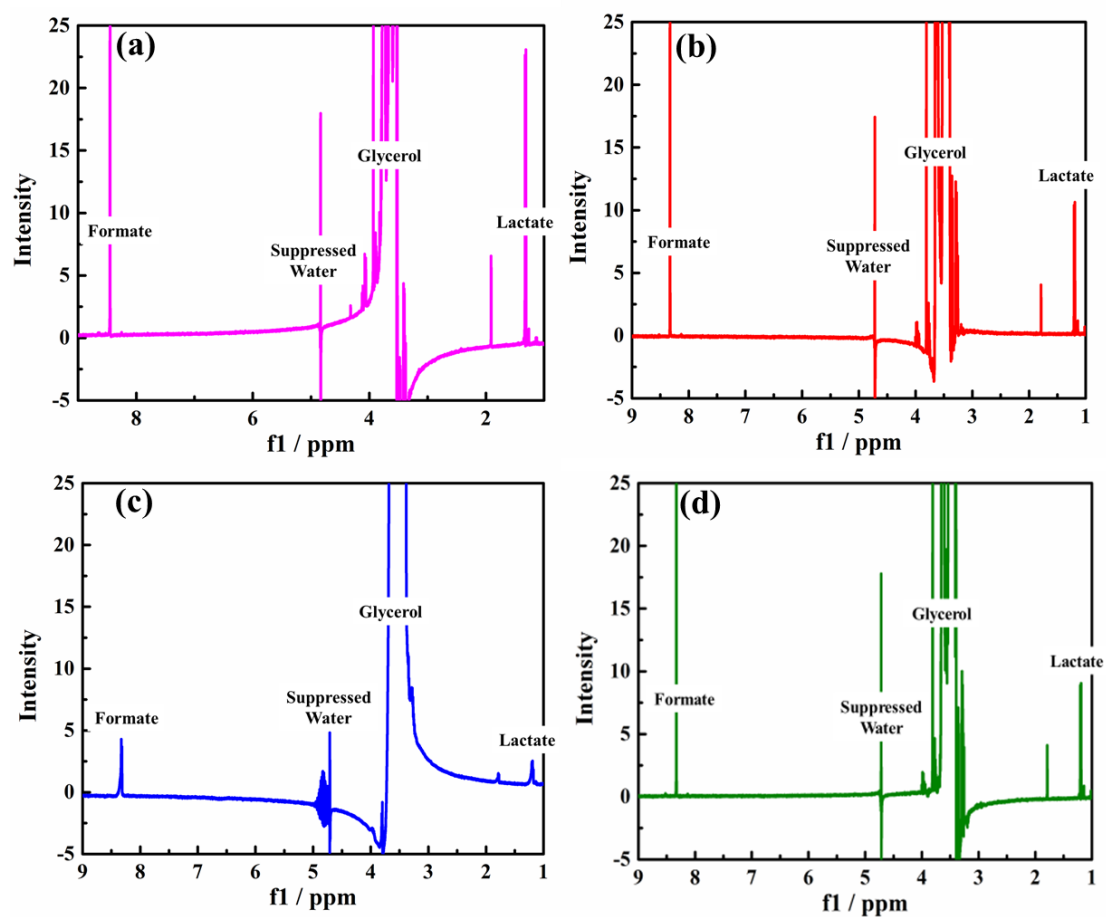


Figure F25. ^1H NMR spectra of 2.0 M KOH + 2.0 M glycerol solution at -1.5 V cell potential on a) Pt, b) $\text{Ni}_{0.9}\text{Au}_{0.1}/\text{C}$ c) $\text{Ni}_{0.95}\text{Pd}_{0.05}/\text{C}$ and (d) $\text{Ni}_{0.95}\text{Bi}_{0.05}/\text{C}$.

Chapter 9

9 Conclusions and Recommendations

9.1 Conclusions

The strategy for the modification of polycrystalline Ni surface for increased catalytic activity toward the GEOR was seen to work as expected in chapter 3. The electrochemical method that governs a sinusoidal-wave potential resulted in a 6-folds increase in electrochemical surface area and nine times enhanced catalytic activity during chronoamperometric measurements. This is the first ever electrochemical treatment exploiting the slow place-exchange process to create a good dispersion of sites for GEOR on polycrystalline Ni.

In chapter 4, a unique study involving direct visualization of Ni structural transformations to Ni hydroxides using various electron microscopies for different shapes of freestanding Ni microstructures. However, the product distributions were similar during GEOR for all three different shapes of Ni materials. This was based on the identification of surface and bulk solution species by *in-situ* PM-IRRAS technique. Furthermore, DFT calculation demonstrated that the (001) surface was the most thermodynamically stable for both β -Ni(OH)₂ and β -NiOOH structures. While, the β -NiOOH (001) with Ni atom exposed on the outmost layer was more reactive with an ϵ_d closer to the Fermi level; thus, a suitable candidate for glycerol electrooxidation.

In chapter 5, core double-shell Ni_xPd_{1-x} nanoparticles were synthesized with highly dispersed Pd atoms on the Ni shell. This configuration resulted in increasing the mass activity of GEOR at lower overpotentials due to both Ni and Pd synergetic effect and Ni_xPd_{1-x} smaller particle sizes. In addition, PM-IRRAS showed that the main reaction products on Ni_xPd_{1-x} (x = 100 – 80 at.%) led to a similar selectivity towards glyceraldehyde, carbonyl groups for mesoxalate and tartronate ions, carboxylate ions and traces of carbon dioxide.

In chapter 6, we investigated for the first-time an inexpensive Bi to Ni-nanostructured catalysts (Ni_xBi_{1-x}, x = 100 – 90 at. %) for selective oxidation of glycerol to C3 and C2 products (glycerate, tartronate and oxalate). Addition of small quantities of Bi adatom (≤ 10 at.%) has shown positive effects on catalytic performance and catalyst stability. This is mainly attributed to the Ni-Bi double shell-core structure, which includes highly dispersed Bi clusters on the outer Ni shell, affecting the formation of the Ni³⁺ phase.

Furthermore, the effect of aging was also investigated, showcasing a higher mass activity ($\times 2$) after two weeks due to structural shape modification. Whereas HPLC analysis reveals that Bi adatom actively influences the reaction products by suppressing the pathways with C–C bond cleavage, hindering the production of formate and improving the production of tartronate, oxalate and glycerate at different applied potential and temperature.

In chapter 7, we synthesised bi-metallic Pd@Ni and Au@Ni core-shell like NPs by the heatless NaBH₄ co-reduction method, which could be easily scaled up. The addition of Pd and Au was capable of promoting the activity of Ni due to synergistic and electronic effects between the bi-phases of Ni-Pd and Ni-Au. Among different electrocatalyst, Ni₈₀Pd₂₀ displayed the highest current densities of 543 A.g⁻¹_{Ni}, which were $\sim 4.5\times$ and $2.5\times$ higher than spherical Ni and previously synthesised Ni₈₀Pd₂₀ (chapter 5), respectively. Notably, our DFT calculations matched the experimental results, showing that Pd@Ni NP is the most stable and reactive system compared to Au@Ni and monometallic Ni systems as demonstrated by the excess energy, strain, electronic structure, Bader charge and work function. In addition, Ni-rich bi-metallic catalysts generated better selectivity to C₃ products in the GEOR electrolysis system.

In chapter 8, we studied carbon supported Ni_xM_{1-x} (M = Bi, Pd and Au) nanomaterials with different atomic ratios (M atomic ratio $\leq 20\%$) for GEOR with Pt/C and commercial Ag NPs for cathodic H₂ production and CO₂ electro-reduction, respectively. Addition of small quantities of second metal (≤ 20 at.%) has shown positive effects on catalytic performance and catalyst stability, generating 100% selectivity towards formate with 100% conversion. Among different materials, the Ni₉₀Au₁₀/C electrocatalyst displayed the highest current density, reaching 46 mA.cm⁻² with a concurrent onset potential at $\sim +0.12$ V vs. Hg/HgO, which is approximately 190, 290 and 370 mV lower than Ni/C, unsupported Ni (chapter 4) and bulk Ni (chapter 3), respectively. Similarly, co-electrolysis of CO₂ and glycerol process showed that Ni₉₀Au₁₀/C catalyst attained the highest partial current density for CO and the lowest onset cell potential. This chapter was a pioneer in showing 100% selective oxidation of glycerol and combining glycerol and CO₂ valorization using Ni-rich materials.

9.2 Recommendations

Despite the relative success of the research presented in this thesis, there remains a significant amount of both experimental and theoretical work that can be done. These will be presented as several recommendations for future work in this section.

- Firstly, the transition to synthesizing and analyzing bimetallic noble/non-noble catalysts must be continued. A synergetic effect in combining noble/non-noble metals was found to be better than using mono-metallic Ni. Therefore, new studies could be performed on the influence of the size and shape of Ni, NiBi, NiAu, NiPt and Ni(OH)₂ particles on their activity towards the GEOR. Similar research could be performed on the stability, durability and product selectivity of these nanomaterials in relation to the composition and concentration of aqueous electrolytes.
- Throughout this research, one of the most interesting findings was the effect of metal-support on product selectivity. In the case of GEOR, the activity, overpotential and selectivity towards the partial oxidation product was greatly improved by supporting Ni-rich catalysts on carbon. Therefore, it is worthwhile to screen other metal-support interaction experiments, special consideration to be given to 3D and/or mesoporous materials such metal-organic-frameworks (MOFs) and metal oxides, such as cerium oxide (CeO₂), titanium dioxide (TiO₂) and tin oxide (SnO₂).
- pH and concentration effects are the most important factors that should be considered in future studies. Our preliminary experiments (chapter 3, 4 and 5) have shown that there is an optimum concentration where the highest current can be achieved, higher concentrations than the optimum value led to surface deactivation due to surface blockage by adsorbed glycerol. The effect of pH and proton or hydroxide diffusion on nickel hydroxide and oxyhydroxide formation will provide more information on the mechanism and its changes in different environments. In addition, buffer and ionic liquids usage are also recommended for further study in order to solve the issue of the changing pH in the double layer during GEOR. The consideration for ionic liquids is expected to improve the reaction selectivity by mitigating the issue of carbonate precipitation which occurs as a result of the reaction between CO₂ and KOH.
- It is evident that a range of analytical tools (PM-IRRAS, HPLC, NMR and XPS) should be the standard complementary techniques in future studies, since they capture the complete details of the reaction mechanism. Raman spectroscopy is also

recommended in order to study the formation and reduction of surface oxides in the sub-monolayer and monolayer regions.

- When it comes to theoretical modeling of GEOR process, it will be interesting to study further the case of glycerol electrooxidation on surface oxides, mono- and bi-metallic. DFT insights will provide valuable information of the elementary reaction steps and kinetic parameters, required to pave the way for the rational design of selective and stable catalysts.
- Finally, an ideal future objective in bio-refineries would be crude glycerol transformation, which contains impurities such as NaOH, methanol, residual heterogenous or homogeneous catalysts and other salts. It will be an enormous step forward to find stable and active electro-catalysts which can catalyze the crude glycerol reaction and be utilised in the industry. However, this approach is scarcely investigated and only a few studies that address this issue are currently available in the literature. Evading the purification process of crude glycerol and its direct usage to generate value-added chemicals might be a promising approach to make the biodiesel production economically-feasible. Although great advancements have been and will continue to be made on the fundamental aspects of GEOR, researchers could tackle the crude glycerol purification process to develop the most economically and practically efficient processes.

Appendix

Scholarly Contributions

Publications

1. **Houache M. S. E.**, Safari R., Uzoma O. N., Thibault R., Botton G. A., Paul J. A. K., Baranton S., Coutanceau C., Baranova E. A., (2020), *Selective Electrooxidation of glycerol to Formic acid over Carbon Supported $Ni_{1-x}M_x$ ($M = Bi, Pd$ and Au) Nano-catalysts and Co-Electrolysis*. ACS Appl. Energy Mater. 3(9), 8725-8738. (IF = 4.473)
2. Cossar E., **Houache M. S. E.**, Zhang Z., Baranova E. A., (2020), *Comparison of Electrochemical Active Surface Area Methods for Various Ni Nanostructures*. J. Electroanal. Chem. 870, 114246. (IF = 3.218)
3. Lamsal R., **Houache M. S. E.**, Williams A., Baranova E. A., Jerkiewicz G., Beauchemin D., (2020), *Single Particle Inductively Coupled Plasma Mass Spectrometry with and without Flow Injection for the Characterization of Nickel Nanoparticles*. Analytica Chimica Acta. (IF = 5.256)
4. **Houache M. S. E.**, Hughes K., Safari R., Botton G. A., Baranova E. A., (2020), *Modification of Nickel Surfaces by Bismuth: Effect on Electrochemical Activity and Selectivity towards glycerol*, ACS Applied Materials & Interfaces, 12(13), 15095-15107 (IF = 8.46)
5. **Houache M. S. E.**, Hughes K., Ahmed A., Safari R., Liu H., Botton G. A., Baranova E. A., (2019), *Electrochemical Valorization of Glycerol on Ni-rich Bimetallic NiPd Nanoparticles: Insight into product selectivity using in-situ PM-IRRAS*, ACS Sustain. Chem. Eng., 7(17), 14425-14434. (IF = 6.97)
6. Hajar Y. M., Venkatesh B., **Houache M. S. E.**, Liu H., Safari R., Prabhudev S., Botton G. A., Baranova E. A., (2019), *Electrochemical promotion of Bi-metallic Ni9Pd core double-shell nanoparticles for complete methane oxidation*. Journal of Catalysis, 374, 127-135. (IF = 7.723)
7. **Houache M. S. E.**, Hughes K., Baranova E. A., (2019), *Study on catalyst selection for electrochemical valorization of glycerol*. Sustainable Energy & Fuels, 3, 1892-1915. (IF = 4.912)
8. **Houache M.S.E.**, Cossar E., Ntais S., Baranova E.A., (2018), *Electrochemical Modification of Nickel Surfaces for Efficient Glycerol Electro-oxidation*. Journal of Power Sources, 375, 310-319. (IF = 7.467)
9. Hajar Y. M., **Houache, M.S.E.**, Tariq U., Vernoux P., Baranova E. A., (2017), *Nanoscope Ni Interfaced with Oxygen Conductive Supports: Link between Electrochemical and Catalytic Studies*. ECS Transactions, 77(10), 51-66. (IF = 0.47)

In preparation

10. **Houache M. S. E.**, Shubair A., Sandoval M.G, Safari R., Jasen P.V., González E. A., Botton G. A., Baranova E. A., (2020), *Influence of Pd and Au on electrochemical valorization of glycerol over Ni-rich surfaces*. (In preparation).
11. **Houache M. S. E.**, Sandoval M.G., Safari R., F. Gaztañaga, Escudero F., Hernández-Laguna A., Sainz-Díaz C.I., Botton G. A., Jasen P.V., González E. A., A. Juan, Baranova E. A., (2020), *Glycerol Morphology Alteration of Nickel Microstructures for Glycerol Electrooxidation*. (In preparation)

Conferences and meetings

1. **Houache M. S. E***, Shubair A., Hughes K., Safari R., Botton G. A., Baranova E. A., (2020) *Electrochemical Modification of Ni-Rich Bimetallic $Ni_{1-x}M_x$ ($M= Bi, Pd$ and Au) Nanoparticles for Glycerol Electro-Oxidation in Alkaline Media*. **Oral presentation** at 237th ECS with the 18th International Meeting on Chemical Sensors IMCS May 10-14th, Montreal, Canada. (Accepted abstract – Cancelled due to COVID-19)
2. Shubair A., **Houache M.S.E***, Baranova E.A., (2019) *Carbon Supported Nickel-Bismuth Catalyst for the Selective Electrooxidation of Low-grade Glycerol to Value-added Chemicals*. **Oral presentation** at 69th Canadian Chemical Engineering Conference, Oct 21st, Halifax, Nova Scotia, Canada.
3. **Houache M.S.E.*** (2019) *Electrochemical Valorization of Glycerol on Ni-rich Bimetallic Nanoparticles: Insight into Activity and Product Selectivity*. **Oral presentation (Keynote)** at Universidad Nacional del Sur, June 28th, Bahía Blanca, Argentina
4. Lamsal R.P., **Houache M.S.E.***, Baranova E.A., Jerkiewicz G., Beauchemin D., (2019) *Analyse de nanoparticules de nickel par spectrométrie de masse à plasma inductif avec et sans injection en flux continu*. **Oral presentation** at Spectr'Atom, June, Montreal, Canada.
5. Hajar Y.M, Venkatesh B., **Houache M.S.E***, Liu H., Safari R., Botton G., Baranova E.A., (2018) *Non-Faradaic Enhancement of Catalytic Activity of Core/Shell PdNi for complete methane oxidation*. **Oral presentation** at 68th Canadian Chemical Engineering Conference, Oct 31st, Toronto, Ontario, Canada.
6. Cossar E., **Houache M.S.E***, Baranova E.A., (2018) *Comparison of Electrochemical Active Surface Area Methods for Various Ni Nanostructures*. **Oral presentation** at 68th Canadian Chemical Engineering Conference, Oct 30th, Toronto, Ontario, Canada.
7. **Houache M.S.E***, Hughes K. A., Ahmed A., Safari R., Botton G., Baranova E. A., (2018) *Nanostructured Ni and Ni-Pd Catalysts for Glycerol Electro-Oxidation in Alkaline Media*. **Oral presentation** at ECS and SMEQ Joint International Meeting, Oct 1st, Cancun, Mexico.

8. **Houache M.S.E***, Hughes K. A., Ahmed A., Baranova E. A., (2018) *Electrochemical Valorization of Glycerol on Bimetallic Nickel-Rich Nanoparticles: The Role of Pd and Bi on Product Selectivity*. **Oral presentation** at 9th Annual Meeting of the International Society of Electrochemistry, Sept 2nd, Bologna, Italy.
9. **Houache M.S.E.***, (2018) *Investigation of glycerol electro-oxidation reaction on Ni-based nano-catalysts using in-situ PM-IRRAS technique*. **Oral presentation** at East coast spring 2018 NiElectroCan Symposium, INRS, April 27th, Montreal, Québec, Canada.
10. Lamsal R.P., **Houache M.S.E.***, Baranova E.A., Beauchemin D., Jerkiewicz G., (2018) Single Particle Inductively Coupled plasma Mass Spectroscopy Method for the Characterization of metallic nanoparticles for Fuel Cell Applications. **Oral presentation** at winter conference on plasma spectrochemistry, January 11th, Amelia Island, Florida, USA.
11. **Houache M.S.E.***, Cossar E., Baranova E.A., (2017) Electrochemical modification of nickel electrode for glycerol electro-oxidation. **Oral presentation** at the 68th annual meeting of the international society of electrochemistry, August 29th, Providence, RI, USA.
12. **Houache M.S.E.*** (2017) *Glycerol electrochemical valorization using Ni based catalyst*. **Oral presentation** in CANOPENER at NTNU, June 20th, Trondheim, Norway.
13. Hajar Y.M, **Houache M.S.E.***, Tariq U., Baranova E.A., (2017) *Nanoscale Ni interfaced with oxygen conductive supports: link between electrochemical and catalytic studies*. **Oral presentation** at 231st ECS meeting, May 28- June 1, New Orleans, USA.
14. **Houache M.S.E.***, Cossar E., Baranova E.A., (2017) *Electrochemical modification of nickel electrode for glycerol electro-oxidation*. **Oral presentation** at the 100th Canadian Chemistry Conference and Exhibition, May 28- June 1, Toronto, Ontario, Canada.
15. **Houache M.S.E.*** (2017) *Insights of Glycerol Electro-oxidation on Ni electrode using Spectro-electrochemical Characterizations*. **Oral presentation** at 5th joint workshop on Engineered Nickel Catalyst for Electrochemical Clean Energy at University of Toronto, May 10th, Toronto, Ontario, Canada.
16. **Houache M.S.E.*** (2016) *Application of Ni-based Catalysts for Glycerol Electro-oxidation*. **Oral presentation** in 3rd joint workshop on Electrocatalysis, Materials Science and Analytical Chemistry of Nickel-Based Materials at Queen's University, December 7th, Kingston, Ontario, Canada.
17. **Houache M.S.E.*** (2016) *Application of Ni-based catalysts for Glycerol electro-oxidation*. **Oral presentation** in 2nd joint workshop on Electrocatalysis, Materials Science and Analytical Chemistry of Nickel-Based Materials at Queen's University, May 25th, Kingston, Ontario, Canada.

Poster presentations

1. **Houache M. S. E***, Hughes K., Safari R., Botton G. A., Baranova E. A., (2019) *Modification of Nickel Surfaces by Bismuth: Effect on Electrochemical Activity and Selectivity towards glycerol*. **Poster presentation** at ECS Canadian Section 2019 Fall Symposium, Queens University, December 19, Kingston, Ontario, Canada.
2. Shubair A., **Houache M. S. E***, Baranova E. A., (2019) *Supported Nickel-Bismuth Catalyst for the Selective Electrooxidation of Glycerol*. **Poster presentation** at ECS Canadian Section 2019 Fall Symposium, Queens University, December 19, Kingston, Ontario, Canada.
3. **Houache M. S. E***, Hughes K., Safari R., Botton G. A., Baranova E. A., (2019) *Modification of Nickel Surfaces by Bismuth: Effect on Electrochemical Activity and Selectivity towards glycerol*. **Poster presentation** at ECS Canadian Section 2019 Fall Symposium, Queens University, December 19, Kingston, Ontario, Canada.
4. Shubair A., **Houache M. S. E***, Baranova E. A., (2019) *Supported Nickel-Bismuth Catalyst for the Selective Electrooxidation of Glycerol*. **Poster presentation** at NSERC Discovery Frontiers: Engineered Nickel Catalysts for Electrochemical Clean Energy, Y4 Annual Review Meeting, Queens University, December 17-18, Kingston, Ontario, Canada.
5. **Houache M.S.E***, Hughes K. A., Ahmed A., Safari R., Botton G., Baranova E. A., (2018) *Tuning Activity and Selectivity of Nano-sized Ni for Glycerol Electro-oxidation: Shape and Pd Addition Effects*. **Poster presentation** at NSERC Discovery Frontiers: Engineered Nickel Catalysts for Electrochemical Clean Energy, Y3 Annual Review Meeting, University of Ottawa, August 14-15, Ottawa, Ontario, Canada.
6. **Houache M.S.E.*** Abdulgadir A., Baranova E.A., (2017) *Preparation of Ultrafine Nickel Nanoparticles and Spectro-electrochemical Characterization towards Glycerol Valorization*. **Poster presentation** at Canadian Section of the ECS Fall Symposium, Queen's University, November 3rd, Kingston, Ontario, Canada.
7. **Houache M.S.E.***, Cossar E., Baranova E.A., (2017) *Electrochemical Modification of Bulk Nickel for Efficient Glycerol Electro oxidation*. **Poster presentation** at Canadian Section of the ECS Fall Symposium, INRS, November 3rd, Kingston, Ontario, Canada.
8. Hajar Y.M., Venkatesh B., **Houache M.S.E.***, Baranova E.A., (2017) *Effect of Electrochemical Promotion of Ni₉₀Pd₁₀ Catalyst on Methane Oxidation*. **Poster presentation** at Canadian Section of the ECS Fall Symposium, Queen's University, November 3rd, Kingston, Ontario, Canada.
9. **Houache M.S.E.*** Abdulgadir A., Baranova E.A., (2017) *Preparation of Ultrafine Nickel Nanoparticles and Spectro-electrochemical Characterization*

towards Glycerol Valorization. **Poster presentation** at NSERC Discovery Frontiers: Engineered Nickel Catalysts for Electrochemical Clean Energy, Simon Fraser University, August 9-10, Vancouver, British Columbia, Canada.

10. **Houache M.S.E.***, Cossar E., Baranova E.A., (2017) *Electrochemical Modification of Bulk Nickel for Efficient Glycerol Electro oxidation*. **Poster presentation** at NSERC Discovery Frontiers: Engineered Nickel Catalysts for Electrochemical Clean Energy, Simon Fraser University, August 9-10, Vancouver, British Columbia, Canada.
11. Lamsal R.P., **Houache M.S.E.*** (2017) *Single Particle Inductively Coupled plasma Mass Spectroscopy Method for the Characterization of NiNPs for Alkaline Fuel Cell Applications*. **Poster presentation** at NSERC Discovery Frontiers: Engineered Nickel Catalysts for Electrochemical Clean Energy, Simon Fraser University, August 9-10, Vancouver, British Columbia, Canada.
12. **Houache M.S.E.*** Abdulgadir A., Baranova E.A., (2017) *Preparation of Ultrafine Nickel Nanoparticles and Spectro-electrochemical Characterization towards Glycerol Valorization*. **Poster presentation** at University of Ottawa, March 30th, Ottawa, Ontario, Canada.
13. **Houache M.S.E.*** Cossar E., Baranova E.A., (2016) *Nickel based electrocatalysts for glycerol electro-oxidation in alkaline media*. **Poster presentation** at Toronto University, August 17th, Toronto, Ontario, Canada.