

**ENGINEERING LOW-COST SPINEL NANO CATALYSTS
FOR SUSTAINABLE GREEN HYDROGEN PRODUCTION
VIA WATER SPLITTING: A DFT SUPPORTED STUDY**

BY

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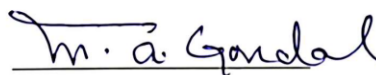
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DEDICATION

To my beloved parents, whose sacrifices and prayers have been the cornerstone of my aspirations; to the devoted faculty, whose knowledge shaped my curiosity into purpose; and to the entire staff of Darul-Hijra Islamic School, whose unwavering support and quiet encouragement laid the foundation of this journey.

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LIST OF ABBREVIATIONS

NECs	:	Nanoelectrocatalysts
DOS	:	Density of States
DFT	:	Density Functional Theory
PDOS	:	Partial Density of States
ZnCo	:	ZnCo_2O_4
ZnPd	:	$\text{ZnCo}_{2-x}\text{Pd}_x\text{O}_4$
ZNS	:	ZnCo_2S_4
ZnPds	:	$\text{ZnCo}_{2-x}\text{Pd}_x\text{S}_4$
XRD	:	Xray Diffraction
TEM	:	Transmission Electron Microscopy
HRTEM	:	High Resolution Transmission Electron Microscopy
NF	:	Nickel Foam
ECSA	:	Electrochemical Active Surface Area
HER	:	Hydrogen Evolution Reaction
OER	:	Oxygen Evolution Reaction
EIS	:	Electrochemical Impedance Spectroscopy
CHE	:	Computational Hydrogen Electrode

TOF	:	Turnover Frequency
LSV	:	Linear Sweep Voltammetry
F.E.	:	Faradaic Efficiency
ORR	:	Oxygen Reduction Reaction
COR	:	Carbon Oxidation Reaction
PEME	:	Proton Exchange Membrane Electrolysis
AWE	:	Alkaline Water Electrolysis
SOEC	:	Solid Oxide Electrolysis Cell
LDA	:	Local Density Approximation
PBE-GGA	:	Perdew Burke Ernzhof General Gradient Approximation
EDX	:	Electron Dispersive Xray
VB/VBM	:	Valence Band Maximum
CB/CBM	:	Conduction Band Maximum
CP	:	Chronopotentiometry
Cdl	:	Charge Double layer

ABSTRACT

Full Name : Mubarak Abdulwahab Adebunmi
Thesis Title : Engineering Low-Cost Spinel Nanocomposite Catalysts for Sustainable Green Hydrogen Production Via Water Splitting: A DFT-Supported Study.
Major Field : Materials Science and Engineering
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As the world's demand for sustainable energy continues to increase, there is a need to have a balance between energy generation, the economy, and the environment. Hydrogen fuel has been considered an alternative to fossil fuels due to its low carbon footprint compared to fossil fuels. To achieve sustainable production of hydrogen, the development of low-cost and highly effective electrocatalysts is necessary. This study investigates the impact of palladium (Pd) doping in enhancing the electrocatalytic activity of ZnCo_2O_4 and ZnCo_2S_4 for the hydrogen evolution reaction (HER). Palladium-doped zinc cobalt oxide ($\text{ZnPd}_x\text{Co}_{2-x}\text{O}_4$, $0.00 \leq x \leq 0.08$) and zinc cobalt sulfide ($\text{ZnPd}_x\text{Co}_{2-x}\text{S}_4$, $0.00 \leq x \leq 0.10$) nanoelectrocatalysts (NECs) were successfully synthesized through hydrothermal methods and coated onto nickel foam (NF). Structural and morphological characterizations, including X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), scanning electron microscopy (SEM), and X-ray diffraction (XRD), confirmed the formation of spinel phases with well-defined nanostructures. Electrochemical performance analysis revealed that Pd doping significantly enhances HER activity. The optimized $\text{ZnPd}_{0.08}\text{Co}_{1.92}\text{O}_4@\text{NF}$ catalyst achieved a low overpotential of 31 mV, a Tafel slope of 54.36 mV/dec, and remarkable stability for over 72 hours. Similarly, $\text{ZnPd}_{0.06}\text{Co}_{1.94}\text{S}_4@\text{NF}$ exhibited an overpotential of 166 mV and a Tafel slope of 127.7 mV/dec, and sustained activity for over 40 hours. The superior performance of these catalysts is attributed to an increased electrochemical

active surface area (ECSA) and enhanced charge transfer kinetics at the semiconductor-electrolyte interface.

Density functional theory (DFT) calculations were performed to further support these findings. The theoretical investigation reveals that Pd doping in $\text{ZnPd}_x\text{Co}_{2-x}\text{O}_4$ optimizes the electronic structure, reduces the energy barrier for water dissociation to a thermoneutral energy of (0.03 eV), and accelerates the Volmer step, leading to improved HER kinetics. Similarly, the Pd doping in $\text{ZnPd}_x\text{Co}_{2-x}\text{S}_4$ optimizes the electronic structure, reduces the energy barrier for water dissociation to an energy of (-0.012 eV), and accelerates the Volmer step, leading to improved HER kinetics. These results demonstrate that Pd-doped ZnCo_2O_4 and ZnCo_2S_4 catalysts exhibit HER activity, with the oxides exhibiting activity comparable to commercial Pt electrodes, offering a promising low-cost alternative for large-scale green hydrogen production. The comparative analysis of oxide and sulfide performance provides insights into the tunability of spinel-based materials for efficient electrocatalysis.

Keywords: *Electrocatalysts, Hydrogen fuel, Density Functional Theory (DFT), Spinel oxides & Spinel sulfide.*

ملخص البحث

الاسم الكامل: مبارك عبد الوهاب أديبني

عنوان الرسالة: تصميم محفزات نانوية مركبة من نوع السبيل منخفضة التكلفة لإنتاج الهيدروجين الأخضر المستدام عبر

تحليل الماء: دراسة مدعومة بنظرية الكثافة الوظيفية (DFT).

التخصص الرئيسي: علوم وهندسة المواد

تأريخ الحصول على الدرجة: مايو 2025

مع تزايد الطلب العالمي على الطاقة المستدامة، تبرز الحاجة إلى تحقيق توازن بين توليد الطاقة، والاقتصاد، وحماية البيئة. يُعدّ الهيدروجين وقودًا بديلاً واعداً للوقود الأحفوري نظرًا لبصمته الكربونية المنخفضة مقارنة بالوقود الأحفوري. ولتحقيق إنتاج مستدام للهيدروجين، من الضروري تطوير محفزات كهربائية منخفضة التكلفة وذات كفاءة عالية. تبحث هذه الدراسة تأثير تطعيم البلاديوم (Pd) في تعزيز النشاط التحفيزي الكهربائي لأكسيد الزنك والكوبالت (ZnCo_2O_4) وكبريتيد الزنك والكوبالت (ZnCo_2S_4) لتفاعل إنتاج الهيدروجين (HER). تم بنجاح، تصنيع محفزات نانوية كهربائية (NECs) من أكسيد الزنك والكوبالت المطعم بالبلاديوم ($\text{ZnPd}_x\text{Co}_{2-x}\text{O}_4$)، حيث ($0.00 \leq x \leq 0.08$) وكبريتيد الزنك والكوبالت ($\text{ZnPd}_x\text{Co}_{2-x}\text{O}_4$)، حيث ($0.00 \leq x \leq 0.10$) باستخدام طريقة التحلل المائي، ثم تم طليها على رغوة النيكل (NF). أكدت التحليلات التركيبية والمورفولوجية، بما في ذلك مطيافية الأشعة السينية للإلكترونات (XPS)، والمجهر الإلكتروني النافذ (TEM)، والمجهر الإلكتروني الماسح (SEM)، والحيود بالأشعة السينية (XRD)، تكوين الطور السبيلي بتركيبة نانوية واضحة. كشفت تحليلات الأداء الكهروكيميائي أن تطعيم البلاديوم يعزز بشكل كبير نشاط تفاعل HER. فقد حقق المحفز $\text{ZnPd}_{0.08}\text{Co}_{1.92}\text{O}_4@\text{NF}$ قيمة جهد إضافي منخفضة بلغت 31 مللي فولت، وانحدار تأفل مقداره 54.36 مللي فولت/عقد، واستقرارًا ملحوظًا لأكثر من 72 ساعة. وبالمثل، أظهر المحفز $\text{ZnPd}_{0.06}\text{Co}_{1.94}\text{S}_4@\text{NF}$ جهدًا إضافيًا قدره 166 مللي فولت وانحدار تأفل مقداره 127.7 مللي فولت/عقد، مع نشاط مستدام لأكثر من 40 ساعة. تُعزى الأداءات الفائقة لهذه المحفزات إلى زيادة المساحة السطحية النشطة كهربائيًا (ECSA) وتحسين ديناميكيات انتقال الشحنة عند واجهة شبه الموصل/الإلكتروليت.

تدعم حسابات نظرية الكثافة الوظيفية (DFT) هذه النتائج بشكل إضافي، حيث تكشف أن تطعيم البلاديوم في $\text{ZnPd}_x\text{Co}_{2-x}\text{O}_4$ يُحسن البنية الإلكترونية، ويقلل من حاجز الطاقة لتفكك جزيئات الماء إلى طاقة معتدلة تبلغ (0.03 إلكترون فولت)، ويُسرّع خطوة فولمر، مما يؤدي إلى تحسين ديناميكيات تفاعل إنتاج الهيدروجين HER. وبالمثل، فإن تطعيم البلاديوم في

$\text{ZnPd}_x\text{Co}_{2-x}\text{S}_4$ يُحسّن البنية الإلكترونية، ويقلل من حاجز طاقة تفكك الماء إلى طاقة تبلغ (0.012- إلكترون فولت)، ويُسرّع خطوة فولمر، مما يؤدي إلى تحسين ديناميكيات تفاعل HER. تُظهر هذه النتائج أن محفزات ZnCo_2O_4 و ZnCo_2S_4 المطعّمة بالبلاديوم تُظهر نشاطاً في تفاعل HER، حيث يُظهر الأكسيد نشاطاً مماثلاً لأقطاب البلاتين التجارية، مما يجعله بديلاً واعدًا ومنخفض التكلفة لإنتاج الهيدروجين الأخضر على نطاق واسع. ويوفّر التحليل المقارن بين أداء الأكسيد والكبريتيد رؤى مهمة حول قابلية ضبط مواد السبيل لت تحقيق تحفيز كهربائي عالي الكفاءة.

الكلمات المفتاحية:

المحفزات الكهربائية، وقود الهيدروجين، نظرية الكثافة الوظيفية (DFT)، أكاسيد السبيل، كبريتيدات السبيل

CHAPTER ONE

INTRODUCTION

This section presents a brief background of the study, offering an overview of the research problem, its justification, and the motivation behind the investigation. It also introduces key concepts and terminologies relevant to the research and essential for understanding the discussions in the subsequent chapters.

1.1 Background of The Study

As global energy demand continues to rise, the exploitation, mining, and burning of fossil fuels are also expected to increase, as they remain the primary source of the world's energy supply. Reports suggest that approximately 80% of global energy is derived from conventional energy resources such as crude oil, coal, and natural gas [1], [2], [3]. The reliance on this kind of energy source for a long time comes along with adverse side effects, including environmental degradation and atmospheric pollution. The release of greenhouse gases such as CO₂ and NO₂ as by product of fossil fuels into the environment leads to trapping of more heat on the earth surface leading to rising temperature on the earth surface an effect termed as global warming, many studies have established a correlation between global warming and CO₂ emission [4] [5]. As a result of this, the call for a shift from sole reliance on fossil fuel-based energy sources to renewable energy sources has intensified in recent years [6].

Among the renewable energy sources, hydrogen has been identified as a potential replacement for fossil fuels due to its ability to address the problem inherent in renewable energies, such as seasonal and regional dependence [7] [8]. Hydrogen is a highly dense energy carrier, environmentally friendly as its by-product is CO₂-free [9]. Hydrogen is not just an energy carrier but also an

important feedstock in the chemical industry for manufacturing ammonia and petroleum refining [10]. There are many ways by which hydrogen can be produced; these include steam reforming of methane, electrolysis, and biomass conversion [11], [12], [13]. Among all these methods, electrolysis has proven to be the most efficient way to produce green hydrogen capable of decarbonizing the Earth. Most of the commercial production of hydrogen has been through steam methane reforming, which relies on fossil fuels, and hence, the process is not CO₂-free [7], [14]. The commercial production of hydrogen through electrocatalysis, despite its greener nature, has been slowed down by the sluggish nature of the Hydrogen Evolution and Oxygen Evolution Reaction (HER & OER), which requires a large overpotential to initiate the reaction [15]. The electrocatalysts that exhibit lower overpotential for water splitting are mostly noble metal-based electrocatalysts such as platinum (Pt), palladium (Pd), ruthenium (Ru), iridium (Ir), and their respective oxides, including iridium and ruthenium oxide (IrO₂, RuO₂). Although the noble metal and their oxides exhibit lower overpotential, their long-term sustainability is threatened by their pricey nature and scarcity. Therefore, there is a need to devote considerable effort to the search for low-cost non-noble electrocatalysts [16]. Among the non-metal-based catalyst that have been identified as viable and sustainable replacements are the spinel compounds which has a structure of AB₂X₄ (X = O, S, Se), and have received significant attention from researchers as potential electrocatalysts for hydrogen production due to their low-cost synthesis, low density, diverse structures, high stability and relative abundance on the earth crust [17].

This work aims to synthesize efficient spinel-based electrocatalysts for the HER by systematically screening anion substitutions that optimize the spinel composition. The study further investigates the effect of Pd doping on enhancing the catalytic performance of the spinel electrocatalysts. To

obtain an insight into the role of Pd in improving the reaction kinetics and mechanism of these catalysts, the experimental analysis is supported by Density Functional Theory (DFT) calculations.

1.2 Aim and Objectives

1.2.1 Aim

This work aims to investigate the electrocatalytic activity of ZnCo_2X_4 ($\text{X} = \text{O}, \text{S}$) spinel-based structures for water splitting applications by screening various anions that optimize the activity of the spinel structures. The study will further explore the effect of Pd doping on enhancing the catalytic activity of these spinel composites using a range of electrochemical characterization techniques. In addition, DFT calculations will be employed to provide mechanistic insights into how Pd dopants influence the kinetics and reaction pathways of the HER reactions.

1.2.2 Objectives

The primary objectives of this study include:

1. To synthesize cobalt-based spinel compounds (ZnCo_2X_4 , $\text{X} = \text{O}, \text{S}$) via the hydrothermal method, with compositional tuning through anion substitution and transitional metal doping of the B-site.
2. To characterize the synthesized spinel electrocatalysts using techniques such as X-ray diffraction (XRD), scanning electron microscopy (SEM), Raman spectroscopy, and electrochemical impedance spectroscopy (EIS), to confirm their structural, morphological, and conductive properties.
3. To evaluate the electrocatalytic performance of the spinel compounds for the HER through electrochemical characterization techniques, such as linear sweep voltammetry (LSV), cyclic voltammetry (CV), and to determine key parameters such as overpotential, Tafel slope, exchange current density, and long-term stability.
4. To compare the activity of spinel oxides and sulfides by identifying compositional trends that govern their catalytic efficiency.

5. To perform DFT calculations to investigate the electronic structure (band structure, DOS, PDOS) and understand how these properties influence HER/OER activity.
6. To identify favorable adsorption sites and calculate the adsorption energies of key reaction intermediates (H_2O^* , H^*), and determine reaction pathways and energy barriers for HER through Gibbs Free energy Calculation.

1.3 Scope of the Study

This research employs both experimental analysis and theoretical studies to evaluate the effect of Pd doping in tuning the electrocatalytic activity of spinel structures. The experimental analysis revolves around the synthesis, structural, and morphological characterizations of spinel structures, followed by the evaluation of electrocatalytic activity using various electrochemical characterization techniques. The theoretical studies employ DFT for the computation of adsorption and dissociation energy of HER intermediates, and the results will be used to compute the Gibbs Free energy using the computational Hydrogen model (CHE).

1.4 Limitations

Due to the limitation imposed by the inability of computational methods to model all experimental phenomena, we restricted our predictions of the electrocatalyst efficiencies to the computation of the Gibbs free energies for the adsorption of hydrogen (H^*) and water (H_2O^*) on the electrocatalyst, a key descriptor in predicting catalyst efficiency in alkaline media.

CHAPTER 2

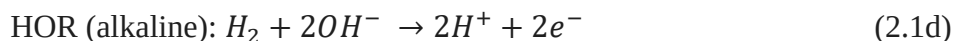
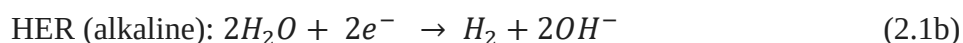
LITERATURE REVIEW

2.1 Electrocatalysis

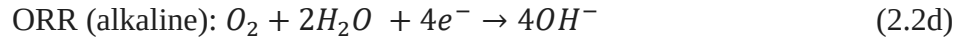
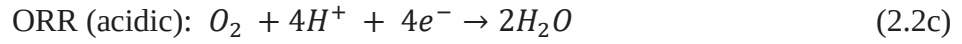
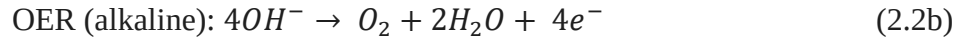
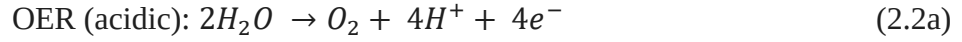
Electrocatalysis explores how the properties of electrode materials influence reaction mechanisms and rates at the electrode–electrolyte interface. Its main goal is to lower the overpotential and boost reaction rates by reducing activation energy, typically through favorable interactions between the electrode surface and reacting species or by altering the reaction pathway.

The field of electrocatalysis is deeply associated with the study of the HER, with early recognition by Kobosev and Monblanova that the cathode catalyzes HER [18]. German chemist Fritz Foerster also highlighted catalysis in his description of cathodic HER [18]. Today, electrocatalysis plays a key role in clean energy technologies. Recent progress has centered on designing high-performance electrocatalysts for applications like fuel cells and electrolyzers, propelled by advanced structural engineering approaches.

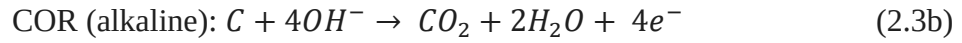
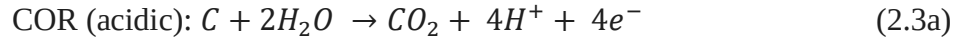
Thus, the most extensively investigated electrode reactions in electrocatalysis include the HER and the hydrogen oxidation reaction HOR, presented in equations 2.1 (a-d) for acid and alkaline media, respectively. In addition, considerable attention has been given to the oxidation of various organic (e.g., methanol, ethanol, etc.) and inorganic fuels (e.g., borohydride, hydrazine) due to their relevance in direct fuel cell applications.



Similarly, the OER and the oxygen reduction reaction (ORR) can be described by equations 2.2 (a-d) for the acidic and alkaline media, respectively.



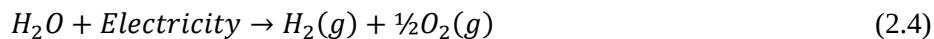
The carbon oxidation reaction (COR), which often accompanies the OER on carbon-based electrodes, is shown in equations 2.3 (a & b).



2.2 General Overview of Water Splitting

Water splitting refers to the process by which a water molecule is split into its components, hydrogen (H₂) and oxygen (O₂). If this process is achieved through the application of electrical energy, it is termed electrocatalytic water splitting [19],[14]. Water electrolysis offers a significant potential for green hydrogen production due to abundant and readily available resources, with an estimated 1.4×10⁹ km³ of water available on Earth, hydrogen production via electrolysis is regarded as a crucial long-term solution in addressing the global energy crisis and long-term environmental degradation caused by energy generation and consumption [20]. Despite its potential, only 4% of hydrogen produced currently comes from electrolysis utilizing renewable energy sources, primarily because of economic factors (including the lack of widely accessible low-cost renewable energy systems, huge capital cost, and intensive energy-input requirement) [21]. This is expected to change shortly as this technology is receiving considerable attention from

many research fields. Electrocatalytic water splitting can simply be expressed by the following overall equation:



This is a thermodynamic reaction with positive Gibb's free energy of ($\Delta G = 237J$).

A typical water electrolyzer setup comprises an electrode (an anode and a cathode), an electrolyte, and an external power supply as displayed in **Figure 1a**. The electrodes are separated to prevent recombination of the generated gases. The nature of electrolyte and operating temperature form the basis for the classification of the water-splitting process into three main divisions, including polymer electrolyte membrane electrolysis (PEME), alkaline water electrolysis (AWE), and solid oxide electrolysis (SOE) [22]. Alkaline and polymer electrolyte membranes are commonly used in low-temperature water electrolysis, while SOEs are employed in high-temperature electrolysis [23]. The operating principles for each class of water electrolysis are presented in **Figure 1(b-d)**.

2.2.1 The Alkaline Water Electrolysis

The AWE cell consists of an anode and cathode submerged in a liquid alkaline electrolyte, typically potassium hydroxide (KOH). A gas-tight diaphragm separates the two electrodes, allowing hydroxide ions (OH^-) to pass through while preventing the crossover of hydrogen (H_2) and oxygen (O_2) gases. This setup facilitates efficient ion transport while maintaining gas purity. AWE is recognized as the most advanced and widely adopted commercial technology for producing hydrogen energy from water [14],[24]. Suppliers like De Nora SAP, Norsk Hydro, Electrolyzer Corp, Teledyne Energy Systems, and General Electric have embraced this production approach [25]. The major reason for its wide adoption is its compatibility with noble and non-noble metal electrodes as the systems typically operate between 40 and 90 °C, with an efficiency range of 60 to 80% [26]. Another reason is that the process is associated with low cost and long-

term stability [21]. The main drawback of this method is the degradation of the diaphragm due to corrosion, which poses a risk of H_2/O_2 gas crossover. Moreover, the operation at low temperatures results in limited electrolysis current densities (400 mA cm^{-2}), low partial loads, and low operating pressures, possibly leading to low energy efficiencies. Furthermore, the toxicity of asbestos used as a diaphragm has prompted manufacturers to search for a replacement with other non-hazardous materials such as ceramics and polymers [14]. Additionally, the diaphragm restricts the flow of OH^- electrolytes, reducing the medium's conductivity, increasing the ohmic resistance, and lowering the general efficiency of the process [27]. A schematic diagram of the AWE technique is displayed in **Figure 1b**.

2.2.2 Proton Exchange Membrane Electrolysis

To overcome the drawback associated with alkaline electrolysis, the PEM water electrolysis was first conceptualized by Grubb in the 1950s, and later developed by General Electric in 1996 [28]. It uses proton-conducting polysulfonated membranes (Nafion, fumaprem) as both electrolyte and separator, eliminating the need for additional electrolytes, so that the process can operate using only deionized water.

Water is pumped to the anode where it splits into Oxygen (O_2), protons (H^+), and electrons (e^-). The membrane conducts protons to the cathodic side while the electrons flow through an external circuit, generating the potential driving the reaction. Hydrogen is produced at the cathode through the recombination of the protons (H^+) and electrons (e^-) [29], [14]. This technology offers several advantages, such as the ability to operate at high current density, higher energy efficiency, high proton conductivity, very compact design, and the capacity of operation at high pressure [24]. A key strength is its effectiveness in mitigating gas crossover, making it the most mature technology of water-splitting that guarantees safety from gas mixtures [30]. However, its dependence on noble

metal electrodes, due to the acidic media created by the membrane, results in expensive setup costs [25], [31]. To solve this problem, researchers are developing alloy catalysts or noble-metal-doped electrodes, which would boost intrinsic catalytic activity and decrease dependency on precious metals, lowering costs and boosting the scalability of the technique. An illustration of the PEM electrolysis set is shown in **Figure 1c**.

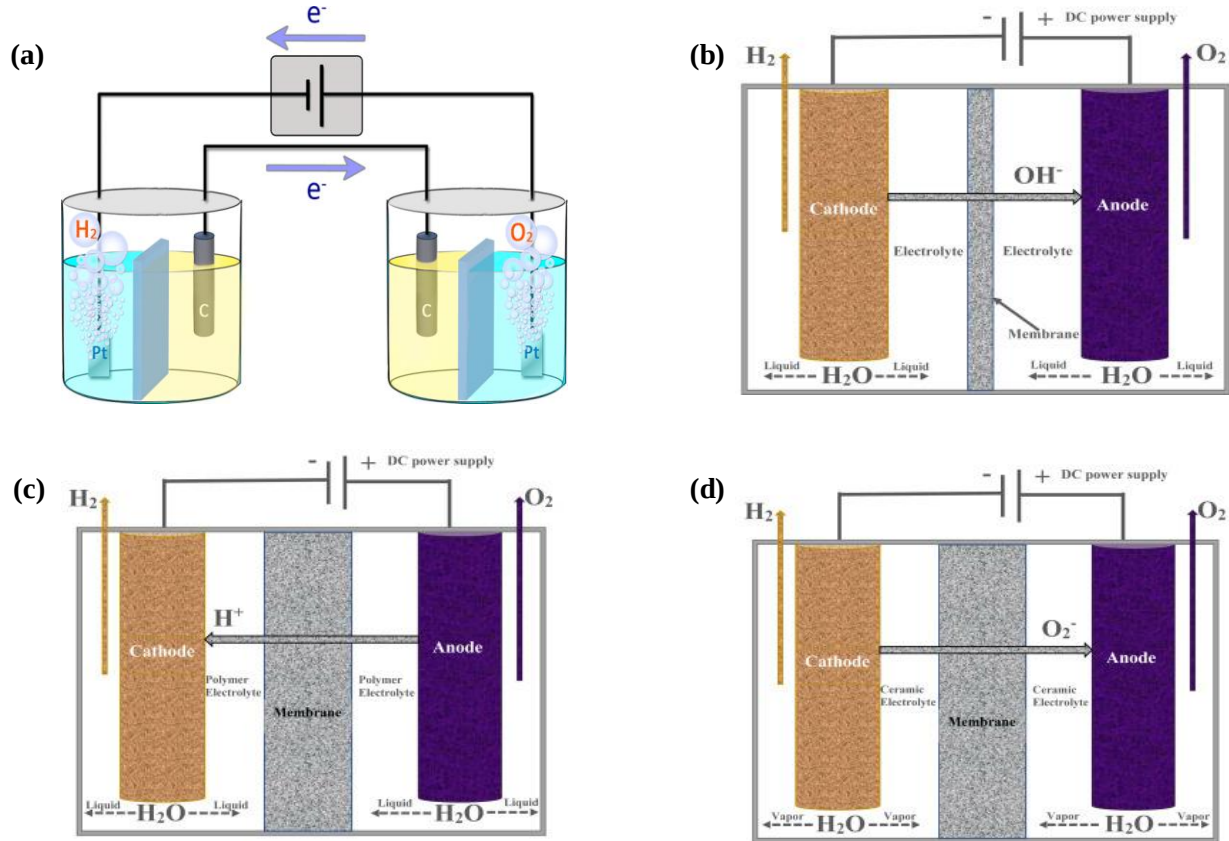


Figure 1: Schematic diagram of alkaline water electrolysis (AWE) technique (a) Water electrolysis complete set up (b) Proton Exchange Membrane Electrolysis (PEME) (c) Solid oxide water electrolysis [21], [20].

2.2.3 Solid Oxide Electrolysis

The Solid Oxide Electrolysis Cell (SOEC) operates at high temperatures (500-1000 °C) and pressure. Water at this temperature converts to steam, requiring heat and electricity input. This gives the procedure two advantages over the low-temperature AWE and PEM method. Firstly, a

high-temperature electrolysis process is more effective than standard room-temperature electrolysis, as heat energy is less expensive than electrical power. Secondly, very little energy is used in high-temperature electrolysis because of the low theoretical breakdown voltage at high steam temperatures [32]. The process operates by supplying steam and recycled hydrogen (H_2) to the cathode, where water molecules are reduced to produce two molecules of H_2 and one molecule of oxide anions O_2^- . The O_2^- anions emerging from the cathodic chamber move to the anode via the solid electrolyte, where they recombine to produce O_2 by releasing their electrons, completing the circuit with the electrons initially released at the cathode. The SOECs rely on solid ceramic electrolytes, offering them a more dynamic kinetics and faster response upon application of electricity.

The most widely used cathodic materials are cermet made of nickel stabilized Zirconia, yttrium stabilized zirconia (YSZ), and strontium-doped lanthanum magnetite materials [33]. The anode is often made of Zirconia or perovskite materials, and the solid electrolyte is made of YSZ. This mode of operation of (SOECs) leverages high-temperature operation to enhance efficiency by lowering the energy required for splitting water. The use of solid electrolytes improves ionic conductivity and enables compact design but introduces challenges related to material stability at elevated temperatures. Although ceramic electrolytes suppress gas permeation, the possibility of their breakdown or cracking at high operation temperatures over a long time poses a risk to the gas mixture. To mitigate this issue, proton-conducting oxides are currently being explored as a potential substitute for O_2^- conducting electrolytes to enhance the process efficiency by reducing the operating temperature range, and improving ionic conductivity, thereby ensuring both safety and increased efficiency [34], [22]. A schematic diagram of the PEM electrolysis is illustrated in

Figure 1d. Furthermore, **Table 1** provides a comparison of the different technologies currently being explored for electrocatalytic water splitting.

Table 1: Comparative analysis of water electrolysis technologies, highlighting their advantages and limitations

Method	Temperature (°C)	Electrolyte	Efficiency (%)	Electrocatalyst	Advantage	Disadvantage
Alkaline	40-90	Liquid	70-80	Ni alloys, Co, Fe oxides, perovskite materials, and spinel materials	Conventional technology, commercialized, non-noble metal catalyst, slow dynamics.	Low current density, Low activity, corrosive electrolyte, gas permeation.
SOE	500-100	Solid	90-800	Ni-YSZ, Perovskite	Non-noble catalyst, high pressure, higher output, low capital cost, enhanced kinetics.	Heavy system design, lab-scale production, brittle electrodes, low durability.
PEME	20-100	Solid	80-90		High current density, small and compact design, High purity of H ₂ , High activity, near-term commercialization.	Precious metal catalyst, corrosive electrolytic medium, less durable, high cost.

Regardless of the electrolyzers or techniques employed, the overall reaction of complete water splitting involves two half-cell reactions (HER and the OER). In the HER, H_2O is reduced at the cathode to produce H_2 gas, while in the OER, it is oxidized at the anode to produce O_2 gas.

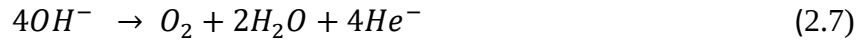
Depending on the electrolyzers, the process can occur in either alkaline or acidic media. The overall reaction is shown in the reaction below:



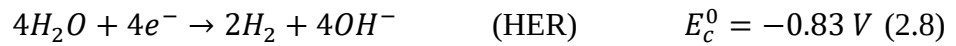
The following equation describes the HER at the cathode under acidic conditions, through the combination of protons and electrons to produce hydrogen gas (H₂):



The OER under a basic condition follows this reaction:



In an alkaline media, the HER and OER each follow these reactions;



In general, the acidic medium offers higher efficiency for the HER and OER due to the lower potential required to initiate the reaction compared to the alkaline medium. As a result, the PEM and SOECs display higher efficiency than the AWE. However, due to the requirements of the acidic medium, OER electrocatalysts in the media are limited to noble metals and their oxides, meaning that the state-of-the-art catalysts in these conditions are restricted to metals and their oxides, making PEM and SOECs more costly than the AWE techniques [6].

2.3 Key Parameters for Evaluation of Electrocatalytic Performance

An electrocatalyst is a catalyst that facilitates electrochemical reactions due to the multiple charge transfers involved in the process. An example is the water electrolysis reaction illustrated in equation (1) above. An electrocatalyst is used in 2 ways: it can either be employed for electrode surface modification or employed to function as the electrode itself [18]. The main purpose of an electrocatalyst, regardless of how it is used, is to adsorb reactants onto its surface to create an

adsorbed intermediate, which enables it to enhance the transfer of electrons between the electrode and the reactant. The performance of an electrocatalyst can be evaluated based on various parameters, the major ones include (1) Activity, which can deduce based on the following parameters: the Tafel slope which is a plot of ($\log(J)$ Vs η), the exchange current density (J), and the overpotential (η). (2) Stability and (3) Efficiency, which comprises Faradaic efficiency and Turnover Frequency (TOF). These variables are crucial and can give important information about the electrochemical reaction's kinetics and process. For this reason, we provide a basic introduction to these experimental kinetic parameters to relate them to the theoretical Descriptor in the next section.

2.3.1 The Overpotential

One of the most crucial metrics for assessing the effectiveness of an electrocatalyst is overpotential (η). The overpotential is the extra potential required to overcome the intrinsic kinetic barriers and initiate an electrochemical water splitting reaction beyond the estimated theoretical equilibrium value [35]. Ideally, the applied potential for initiating a particular reaction should coincide with the reaction's equilibrium potential, which is evaluated as 1.23V for water splitting. In reality, during water splitting this energy is not enough to initiate the process, there is a need for an applied potential that will enable the reaction to proceed and overcome the electrode kinetic barrier, this energy is much higher in magnitude than the estimated equilibrium value. This extra energy required to initiate the reaction is referred to as the overpotential [19].

Theoretically, at room temperature, 0 V and 1.23V of potential voltage is required to activate the HER and OER respectively. Even with this, a lot of energy is still required for the reactions to proceed at a fast-enough rate. The required voltage to achieve a specific current density is termed as the overpotential (η). The primary goal of effective electrocatalysts is to reduce the reaction's

overpotential to the bare minimal level at equilibrium. The applied potential for the reaction can be obtained in accordance with the Nernst equation given below,

$$E = E^0 + \frac{RT}{nF} \ln \frac{C_0}{C_R} \quad (2.10)$$

The applied potential in this context is denoted by E , and the reaction's equilibrium potential is represented by E_0 . R denotes the universal gas constant; F the Faraday constant; T the absolute temperature; n is the number of electrons exchanged during the reaction is n ; the concentrations of the oxidized and reduced species are C_R and C_0 , respectively. Another way to express the overpotential (η) is to represent it as a difference between the equilibrium potential (E_{eq}) and the applied potential (E) required to reach a specific current density.

$$\eta = E - E_{eq} \quad (2.11)$$

Thus, the overpotential at any current density, without accounting for iR drop, can be expressed as $\eta_{HER} = E_{RHE} - 0 \text{ V}$ for HER and $\eta_{OER} = E_{RHE} - 1.23 \text{ V}$. The benchmarked overpotential (η) of the system is usually measured at a standard current density benchmarked at 10 mA cm^{-2} , this value serves as a means of comparing the activities of different electrocatalysts. This value is used as a reference because it corresponds to the photocatalysis solar-to-hydrogen efficiency value of 12.3% [36]. For this, it is worth noting that the overpotential (η) adopted for a reaction is the value of the potential that must be applied to produce a particular current density, usually @ 10 mA cm^{-2} . An electrocatalyst that operates at a lower overpotential in a specific electrolysis system indicates its higher electrocatalytic ability and its efficiency for that reaction. Furthermore, to satisfy the demands of industrial water electrolysis, electrocatalysts must exhibit excellent catalytic activity at higher current densities (such as $500 \text{ or } 1000 \text{ mA cm}^{-2}$). Therefore,

overpotentials at higher current density are also crucial for evaluation of activity of electrocatalyst activity [37].

2.3.2 Exchange current density (J).

Another key parameter to evaluate electrocatalytic kinetics of a reaction is the exchange current density, denoted as (j). For an electrochemical system, j represents the charge transfer dynamics that occur at the electrode/electrolyte interface at equilibrium or an open circuit [38]. The overall current (I) flowing in the system equals the sum of anodic (I_a) and cathodic (I_c) currents. Typically, the exchange current density for an electrocatalytic reaction is determined by fitting the Butler-Volmer relation, which correlates between the voltage and anodic-cathodic current as shown in Equations 2.12 (a-c) respectively [39], [40]. The relationship connecting the overpotential with the current at the electrode-electrolyte interface is described below.

$$I = I_a + I_c \quad (2.12a)$$

$$I_a = I_0 \exp\left(\alpha_a \frac{nF}{RT} \eta\right) \quad (2.12b)$$

$$I_c = I_0 \exp\left(\alpha_c \frac{nF}{RT} \eta\right) \quad (2.13c)$$

I_a and α_a denote the anodic transfer coefficient and anodic half reaction rate constants, respectively. However, I_c and α_c are the cathodic-half reaction rate constant and transfer coefficient, respectively while I_0 is the exchange current density [40],[41].

This can be combinedly written as:

$$I = I_0 \left[\exp\left(\alpha_a \frac{nF}{RT} \eta\right) - \exp\left(\alpha_c \frac{nF}{RT} \eta\right) \right] \quad (2.14)$$

The exchange current can be obtained through the extrapolation of the linear sweep voltammogram (LSV) curve to the point of intersection of the equilibrium potential (zero overpotential) with the

current density on the logarithmic scale [42]. This is because the reaction attains its equilibrium conditions when ($\eta = 0$; $E = E_{eq}$), at this point the anodic current (I_a) equals the cathodic current (I_c), which leads to a zero total net current as shown in Figure 2(a). In simpler terms, the value of the intercept when the overpotential (η) is zero represents the exchange current, denoted by (I_0). The exchange current density (j_0) is obtained when the exchange current (I_0) is being divided by the active surface area of the electrode (A) as in the equation below [43].

$$j_0 = \frac{I_0}{A} \quad (2.15)$$

The exchange current density (j_0) magnitude represents the intrinsic bonding-charge transfer interactions between the reactant and the electrocatalyst. In contrast to the case of overpotential (η) a good electrocatalyst should possess high exchange current density (J_0) [44]. For example, platinum shows very high exchange current densities in HER systems when compared to other precious metals, and iridium exhibits very high exchange current densities among other precious metals in OER systems.

2.3.3 The Tafel slope

A key parameter for evaluating the activity of electrocatalysts is the Tafel slope. The Tafel plot depicts the linear correlation between the overpotential and the total kinetic current of an electrochemical reaction, while the Tafel slope expresses their relationship. The relation is expressed as:

$$\eta = a + b \log(j) \quad (2.16)$$

j in this equation denotes the current density, η represents the overpotential a is a constant related exchange current density (j_0) through the relation $a = -b \log(j_0)$. Therefore equation 2.17 can be rewritten as:

$$\eta = b \log(j/j_0) \quad (2.17)$$

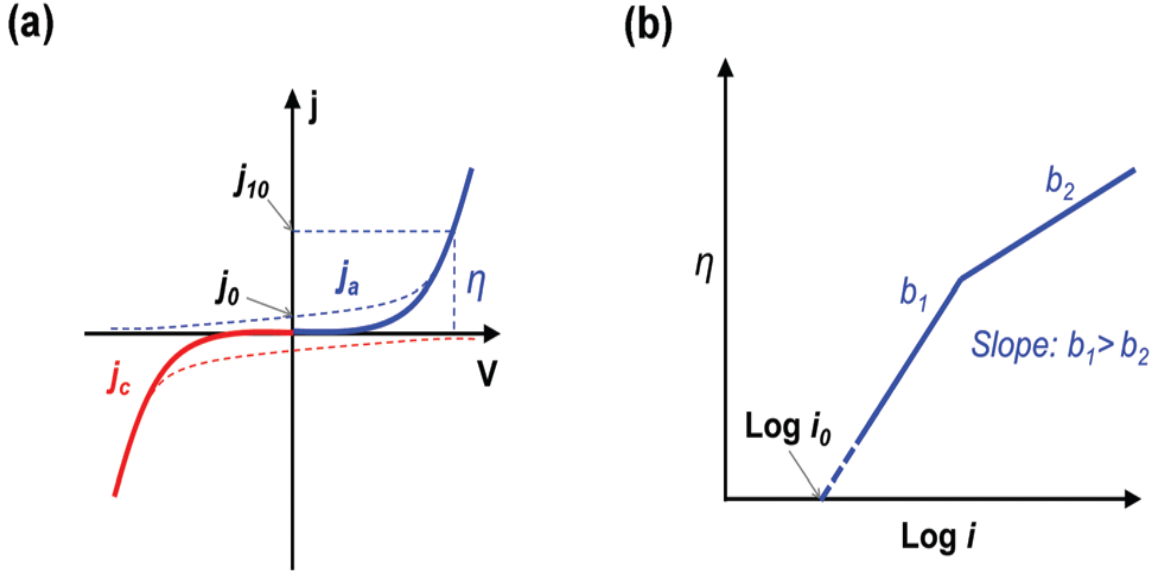


Figure 2: (a) Cathodic (red) and anodic (blue) electrode Polarization curves showing the exchange current density (j_0) (b) Tafel Plot showing the Tafel slope (b_1 - b_2) and the exchange current density ($\log i_0$) [39].

By plotting η as a function of $\log |j|$ the Tafel plot can be obtained. The Tafel plot depicted in **Figure 2b** provides a connection between the overpotential and the exchange current density (j_0). By analyzing the Tafel plot around the linear regions, two (2) key kinetic parameters can be obtained. The first is exchange current density (J_0), which can be obtained by determining the current at zero overpotential (η). The second deducible parameter from the Tafel plot is the Tafel slope (b). The Tafel slope is associated with the mechanism of the catalytic reaction in terms of electron transfer kinetics. A lower Tafel slope indicates rapid electrocatalytic reaction kinetics and a significant increase in the current density for any change in the overpotential. An efficient electrocatalyst is characterized by a lower overpotential (η) and Tafel slope (b), along with a higher increase in the corresponding current density (I) [19]. This is because faster electron-transfer

kinetics are indicated by smaller (b), which indicates that less η is needed to achieve a given increase in the same current density.

2.3.4 Faradaic efficiency

The faradaic efficiency (F.E.) is a parameter used to determine the electrocatalytic activity of a catalyst by comparing the actual products to predicted theoretical products [44]. In general, it describes the potential of an electron and the extent to which it contributes to an electrochemical reaction. The F.E. in Water electrolysis specifically denotes the efficiency of transforming electrical energy into chemical energy stored in the form of hydrogen and oxygen gas. It compares the volume of gas produced experimentally to that which is theoretically predicted under identical conditions [45], [46]. In other words, the F.E. tells us how well we are doing experimentally compared to the theoretical predictions. To measure the F.E., gas chromatography is employed to estimate the no. of moles of hydrogen generated experimentally at a specific time, while the no. of moles of hydrogen that should be generated theoretically under the same condition is calculated from the current-time data. Mathematically, the F.E is written as;

$$FE = \frac{\text{No of moles of } H_2 \text{ produced experimentally}}{\text{No of moles of } H_2 \text{ produced theoretically}} 100\% \quad (2.17)$$

$$FE = \frac{4FnH_2}{It} \times 100\% \quad (2.18)$$

Where nH_2 is the no. of molecular Hydrogen produced, I represent the applied current, t is the reaction time, & F is Faraday's constant (96485 Cmol^{-1}).

2.3.5 Turnover frequency (TOF)

Michel Boudart was the first to adopt the turnover frequency (TOF) as an evaluation parameter in 1968 [16]. For each active site, it indicates the quantity of molecules transformed into products in

a given amount of time. It is typically expressed as the no. of reaction products (H_2 & O_2) produced per active site in a given amount of time [18]. In comparing the catalytic activity for several electrocatalysts, the TOF is helpful despite its imprecision. The imprecision arises because not all active sites are involved in the reaction. Certain reaction conditions or inappropriate surface area are two reasons leading to the inactivity of some sites. In reporting the TOF, some researchers only consider the exposed area while others consider the entire area. Active sites are determined based on their surface density and surface area. The TOF can also be written as

$$TOF = \frac{j \times N_A}{n \times F \times \tau} \quad (2.19)$$

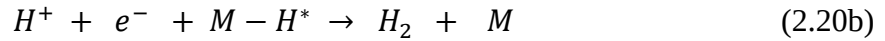
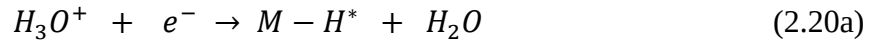
In this equation j is the current density, N_A is the Avogadro number, n is the number of electrons involved in the reaction and F is the Faraday constant. τ is the total/surface concentration of active sites of the catalysts.

A higher TOF value often indicates stronger electrocatalytic HER & OER performance, hence electrocatalysts with higher TOFs are preferred for effective hydrogen and oxygen production.

2.4 Hydrogen Evolution Reaction

HER is the first among the two (2) reactions that play a major role in electrocatalytic water splitting. HER is a two-electron reduction reaction that occurs at the cathodic electrode of the electrocatalysis setup independent of the media used to perform water electrolysis. Although the no. of electron transfer is independent of the media, the HER intermediate varies between acidic and alkaline media. Water molecules (H_2O) are reduced to H_2 in alkaline media by HER, whereas protons (H^+) are reduced to generate hydrogen molecules (H_2) in acidic media. The HER in acidic media can proceed through three possible steps, which are mechanistically classified into two pathways: the Volmer-Heyrovsky mechanism and the Volmer-Tafel mechanism [6],[47].

The Volmer reaction is the first step and acts as an intermediate for HER, this involves the reaction of a proton (H^+) with an electron, to generate an adsorbed hydrogen (H^*) on the electrocatalyst surface labelled as (M), the proton originates from the reduction of hydronium cation (H_3O^+). The reaction can then proceed through any of these two subsequent steps at its later stage, either through the reaction of a proton in the solution with an electron to form a hydrogen atom on the same active site as the former which then combines with the initially adsorbed hydrogen on that site forming a Hydrogen molecule. If the reaction proceeds through this mechanism it is referred to as the Volmer-Heyrovsky pathway. Alternatively, the reaction may proceed from the first step directly to a third step which involves the combination of two adsorbed hydrogen on different active sites on the surface of the electrocatalyst to generate a hydrogen molecule (H_2), this mechanism is termed as the Volmer-Tafel reaction pathway [48]. The three reaction steps are represented in the equations below: Where M represents- the surface of the electrocatalyst.



The HER mechanism in the alkaline and neutral environment involves three basic reaction steps comparable to that of the acidic media reaction pathway; the differences are in the reactive species involved in each stage [7]. The first step constitutes the Volmer step (2.21), which involves the dissociation of a water molecule and the subsequent adsorption of hydrogen onto a free site of the electrocatalyst surface. The reaction can then proceed by the subsequent production of hydrogen through either an electrochemical process where another water molecule dissociates to form

adsorbed hydrogen and combines with the initially formed hydrogen on the catalyst surface to form a hydrogen molecule (H_2) this is termed (Heyrovsky step). Alternatively, the reaction can proceed by a chemical process that involves the combination of two adsorbed hydrogen on the electrocatalyst surface to form a hydrogen molecule. This process is termed as the Heyrovsky process. A schematic description of HER in an acidic medium is provided in **Figure 3**.



The dissociation of hydronium ions (H_3O^+) to create M-H intermediates in acidic media, whereas the dissociation of H_2O in alkaline media to obtain the M-H intermediates, is the primary difference between the reaction processes in acidic media and alkaline/neutral media. Even for the most active noble metal electrocatalyst, the activity of HER of catalysts in alkaline/neutral media is generally lower than in its counterpart (acidic), due to the higher overpotential needed to break the stronger covalent bond H-O-H of H_2O molecules is higher than that required to break the dative bond of (H_3O^+) [7], [49]. The major factor that determines the predominant mechanism i.e., the Volmer-Heyrovsky or the Volmer-Tafel, relies on the no. of concentration of active site on the catalyst surface. On surfaces with a low concentration of active sites, the former predominates, while on surfaces with a high no. of active sites the latter predominates. The distance between adjacent site is also a determining factor of which reaction mechanism predominates. When the distance between sites is greater than the van der Waal's radius of the adsorbed two adsorbed hydrogens, the Heyrovsky mechanism predominates, while a smaller distance between adjacent sites leads to

predominance of the Tafel mechanism. The Heyrovsky process takes precedence when the distance between two sites is more than the Van der Waal's radius of the adsorbed hydrogens, but the Tafel mechanism takes precedence when the distance between adjacent sites is smaller [42].

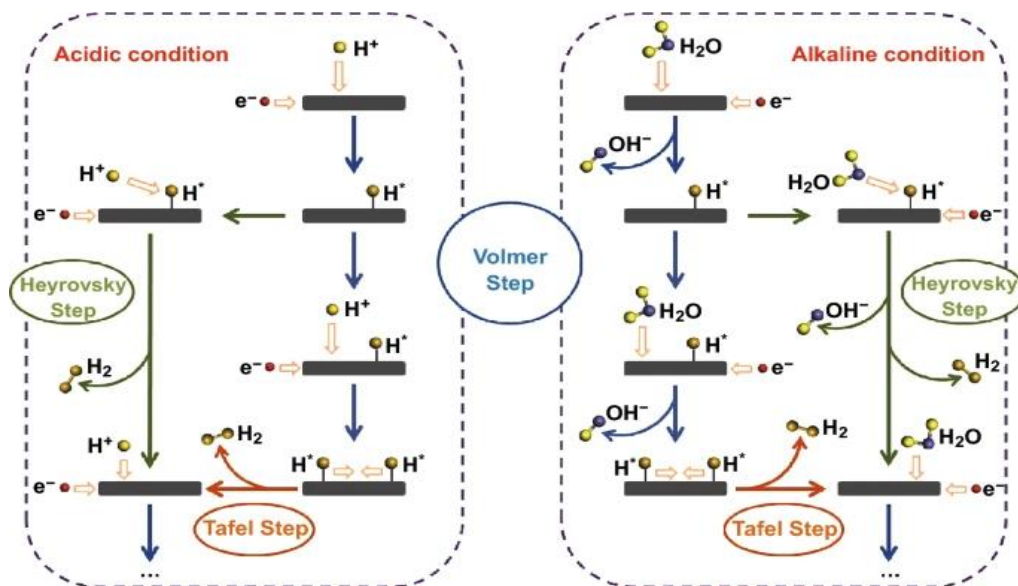


Figure 3: HER mechanism in Acidic and alkaline media [49].

2.5 Spinel Structures

Spinel compounds represent a significant class of chalcogenide minerals with the chemical formula AB_2X_4 , where X represents an anion (typically O, S, Se, or Te), and A and B are cations (commonly Fe, Mn, or Co) [50]. These compounds derive their names from the parent compound $MgAl_2O_4$, known as spinel. These compounds are primarily ionic, formed from the interaction of highly electropositive metal cations and strongly electronegative nonmetal anions. In the general spinel formula AB_2X_4 , the anion X typically adopts a -2-oxidation state, while the A-cation exists in a +2 oxidation state, occupying the tetrahedral voids, and the B-cation assumes a +3 oxidation state, occupying the octahedral voids, resulting in the normal spinel structure $A^{2+}B^{3+}_2X_4$ displayed in **Figure 4a**. Otherwise, the existence of the B-cation in the tetrahedral and octahedral sites leads to the shifting of the A-cation to the octahedral sites, forming the inverse spinel structures

displayed in **Figure 4b**. The most common anions (X) in spinel compounds include O, Si, Se, Te, S, and N, and they are categorized based on these anions; for example, AB_2O_4 represents spinel oxides, while AB_2S_4 denotes spinel sulfide. While the range of anions is limited to specific groups in the periodic table, cations span a broad range of metals, including transition metals, highlighting the structural and compositional versatility of these materials [51].

Due to the flexibility of the spinel structures to accommodate a large variety of cations, nearly all metals in the periodic tables, the tolerance factor serves as an essential tool in predicting the stability of specific cation-anion combinations to form the spinel structures. The tolerance factor for spinel structures as derived from the work of Song et al., is given as [52]:

$$\tau = \frac{\sqrt{3}(r_B + r_X)}{2(r_A + r_X)} \quad (2.23)$$

Where r_A , r_B and r_X are the ionic radii of the A, B, and X site ions.

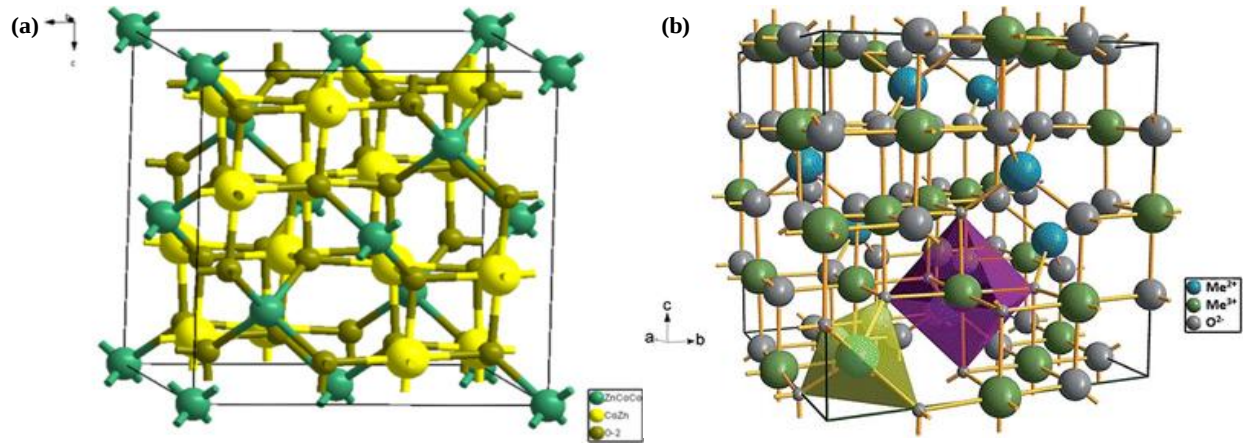


Figure 4: Schematic Representation of (a) Normal Spinel, (b) Inverse Spinel Structure

2.6 Spinel Nanocomposite as Electrocatalyst for Water Splitting

The spinel compounds are a wide class of materials, but many studies have established that the cobalt-based spinel oxides are widely employed as OER electrocatalysts, as they display minimal overpotential requirement for OER. However, cation doping and structural engineering have been

widely adopted strategies to functionalize and enhance the activity of spinel structures towards OER. Bhuvanendran et al., research on integrated abundant O vacancies in Co_3O_4 spinel oxides yields an electrocatalyst that possesses an overpotential of 363 mV @ 10 mA cm^{-2} and a Tafel slope of 89 mV dec^{-1} [53]. According to Zhang et al.'s investigation on CoFe_2O_4 's performance toward OER at various temperatures, CoFe_2O_4 showed a lowered Tafel slope value of 159 mV dec^{-1} at high temperatures and an overpotential value of 446 mV at 10 mA cm^{-2} current density [54]. By incorporating oxygen vacancy into Co_3O_4 , Xiang et al. successfully synthesized ZnCo_2O_4 nanosheets, which require an overpotential of 324 mV to achieve a current density of 10 mA cm^{-2} in 0.1 M KOH. These approaches demonstrate that by doping or vacancy engineering of spinel catalysts, their electrocatalytic performance can be improved.

Recently, efforts have been directed towards the enhancement of spinel oxides as electrocatalysts for HER. By doping of MnCo_2O_4 with vanadium (V), Muhammad et al., synthesized and optimized catalyst which exhibit a Tafel slope of 84 mV/dec, and a low onset potential of 78.9 mV, and a low overpotential of 85.9 mV at a current density of 10 mA/ cm^2 , respectively for HER [55]. Furthermore, Lee *et al.* synthesized a flower-shaped CoMn_2O_4 structure on Ni foam for efficient HER in water splitting, which exhibited an overpotential of 132. mV and a Tafel slope of 136 mV/dec. Additionally, Bibi *et al.* successfully synthesized a dual-spinel cobalt-ferrite-based oxide, $\text{ZnCo}_2\text{O}_4/\text{CoFe}_2\text{O}_4$, which demonstrated promising electrocatalytic performance. The heterostructure electrocatalyst achieved an overpotential of 125 mV and a Tafel slope of 123 mV dec^{-1} at a current density of 10 mA cm^{-2} . The enhanced activity was attributed to optimized cation distribution and improved charge transfer at the interface of the two spinel phases, resulting in a performance enhancement of approximately 20% compared to the individual spinel counterparts. Furthermore, to enhance the catalytic activity of zinc cobaltite (ZnCo_2O_4) for the hydrogen

evolution reaction (HER), Yang *et al.* engineered a $\text{ZnCo}_2\text{O}_4@\text{CoMoO}_4$ heterostructure deposited on nickel foam via a hydrothermal method. The resulting composite exhibited a low overpotential of 114 mV at a current density of 10 mA cm^{-2} , along with a Tafel slope of $114.09 \text{ mV dec}^{-1}$, indicating favorable kinetics for HER. **Table 2** provides a summary of previous work on engineering spinel structures for improved catalytic activity in water splitting.

Although, spinel structures offer considerable tunability through various anion and cation combinations, most research efforts have predominantly focused on spinel oxides, whereas spinel sulfides and selenides have remained relatively underexplored. Notably, the choice of anion plays a crucial role in determining the electrode structure and electrochemical performance of transition metal-based compounds, influencing electrochemical activity parameters such as conductivity, catalytic, and stability [56], [57]. A study conducted by Song *et al.* reported that ZnCo_2S_4 nanoflowers grown on nickel foam ($\text{ZnCo}_2\text{S}_4/\text{NF}$) exhibited notable bifunctional electrocatalytic activity. The material demonstrated an overpotential of 278 mV to 10 mA cm^{-2} towards OER and an overpotential of 185 mV for HER at the same current density, along a Tafel slope of $110.4 \text{ mV dec}^{-1}$ [58]. Moreover, ZnCo_2S_4 synthesized on reduced graphene oxide by Santosh *et al.*, displays an overpotential of 135 mV and a Tafel slope of 47 mV dec^{-1} with an excellent stability up to 36 h, which is comparable to that of the benchmark catalyst of Pt-C [59]. Moreover, Santosh *et al.* synthesized ZnCo_2S_4 supported on reduced graphene oxide, which exhibited an overpotential of 135 mV and a Tafel slope of 47 mV dec^{-1} for HER. The catalyst demonstrated excellent stability over 36 hours of continuous operation, with performance metrics comparable to those of the benchmark Pt/C catalyst [60] [61].

Table 2: Comparative analysis of key electrochemical parameters for the spinel structures electrocatalyst for HER

Electrocatalyst	Overpotential (mV)	Tafel slope (mV/dec)	Stability (h)	Cdl ($\mu F/cm^2$)	Reference
40% Pt (Vulcan XC 72)	40	30	3@305 mA cm ⁻²	235	[62]
CoMn ₂ O ₄ / NNF	132.00	136.00	10@100mA cm ⁻²	640	[63]
ZnCo ₂ O ₄ /CoFe ₂ O ₄	148.00	123.00	200@80mA cm ⁻²	44700	[64]
ZnCo ₂ O ₄ @CoMoO ₄ /NF	114.00	114.09	13@12mA cm ⁻²	14470	[65]
ZnCo ₂ O ₄ @NiCo-LDH	54.30	48.69	13@20 mAcm ⁻²	66	[66]
2%La–Co ₃ O ₄ -350	98	72.8	12@10mA cm ⁻²	238	[67]
ZnCo ₂ S ₄ @Ni(OH) ₂	141.70	129.60	13@ 40mA cm ⁻²	850.41	[68]
CoS ₂ @NiCo ₂ O ₄ @NF	173.00	53.00		10800	[69]
NiPd _x Co _{2-x} O ₄ @NF	191.60	84.70	24@10 mA cm ⁻²	740	[70]
ZnCo ₂ S ₄ /NF	185	110.4	24@10 mA cm ⁻²	—	[58]
ZnCo ₂ S ₄ @CoZn ₁₃	160	61.42	25@10 mA cm ⁻²	70	[71]
Ni/Co ₃ O ₄ @Ti	106	109	12@10 mA cm ⁻²		[72]
CuCo ₂ Se ₄ @Au-glass	125	66.5	4.5@8mA cm ⁻²	213	[73]

Similarly, limited studies have explored the potential of selenide-based catalysts for overall water splitting. In a continued effort, Santosh *et al.* substituted sulfur with selenium to synthesize ZnCo₂Se₄ supported on reduced graphene oxide (ZnCo₂Se₄@RGO) and evaluated its bifunctional electrocatalytic performance for both the oxygen evolution reaction (OER) and oxygen reduction reaction (ORR) in zinc-air batteries. The catalyst exhibited an overpotential of 298 mV for OER, indicating promising activity in alkaline media [61]. Furthermore, Wang *et al.*, successfully synthesized a ternary spinel CoIn₂Se₄ nanomaterial, which exhibited an overpotential of 315 mV

at a current density of 10 mA cm⁻², highlighting its potential as an efficient electrocatalyst for water splitting applications. **Table 2** summarizes selected studies on the synthesis, modification, and performance enhancement of spinel-based materials for the HER.

2.7 Fundamentals of Density Functional Theory

DFT arises as a result of the need to solve the many-particle problem in solids. In investigating the many-particle systems in solids, such as atoms and molecules, one of the fundamental tasks is to find the energy of the ground state. This can be accomplished by finding the solution to the Schrodinger equation, which describes the time-dependent changes in a physical system's quantum state [74].

This equation is given by

$$\hat{H}\Psi(r_i, R_i) = E\Psi(r_i, R_i) \quad (2.24)$$

$\hat{H}$ stands for the Hamiltonian operator given by $\hat{H} = \hat{T} + \hat{V}$, $\Psi(r_i, R_i)$ is the wave function for the electron and nuclei coordinate.

$\hat{V} = \frac{q_i q_j}{|r_i r_j|}$ is the Coulomb potential for a pair of charged electrons, $\hat{T}$ the Kinetic energy operator, and E denotes the system total energy.

To simplify equation (1), the electron and the nuclei dynamics can be separated into different mathematical problems by applying the Born-Oppenheimer approximation. It assumes that nuclei are substantially heavier than electrons and relatively motionless relative to electron mobility, and can be used to treat the dynamics of nuclei and electrons. This allows the decoupling of the nuclei and electrons' dynamics [75]. The wave function can then be decoupled into two wave functions as follows:

$$\psi(r_i, R_i) \rightarrow \psi_N(R_i) * \psi_e(r_i) \quad (2.25)$$

where ψ_N and ψ_e are the wave functions for the nuclei and electron, respectively. R_i and r_i are the coordinates of the electron and nuclei coordinates respectively.

This also follows that the time required for the electron to fill the ground state is much quicker than the nuclei can move. Now we can concentrate on solving only the ground state of the electron.

In Many particle problems for solids, the Schrodinger equation for electrons is solved in the approach described below:

$$\hat{H}\Psi(r_1, r_2, r_3, \dots r_N) = E\Psi(r_1, r_2, r_3, \dots r_N) \quad (2.26)$$

$\hat{H}$ represents the electronic Hamiltonian, which consists of three terms as follows

$$\hat{H} = \frac{-\hbar^2}{2m} \sum_i^{N_e} \nabla_i^2 + \sum_i^{N_e} V_{ext}(r_i) + \sum_i^{N_e} \sum_{j>1} U(r_i, r_j) \quad (2.27)$$

The first term denotes the electron's kinetic energy (with $\hbar$ being the Planck constant and m being the electron's mass), the second term represents the external potential of the interaction with the nuclei, and the third term describes the electron-to-electron repulsion. N_e denotes the number of electrons. Equation (24) shows that the Schrodinger equation is three-dimensional (3N) and a function of all N electrons' coordinates in the system. Considering the number of atoms in solids, this shows that it is either practically impossible to solve the Schrodinger equation for solid materials or the solution is limited to solids with few electronic states [76] [77].

2.7.1 Electron Density

In contrast to the many-electron wave function, the electron density relies spatially on three coordinates and offers an alternative to solving the Schrodinger equation, and can be defined from the wave function as

$$n(r) = \psi^i(r_1, r_2, \dots, r_N) * \psi(r_1, r_2, \dots, r_N) \quad (2.28)$$

Here, $n(r)$ represents the electron density, ψ^i , and ψ denotes the electron's imaginary and real wave function, respectively.

Equation 2.28 shows that the three-N (3N) dimension associated with the Schrodinger equation has been reduced to 3, i.e., the electron density is only three-dimensional (3D) in nature and independent of the number of electrons in a system.

Solving the Schrodinger equation using the electron density involves treating the j^{th} electron as a point charge within the field of all other electrons. This approach simplifies the many-electron problem to many single-electron problems, implying that the single-electron wave functions can be written as:

$$\psi(r_1, r_2, r_3, \dots, r_N) = \psi(r_1) * \psi(r_2) * \psi(r_3) \dots * \psi_N(r_N) \quad (2.28)$$

Equation (26) is regarded as the Hartree Product.

With this approach, it is possible to define the electron density as follows in terms of the individual wave functions:

$$n(r) = 2 \sum_i \psi_i^i(r) * \psi_i(r) \quad (2.29)$$

Adopting the electron density $n(r)$, has the main benefit that it is a function of only three coordinates and incorporates the majority of the physically observable information from the Schrodinger equation full wave function solution, which is a function of 3N coordinates [74].

2.7.2 Hohenberg And Kohn Theorems

DFT is based on the theorem formulated by Hohenberg and Kohn in 1964 [78]. The Hohenberg-Kohn theorem shows that understanding the ground state density of electrons is comparable to

understanding the wave function itself. Kohn and Sham subsequently modified this theorem in what is now known as the Kohn-Sham theory, which states that the density of an interacting electron system in the ground state may be estimated from the density of a non-interacting electron system [79]. These two (2) theorems can be explicitly stated as:

1. The first principle of the Hohenberg-Kohn theorem states that the external potential $V(r)$ is solely determined by the ground-state electron density $n(r)$. In another way, the theorem states that the ground state energy E is a unique functional of the electron density [77].

$$E = E[n(r)] \quad (2.30)$$

where E is the energy of the ground state, and $n(r)$ is the density of the ground state.

2. The electron density that minimizes the energy of the overall functional is the true ground state electron density [74].

$$E[n(r)] > E_0[n_0(r)] \quad (2.31)$$

2.7.3 The Energy Functional

The second hypothesis by Hohenberg and Kohn proposed the energy functional, which can be expressed as

$$E[\psi_i] = E_{known}[\psi_i] + E_{XC}[\psi_i] \quad (2.32)$$

where E_{known} and E_{XC} is the known energy and the exchange – correlation functional respectively

$$E_{known}[\psi_i] = \frac{-\hbar}{m_e} \sum_i \int \psi_i^2 \nabla^2 \psi_i d^3r + \int V(r) n(r) d^3r + \frac{e^2}{2} \iint \frac{n(r)n(r')}{r-r'} d^3r d^3r' + E_{ion} \quad (2.33)$$

The electron potential is the first term in the equation; the coulombic force of attraction is the second; the electron-electron repulsion is the third; and the proton-proton repulsion is the fourth. All the quantum effects which are not included in the known Energy functional term, which will be acquired through approximations, are included in the $E_{xc}[\psi_i]$.

2.7.4 The Kohn-Sham Scheme

The Hohenberg-Kohn theorem does not provide a clear method for identifying the minimal energy solutions of the total energy functional, despite providing an easy means of solving the Schrodinger equation. Kohn and Sham overcame this obstacle by demonstrating that the electron density could be calculated as the solution to a system of equations that each represented a single electron. Typically, they present an iterative method of solving the single-electron wave function until self-consistency is achieved. In DFT, the Kohn-Sham scheme entails solving a set of single-electron wave functions described by $\psi(r)$, which depend only on three spatial variables.

$$\left[\frac{-\hbar^2}{2m} \nabla^2 + V(r) + V_H(r) + V_{xc}(r) \right] \psi(r) = \epsilon_i(r) \psi_i \quad (2.35)$$

The first term represent the Hamiltonian for the single electron, the external potential is represented by the second component $V(r)$, the Hartree potential (electron interacting with electron density) by the third term, $V_H(r)$, and the approximated exchange potential, V_{xc} , is represented by the fourth term [80].

2.8 Exchange Correlation

The primary objective of DFT is to determine the most accurate method for approximating the unknown function that requires approximation. The two simplest common Exchange Correlation Functionals (XC Functionals) employed in DFT are: Local Density Approximation (LDA) & Generalized Gradient Approximation (GGA).

2.8.1 Local Density Approximation

By considering only the electron density, $n(r)$, the LDA determines the exchange-correlation energy at a spatial point (r) . The homogeneous electron gas precise expression is defined by the exchange component of the functional.

$$E_{XC}^{LDA}[\rho(r)] = \int n(r) \varepsilon_{xc}^{hom} n(r) dr \quad (2.36)$$

E_{XC}^{LDA} describes the exchange functional for the local density approximation, and ε_{xc}^{hom} is the exchange functional for the homogenous electron gas, which is mathematically given by:

$$\varepsilon_{xc}^{hom} = \frac{-e^2}{4\pi\epsilon_0} \frac{3}{4} \left(\frac{3n}{\pi} \right)^{\frac{1}{3}} \quad (2.37)$$

2.8.2 Generalized Gradient Approximation

The gradient of the density is introduced to the exchange correlation functional by the generalized gradient approximation (GGA), E_{XC}^{GGA} , to approximate the exchange correlation.

$$E_{XC}^{GGA} = \int n(r) \varepsilon_{xc}(n_s |\nabla \rho|) dr \quad (2.38)$$

The quantity $n(r)$ and $n_s(r)$ are the electron density and its gradient, respectively. Non-locality is added to the gradient of the exchange and correlation functional energy descriptions. This can significantly enhance the function's performance by assisting in the assumption of quickly fluctuating electron density charges that are poorly described by the LDA [80].

2.8.3 Perdew Burke Enzhorf (PBE) Exchange Functional

Perdew Burke Enzhorf version of the GGA, abbreviated (PBE-GGA), offers a simplified and more straightforward approach to the GGA, which does not include any empirical components. It contains components like the gradient of the local electron density and its second-order gradient

in the enhancement factors like $F(x)$ and $F(c)$. As a result of its demonstrated high accuracy and computing efficiency, this function is currently the most widely used functional [80].

2.9 DFT Theoretical Descriptor for Hydrogen Evolution Reaction (HER)

In DFT-based evaluations of the HER, the key descriptor is the Gibbs free energy of hydrogen adsorption (ΔG_{H^*}), which quantifies the strength of interaction between hydrogen intermediates and catalyst surfaces. An optimal catalyst has a (ΔG_{H^*}), close to zero, indicating balanced hydrogen adsorption and desorption behavior. Strong adsorption ($\Delta G_{H^*} < 0$), hydrogen desorption becomes rate-limiting, while weak adsorption ($\Delta G_{H^*} > 0$) impedes hydrogen bonding to the surface. For an alkaline medium, the Gibbs free energy of water adsorption ($\Delta G_{H_2O^*}$) serves as a good descriptor for predicting the HER kinetics and catalyst efficiency.

Electronic structure analysis provides deeper insight into catalytic performance. The d-band center theory correlates the position of the metal's d-band relative to the Fermi level with adsorption energy. A d-band center closer to the Fermi level typically enhances H^* adsorption by increasing the overlap with hydrogen's 1s orbital. Modulating the d-band through alloying or doping is a common strategy to tailor catalytic activity. The HER proceeds via either the Volmer–Heyrovsky or Volmer–Tafel mechanism, and DFT is used to compute the associated energy barriers and reaction pathways. The reaction coordinate involves initial proton adsorption (Volmer step), followed by either electrochemical desorption (Heyrovsky step) or a combination of two adsorbed hydrogens (Tafel step). Transition state energies and reaction profiles derived from DFT enable identification of the rate-determining step and evaluation of kinetic feasibility.

Together, adsorption energy, electronic structure descriptors, and reaction coordinate mapping serve as a predictive framework for designing efficient HER catalysts using DFT.

CHAPTER THREE

MATERIALS AND METHODS

3.1 Chemicals

Analytical grade chemicals were used for the synthesis of the ZnCo-based structures without any additional purification. The chemicals include zinc nitrate $\text{Zn}((\text{NO}_3)_2 \cdot 6\text{H}_2\text{O})$, cobalt (II) nitrate $(\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O})$, Palladium (II) Chloride (PdCl_2) , sodium sulfide $(\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O})$, sodium borohydride (NaBH_4) , and Urea.

3.2 Experimental Synthesis Procedure

The ZnCo-based spinel structures can be synthesized using various techniques, including co-precipitation, hydrothermal synthesis, microwave combustion, sol-gel auto combustion, and spray pyrolysis [81]. In this study, the hydrothermal process was used to synthesize the spinel oxides, sulfides, and selenides following the approach adopted by previous literature [58] [56] [61] [82].

3.2.1 Synthesis Procedure of ZnCo_2O_4 Spinel Structure

The ZnCo_2O_4 oxide spinel catalyst was synthesized via the hydrothermal synthesis method. The nickel foam (NF) substrate was cut initially into $5 \times 5 \text{ cm}^2$ pieces and pre-treated in an ultrasonicated bath containing 3M hydrochloric acid, HCl, for 10 minutes. The oxide layer, which was deposited on top of the NF during the pre-treatment process (i.e., NiO on NF), was removed using ethanol and deionized water (DI water). Specifically, 1 mmol of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 2 mmol of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and 4 mmol of urea were dissolved in 50 mL of Deionized water (DI). The solution was stirred vigorously for 1h to ensure uniform mixing. The homogenous solution was subsequently poured into a 100 ml Teflon-lined stainless-steel autoclave, which was then sealed,

and heated at 160 °C for approximately 7 hours. Afterward, the autoclave was allowed to cool naturally to normal room temperature (RT), ~ 25°C.

The resulting black precipitate from the reaction was collected along with the nickel foam and thoroughly washed multiple times with DI water and ethanol to eliminate the residual nitrates. A vacuum oven was used to dry the sample at 80 °C for 4 hours. Finally, the dried catalyst was subjected to calcination at 350 °C for 3 hours in an electric furnace, yielding the $\text{ZnCo}_2\text{O}_4@\text{NF}$ NECs. A schematic of the synthesis process is presented in Figure 5.

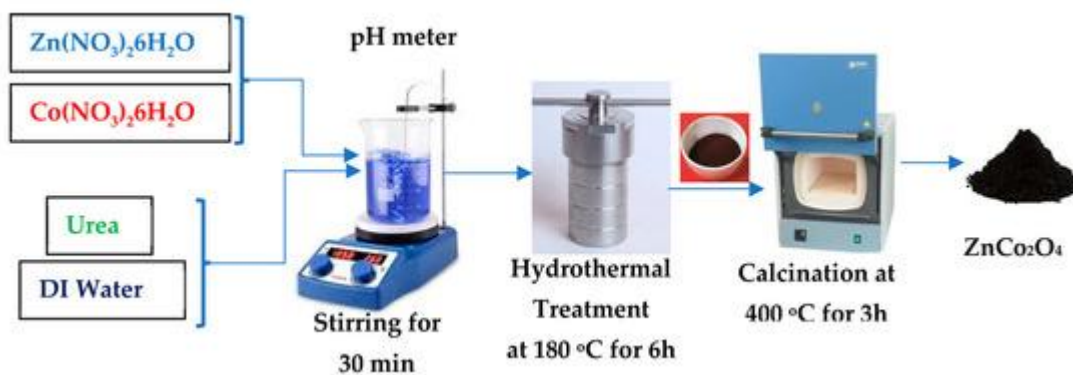


Figure 5: Synthesis Procedure for ZnCo_2O_4 .

3.2.2 Preparation of Pd-doped spinel oxide electrocatalysts

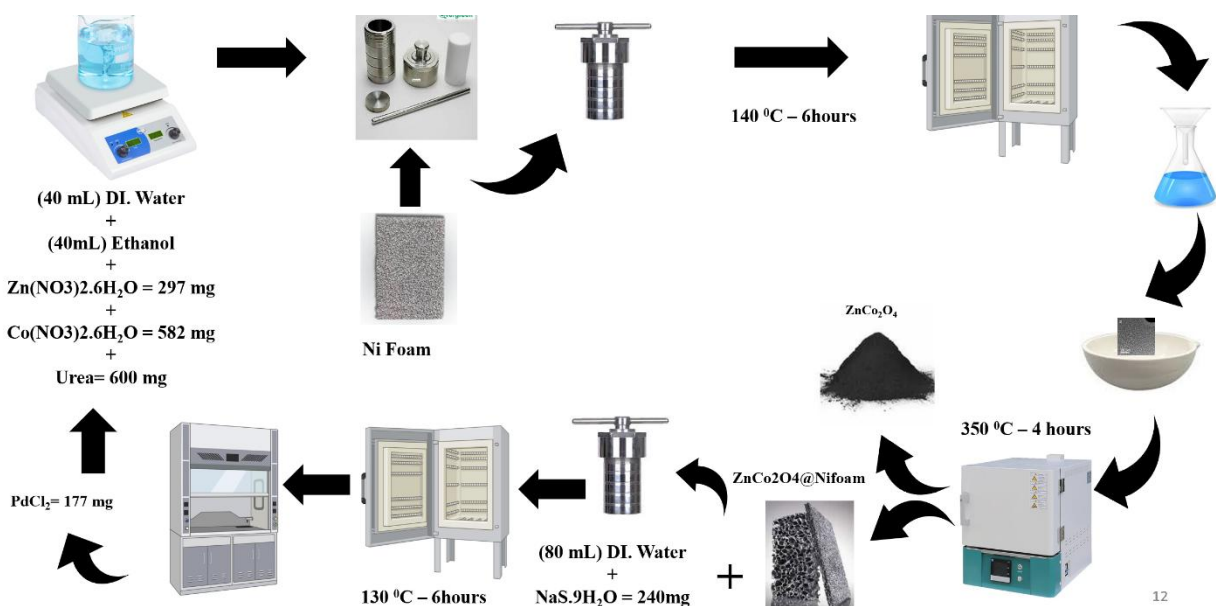
The $\text{ZnPd}_x\text{Co}_{2-x}\text{O}_4$ ($0.00 \leq x \leq 0.08$)@NF NECs were fabricated via a hydrothermal synthesis route. The synthesis process was carried out by varying the concentration of palladium (Pd) to investigate its effect. To synthesize the NECs, accurately measured quantities of Zinc nitrate (98%), Cobalt (II) nitrate (98%), varying concentrations of Pd(II)Chloride (99.9%), and urea were dissolved in 50 mL of deionized water (DI water). Then, the solution was vigorously stirred at room temperature. A piece of pretreated nickel foam (NF) was then immersed in the solution and transferred into a 100 mL Teflon-lined stainless-steel autoclave. The autoclave was securely sealed and heated at 160 °C for approximately 7 hours. The synthesis process then follows a similar procedure to that of $\text{ZnCo}_2\text{O}_4@\text{NF}$ highlighted in section 3.2.1. Finally, the prepared foam of

electrocatalysts was annealed in the electrical furnace for calcination at an elevated temperature of 350 °C for 3h to produce $\text{ZnPd}_x\text{Co}_{2-x}\text{O}_4$ ($0.00 \leq x \leq 0.08$)@NF NECs coated on Ni foam. The synthesis procedure is illustrated in **Figure 6**.

3.2.3 Preparation of Pd-doped spinel Sulfide electrocatalysts

The $\text{ZnPd}_x\text{Co}_{2-x}\text{S}_4$ ($0.00 \leq x \leq 0.10$) NECs coated on Nickel foam, also known as $\text{ZnPd}_x\text{Co}_{2-x}\text{S}_4$ ($0.00 \leq x \leq 0.10$)@NF, were synthesized through a two-step hydrothermal route. Initially, the first step follows a route similar to that of the $\text{ZnPd}_x\text{Co}_{2-x}\text{O}_4$ ($0.00 \leq x \leq 0.10$)@NF as described in section 3.2.2, and displayed in **Figure 6**. Subsequently, to obtain the $\text{ZnPd}_x\text{Co}_{2-x}\text{S}_4$ ($0.00 \leq x \leq 0.10$)@NF from the pre-synthesized $\text{ZnPd}_x\text{Co}_{2-x}\text{O}_4$ ($0.00 \leq x \leq 0.10$)@NF. The pre-synthesized $\text{ZnPd}_x\text{Co}_{2-x}\text{O}_4$ ($0.00 \leq x \leq 0.10$)@NF were inserted in 80 mL of DI water, consisting of 240 mg $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$, and heated inside an autoclave at 140 °C for 12 h to obtain $\text{ZnPd}_x\text{Co}_{2-x}\text{S}_4$ ($0.00 \leq x \leq 0.10$)@NF. Ultimately, the products were dried overnight after being rinsed with deionized water and ethanol on multiple occasions. A schematic illustration of the synthesis procedure is shown in **Figure 6**.

Figure 6: Synthesis Procedure for $\text{ZnCo}_{2-x}\text{Pd}_x\text{O}_4$ @NF & $\text{ZnCo}_{2-x}\text{Pd}_x\text{S}_4$ @NF



3.2.4 Electrocatalysts characterization

The X-ray diffraction (XRD) pattern was used to gain information about the phase of the lattice structure of the NECs of $\text{ZnPd}_x\text{Co}_{2-x}\text{O}_4@\text{NF}$ using $\text{Cu K}\alpha$ of (λ) of 1.54059 Å. TEM technique was employed to analyze the morphology of the $\text{ZnPd}_x\text{Co}_{2-x}\text{O}_4@\text{NF}$ NECs. At the same time, the chemical composition contents agreed with morphology of the NECs were investigated using field-emission scanning electron microscopy (FE-SEM), which is attached to an energy-dispersive X-ray spectroscopy (EDX) module. The chemical compositions and oxidation states of the constituents in $\text{ZnPd}_x\text{Co}_{2-x}\text{O}_4@\text{NF}$ NEC were analyzed using an XPS instrument. The XPS spectra were calibrated by using the C1s of a referenced peak at 284.8 eV. The detailed results of the DFT calculations provide insight into their implications for the electrocatalytic properties of the electrocatalyst under study.

3.2.5 Electrochemical procedure

A 3-electrode glass cell in a KOH (1.0 M) aqueous solution with a pH of 13.6 was used for performing electrochemical measurements. A reference electrode (RE) was Ag/AgCl that was immersed in direct contact with saturated potassium chloride, 3M KCl solution, while for the counter electrode (CE), Pt wire was chosen, and the $\text{ZnPd}_x\text{Co}_{2-x}\text{O}_4$ ($0.00 \leq x \leq 0.08$)@NF NECs was used as working electrode (WE). The potentiostat of (Metrohm AutoLab PGSTAT302N) was used for electrochemical tests. All measurements were performed at room temperature, around 25 °C. Cyclic voltammetry (CV) analysis was conducted within the non-faradic potential region from 0.010 V to 0.021 V at different scan rates from 40-120 mV/s using a range of 20 mV/s. The measurements were used to generate linear plots, where the slope was employed to estimate the double-layer capacitance (C_{dl}). The obtained C_{dl} values were utilized to assess the

electrochemically active surface area (ECSA) of the material, using a standard specific capacitance value of $40 \mu F cm^{-2}$, as commonly reported in literature.

For Linear sweep voltammetry (LSV) analysis, the analysis of results collected from 0.0 to -0.5 V (vs. RHE) at a scan rate of $10 mVs^{-1}$ was utilized to estimate the overpotential of the NECs. Electrochemical impedance spectroscopy (EIS) measurements were carried out to evaluate the electrical characteristics of the electrocatalysts, with particular focus on charge transfer resistance (R_{ct}). The EIS measurements spanned a frequency range from 10 kHz to 0.01 Hz. For further evaluation of the temporal stability of the best performance electrode of $ZnPd_xCo_{2-x}O_4$ ($x=0.08$)@NF NECs, the chronopotentiometry (CP) test was applied at a fixed current of $-20 mA cm^{-2}$ for 72h, while for the $ZnPd_xCo_{2-x}S_4$ ($x=0.08$)@NF NECs, the CP test was carried out for 40h. A minor change in potential is considered negligible for the durable electrocatalyst. The working electrode's $1 \times 1 cm^{-2}$ geometrical surface area was employed to normalize the current density (j).

3.3 Computational Methods

In this study, spin-polarized DFT calculations were carried out using the Perdew-Burke-Ernzerhof (PBE) version of the generalized gradient approximation (GGA) exchange functional as implemented in the Quantum ESPRESSO open source program [83]. The Ultrasoft Pseudopotential (USPP) method was employed to represent the core-valence electron interaction [84]. To obtain an accurate description of the slab and adsorbate configurations, DFT-D2 correction was also included to describe van der Waals interaction due to the weak adsorption of some of the adsorbates involved in the Hydrogen Evolution Reaction (HER) [85]. The valence electronic states were expanded with a kinetic energy cutoff of 80 Ry for the plane wave and

600 *Ry* for the charge densities in all calculations. The Monkhorst-Pack grid of 6 x 6 x 6 was adopted to sample the Brillouin zone. The Broyden-Fletcher-Goldfarb-Shanno (BFGS) method was used for geometry relaxation. The structures were relaxed until a convergence criterion of 1.0×10^{-6} eV and 0.001 eV/Å was achieved for the total energy and the force residue, respectively. To compute the electronic properties, a denser K-mesh of 18 x 18 x 18 was used to sample the Brillouin zone. To model the slabs, a (2 x 2 x 2) supercell was generated from the bulk unit cell to prevent periodic interactions between adsorbates, and was cleaved along the direction of the catalytically active (001) surface to create three (3) layers of the slabs. During the geometry optimization of the slab, the bottom layer was fixed to represent the bulk. In contrast, the top two layers were relaxed, representing the catalyst's surface. To avoid interaction between the periodic images of the repeated slabs, a vacuum space of 15 Å was inserted in the z-direction to ensure proper isolation for each slab due to the imposed periodic boundary conditions [86], [87]. For the slab surfaces, a 3 x 3 x 1 Monkhorst-Pack K-point grid was utilized for energy and structural calculations.

To investigate the effect of the Pd dopant in improving the electrocatalytic activity of the pristine ZnCo₂S₄ catalyst, a palladium atom (Pd) was incorporated into the pristine ZnCo₂X₄ (X = O, S) bulk structures consisting of 56 atoms (Zn = 8, Co = 16, O = 32, S = 32). The substitution of a Pd atom in place of Co represents the efficient dopant percentage observed experimentally (~6.25%). The geometry optimization was then repeated for this structure, following the same procedure performed for the pristine ZnCo₂X₄ bulk structure and slab.

3.4 Free Energy Calculations

The following relations were employed to compute the adsorbate adsorption energies on top of the spinel surfaces [88].

$$\Delta E_{ads} = E_{system} - E_{surface} - E_{adsorbate} \quad (1)$$

Where ΔE_{ads} denotes the adsorption energy, while E_{system} , $E_{surface}$, & $E_{adsorbate}$, represents total energy of the surface with adsorbate, total energy of the slab, and the total energy of the adsorbate in a vacuum respectively.

Consequently, it follows that the adsorption energy for capturing a hydrogen proton (H^+) on top of a catalyst to form a stable adsorption configuration (H^*) is computed as:

$$\Delta E_H = E_{slab+H} - E_{surface} - \frac{1}{2}E_{H_2} \quad (2a)$$

Similarly, the energy change accompanying the adsorption of water (H_2O) molecule on top of a catalyst is computed as:

$$\Delta E_{H_2O} = E_{slab+H_2O} - E_{surface} - E_{H_2O} \quad (2b)$$

To compute the Gibbs free energy of adsorbed hydrogen (ΔG_H), the model put forward by Nørskov *et al.*, was employed to compute the kinetic barriers of the electrochemical reactions through the protonation process [89]. The key assumption of this model is, the free energy change associated with the proton-electron transfer step ($H^+ + e^-$) in the Computational Hydrogen Electrode (CHE) framework can be calculated by adding some correction terms to the hydrogen adsorption energy values (ΔE_H). The ΔG_H can then be expressed according to the following relation [9]:

$$\Delta G_H = \Delta E_H + \Delta E_{ZPE} - T\Delta S \quad (3a)$$

Where ΔE_{ZPE} denotes the change in zero-point energy between the adsorbed H and gas-phase H_2 , and $T\Delta S$ corresponds to the entropy change between the adsorbed state and the gas phase state at room temperature (298.15K).

Furthermore, the ΔE_{ZPE} is obtained as follows:

$$\Delta E_{ZPE} = E_{ZPE}^{H^*} - E_{ZPE}^* - \frac{1}{2}E_{ZPE}^{H_2}$$

Where $E_{ZPE}^{H^*}$, E_{ZPE}^* and $E_{ZPE}^{H_2}$ represents the zero-point energies of the catalyst with adsorbed H , the pure catalyst, and the gas phase H_2 . ΔS can be approximated as:

$$\Delta S_H \approx -\frac{1}{2}S_{H_2}^0$$

Where $S_{H_2}^0$ denotes the entropy of the gas phase H_2 at standard conditions. Similarly, the Gibbs free energy for water adsorption can also be computed following a similar procedure as:

$$\Delta G_{H_2O} = \Delta E_{H_2O} + \Delta E_{ZPE} - T\Delta S \quad (3b)$$

The previous calculations by Nørskov *et al.*, Bin Liu *et al.*, and Yao *et al.*, assume that the value of $\Delta E_{ZPE} - T\Delta S$ for H and H_2O adsorption is 0.24 eV and 0.56 eV, respectively [90], [91], [23].

To fit the computed adsorption energies to an experimentally observed quantity, Nørskov's assumption was employed to obtain the exchange current density, which is defined as [90], [92]:

$$i_0 = -ek_0 \frac{1}{1 + \exp(-|\Delta G_H|/K_b T)}$$

where e represents the electron charge, k_0 is the rate constant assumed to be ($200 \text{ s}^{-1} \cdot \text{site}^{-1}$), K_b refers to the Boltzmann's constant ($8.617 \times 10^{-5} \text{ eV} \cdot \text{K}^{-1}$), and T is the temperature (298 K^{-1}).

CHAPTER FOUR

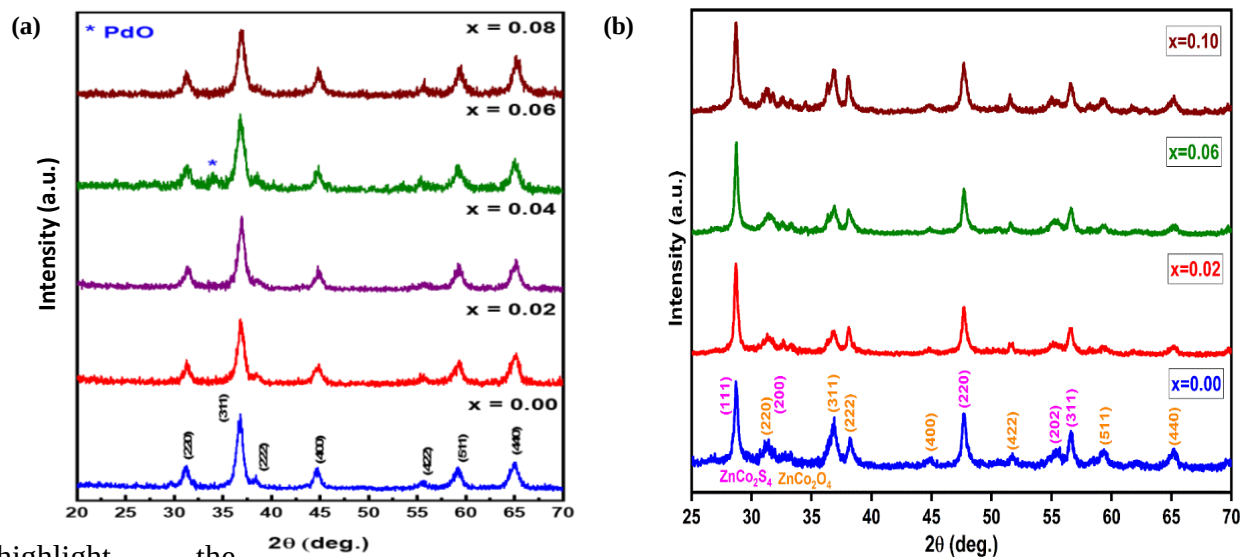
RESULTS AND DISCUSSION

4.1 Phase Analysis and Morphology Evaluation

XRD diffraction powder pattern was performed for investigating the crystal structure and phase purity of the $\text{ZnPd}_x\text{Co}_{2-x}\text{X}_4$ ($0.00 \leq x \leq 0.08$) NECs powder. The obtained diffraction data were further analyzed using Rietveld refinement with Match! 3 and Fullprof software to determine the lattice parameters and crystallite size. For the ZnCo_2O_4 , the presence of the spinel phase was confirmed by the XRD pattern, which displays the characteristic peaks of the ZnCo_2O_4 cubic spinel phase according to Card No. [96-591-0137] as illustrated in **Figure 7a**. In contrast, all the samples of the ZnCo_2S_4 diffraction pattern exhibited the distinctive peaks of ZnCo_2O_4 and ZnCo_2S_4 , indicating the coexistence of a cubic spinel structure [70]. This is ascribed to the two-step preparation method. The ratios exhibited the distinctive peaks of the cubic spinel structure, as depicted in **Figure 7b**. The pattern displayed widened peaks, signifying a smaller crystal size of around 31 nm.

The $\text{ZnPd}_x\text{Co}_{2-x}\text{X}_4@\text{NF}$ NECs morphology was analyzed by SEM at various magnifications, as illustrated in **Figure 8a**. For the $\text{ZnPd}_x\text{Co}_{2-x}\text{O}_4@\text{NF}$, the composition ($x = 0.04$ and $x = 0.08$) was chosen for analysis. The surface morphology analysis for these compositions revealed that the Ni foam was uniformly coated with three-dimensional microspheres composed of interconnected nanosheets. The images further show that an increase in the Pd content results in a reduction in the microsphere size and an increase in their surface density. In contrast, the ($x = 0.04$ and $x = 0.06$) composition for the $\text{ZnPd}_x\text{Co}_{2-x}\text{S}_4@\text{NF}$ was chosen for analysis, as shown in **Figure 8b**. The surface scanning results of the NECs indicate the production of three-dimensional microspheres

and demonstrate surface roughness. The $x=0.06$ sample shows a few nanosheets mixed with spherical particles dispersed randomly on the Ni foam's surface. These morphological changes



highlight the
Figure 7: XRD pattern of the (a) $\text{ZnPd}_x\text{Co}_{2-x}\text{O}_4$ ($0.00 \leq x \leq 0.08$)@NF (b) $\text{ZnPd}_x\text{Co}_{2-x}\text{S}_4$ ($0.00 \leq x \leq 0.10$)@NF NECs

significant influence of surface structure on the electrochemical performance.

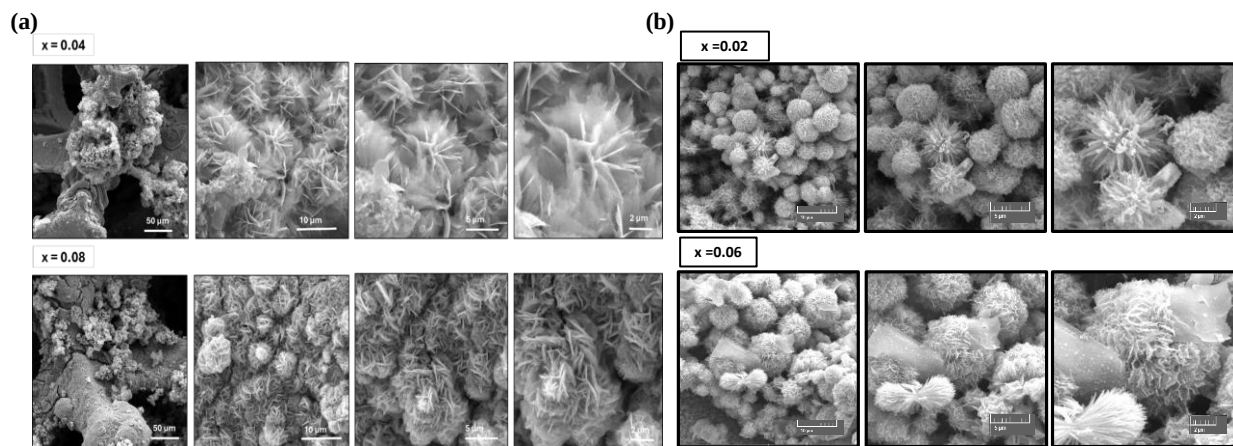


Figure 8: SEM images of (a) $\text{ZnPd}_x\text{Co}_{2-x}\text{O}_4$ ($x=0.04$ and $x=0.08$) (b) $\text{ZnPd}_x\text{Co}_{2-x}\text{S}_4$ ($x = 0.02$ and 0.06) NECs.

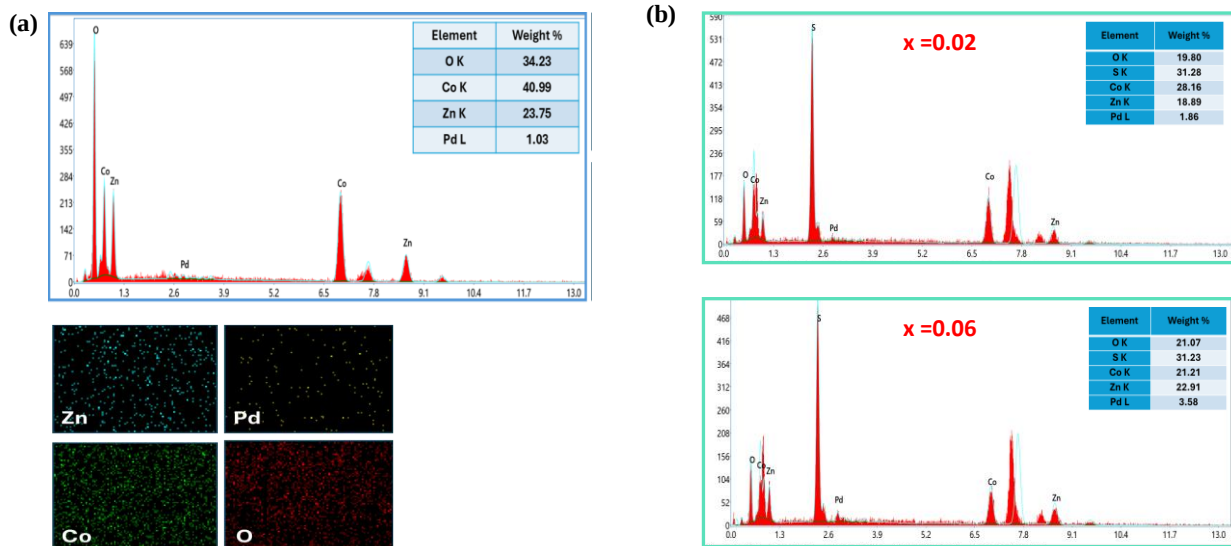


Figure 9: EDX spectra and elemental mapping of (a) $\text{ZnPd}_x\text{Co}_{2-x}\text{O}_4$ ($x=0.08$) (b) $\text{ZnPd}_x\text{Co}_{2-x}\text{S}_4$ ($x=0.02, 0.06$) NECs.

Figure 9 displays the elemental composition and corresponding elemental mapping of the NECs investigated in this study. The results of the EDX analysis for the $\text{ZnPd}_x\text{Co}_{2-x}\text{O}_4$ ($x=0.08$)@NF confirm the presence of Zn, Pd, Co, and O elements, with no evidence of additional peaks. Furthermore, the elemental analysis of $\text{ZnPd}_x\text{Co}_{2-x}\text{S}_4$ ($x = 0.02$ and 0.06)@NF NECs using EDX is displayed in **Figure 9b**. The EDX analysis demonstrates the existence of elements including Zn, Pd, Co, S, and O with no extraneous peaks. This indicates the successful incorporation of the desired elements into the catalyst structure without noticeable impurities. Furthermore, **Figure 10** reveals the TEM analysis of the NECs under investigation. The TEM images confirmed the spherical morphology of $\text{ZnPd}_x\text{Co}_{2-x}\text{O}_4$ ($x=0.08$) particles, as shown in **Figure 10**. Additionally, the High-resolution TEM (HR-TEM) analysis was conducted to measure the lattice fringe spacing using GATAN software, thereby verifying the presence of the spinel oxide phase. Meanwhile, the TEM images displayed in **Figure 10** illustrate the thinner nanosheets of $\text{ZnPd}_x\text{Co}_{2-x}\text{S}_4$ ($x=0.06$) particles. The image depicted the phase interface between the edges and the inside, indicating that sulfur coated the outside surface of ZnCo_2O_4 , forming the ZnCo_2S_4 structure. The HR-TEM

analysis was conducted to ascertain the distance between lattice fringes, revealing distances of 0.13 and 0.14 nm corresponding to the (400) and (440) planes of $\text{ZnPd}_2\text{Co}_{2-x}\text{O}_4$, while 0.16 nm was noted for the (311) plane of ZnCo_2S_4 . These findings confirm the presence of the spinel phase [70].

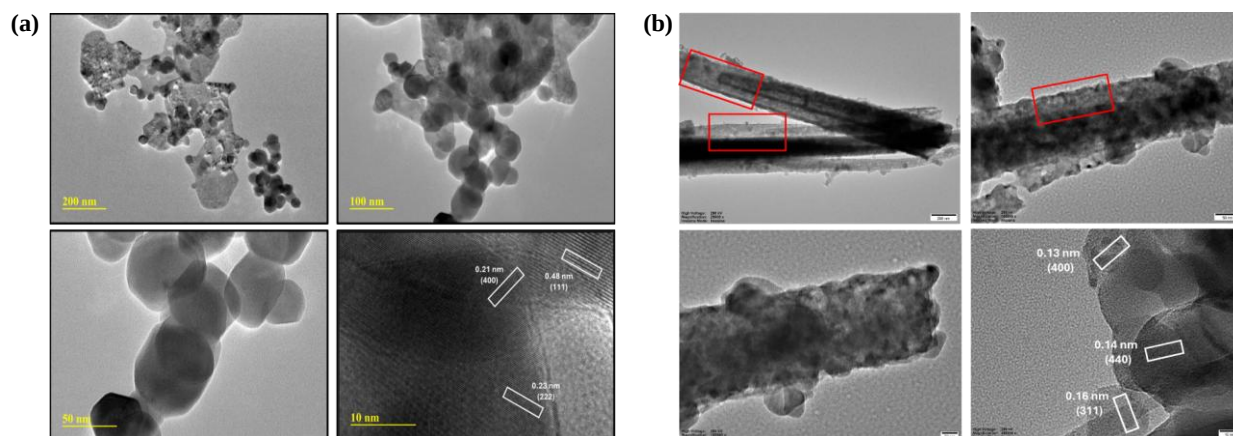


Figure 10: TEM and HRTEM of $\text{ZnPd}_x\text{Co}_{2-x}\text{O}_4$ ($x=0.08$)@NF NECs. (b) TEM and HRTEM images of $\text{ZnPd}_x\text{Co}_{2-x}\text{S}_4$ ($x=0.06$)@NF NECs

4.2 XPS Analysis

XPS was employed to analyze the elemental composition and oxidation states of the synthesized $\text{ZnPd}_x\text{Co}_{2-x}\text{O}_4$ ($x=0.08$)@NF and $\text{ZnPd}_x\text{Co}_{2-x}\text{S}_4$ ($x=0.06$)@NF NECs. The survey scans displayed for the oxide catalyst in **Figure 11** confirmed the existence of Zn, Pd, Co, O, and Ni. Furthermore, the characteristic binding energies for each element in the oxide NECs were analyzed using High-resolution scans. These scans are presented in **Figures 11(b-f)**. The Zn 2p spectra in **Figure 11b** exhibit Zn^{2+} oxidation states, with ($2p_{3/2}$) and ($2p_{1/2}$) observed around ~ 1020 and ~ 1043 , respectively. The Pd 3d spectra exhibited doublet peaks, including the $3d_{5/2}$ and $3d_{3/2}$ states possessing binding energies of ~ 337 eV and ~ 342 eV, thereby verifying the presence of Pd^{2+} and

the successful incorporation of Pd into the spinel framework. The Pd spectra are displayed in **Figure 11c**.

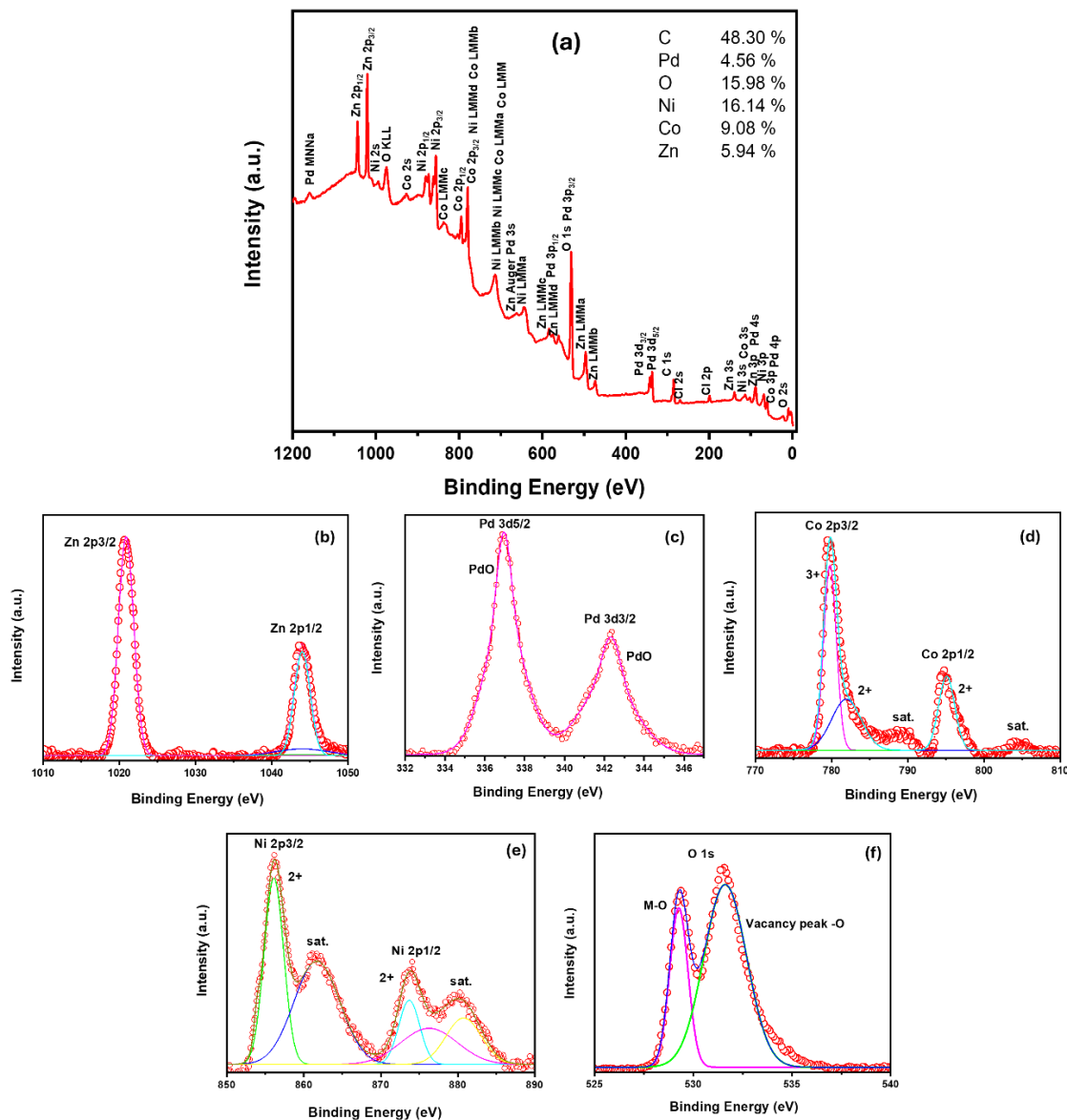


Figure 11: XPS analysis of $\text{ZnCo}_{2-x}\text{Pd}_x\text{O}_4$ ($x=0.08$)@NF NECs with (a) survey scan, and spectrum of (b) Zn 2p, (c) Co 2p, (d) Pd 3d, (e) Ni 2p, and (f) O 1s.

The deconvoluted Co 2p spectra (**Figure 11d**) revealed 2 main peaks at 779 eV and 782 eV, corresponding to the $2p_{3/2}$ orbital, and also confirm the existence of the Co^{3+} and Co^{2+} oxidation states of Co in the NECs. Additionally, a core peak was observed at 794 eV, this peak is assigned

to the $\text{Co}2p_{1/2}$ orbital, which further confirms the presence of Co^{2+} , with satellite peaks at 789 eV and 904 eV. The coexistence of Co^{3+} and Co^{2+} in the sample indicates that cobalt ions occupy both tetrahedral and octahedral sites within the spinel oxide lattice. **Figure 11e** shows the $\text{Ni}2p$ spectrum, confirming the presence of the underlying Ni foam substrate beneath the $\text{ZnPd}_x\text{Co}_{2-x}\text{O}_4$ ($x = 0.08$) NECs layer. The $\text{Ni}2p_{3/2}$ and $2p_{1/2}$ peaks appear at 856 eV and 873 eV, respectively, along with corresponding satellite peaks at 861 eV and 880 eV [93]. Lastly, the O 1s spectrum in **Figure 11f** exhibits two peaks around 529 eV and 531 eV, which are attributed to metal-oxygen bonds and oxygen vacancies within the spinel oxide lattices.

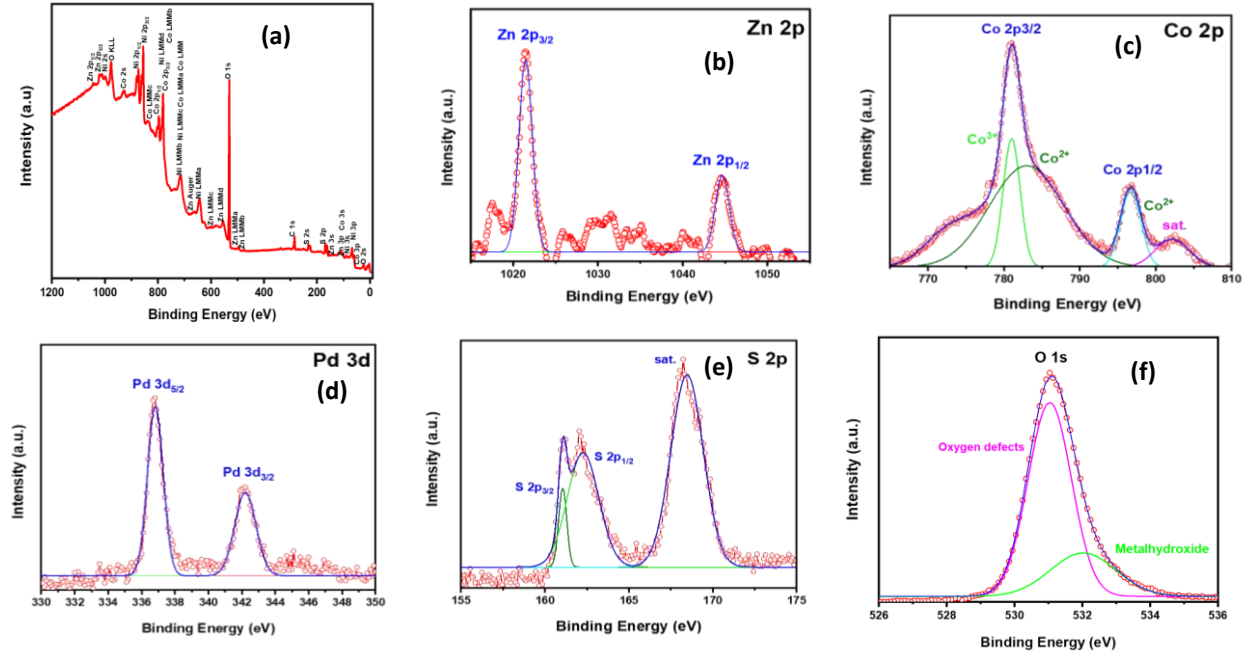


Figure 12: XPS analysis of $\text{ZnCo}_{2-x}\text{PdxS}_4$ ($x=0.06$)@NF NECs with (a) survey scan, and spectrum of (b) Zn 2p, (c) Pd 3d, (d) Co 2p, (e) S 2p, and (f) O 1s.

The XPS of $\text{ZnPd}_x\text{Co}_{2-x}\text{S}_4(0.06)\text{@NF}$ is presented in **Figure 12**. The figure includes the broad survey scan and high-resolution spectra for detailed elemental and chemical state analysis. The survey analysis revealed the presence of the following elements: Co, Zn, Pd, S, and O, as illustrated

in **Figure 12a**. As shown in **Figure 12(b-f)**, the high-resolution analysis was applied to individual elements by scanning within a small range of energy.

As can be seen in **Figure 12b**, the Zn 2p spectra had two split peaks at Zn 2p_{3/2} and Zn 2p_{1/2}. These peaks had binding energies of 1021 eV and 1044 eV, respectively, which indicated the presence of Zn²⁺ [58]. The XPS Pd 3d spectra are displayed in **Figure 12c**, and these spectra present double peaks in the 3d_{5/2} and 3d_{3/2} states, with binding energies of 336.0 eV and 342 eV, respectively, indicating the presence of Pd²⁺ [94]. **Figure 12d** displays the spectra for Co 3p; these peaks are observed at 776 eV, 781 eV, and 796 eV, 797.5 eV corresponding to Co 2p_{3/2} and Co 2p_{1/2}, which indicate the coexistence of Co³⁺ and Co²⁺ [95]. **Figure 12e** shows the XPS spectra of S 2p, which illustrate two peaks at 161 eV and 162 eV, corresponding to S 2p_{3/2} and S 2p_{1/2}, and the bond between zinc and sulfur is represented by the peak at 168 eV, respectively [96]. As illustrated in **Figure 12F**, the O 1s spectra were recorded at 531 eV and 532 eV, which correspond to oxygen defects and metal hydroxide [97].

4.3 Electrochemical HER Performance

4.3.1 ZnPd_xCo_{2-x}O₄@NF HER performance

The electrocatalytic efficiency of ZnPd_xCo_{2-x}O₄ (0.00 ≤ x ≤ 0.08)@NF coated on conductive Ni foam was evaluated using a three-electrode setup in 0.1 M KOH and a pH of 13.6. As shown in **Figure 13a**, linear sweep voltammetry (LSV) curves revealed that Pd doping significantly enhanced the HER activity of the ZnPd_xCo_{2-x}O₄@NF catalyst compared to the undoped ZnCo₂O₄@NF, which possesses an overpotential of 345 mV vs. RHE at a constant current density (J) of -10 mA/cm². The Pd²⁺ incorporation improves the pristine ZnCo₂O₄@NF by modifying the electronic configuration of Co, increasing active sites, and enhancing proton adsorption.

For the various samples of the $\text{ZnPd}_x\text{Co}_{2-x}\text{O}_4@\text{NF}$ analyzed, the $\text{ZnPd}_x\text{Co}_{2-x}\text{O}_4$ ($x=0.08$)@NF exhibited the best HER performance, achieving a low potential of ~ 31 mV as seen in the histogram plot in **Figure 13b**, outperforming all other doping concentrations. To further support this result, the cyclic voltammetry (CV) at different potentials, the electrochemical surface area (ECSA) of the $\text{ZnPd}_x\text{Co}_{2-x}\text{O}_4$ ($x=0.08$)@NF was estimated. **Figure 13c** illustrates the CV curve of the $\text{ZnPd}_x\text{Co}_{2-x}\text{O}_4$ ($x=0.08$)@NF NECs. In **Figure 12d**, the double-layer capacitance (Cdl) exhibits a linear relationship, and the $\text{ZnPd}_x\text{Co}_{2-x}\text{O}_4$ ($x=0.08$)@NF electrode exhibited the highest Cdl capacitance of $4780 \mu\text{F}/\text{cm}^2$. This value represents a remarkable 61.13-fold increase in Cdl compared to the undoped ZnCo_2O_4 electrode Cdl $78.2 \mu\text{F}/\text{cm}^2$, confirming that the Pd^{2+} incorporation significantly enhances HER activity through electrochemically active sites increment.

The ECSA was estimated by calculating the Cdl from the CV measurements performed at different scan rates within the non-faradaic potential region. The histogram plot displaying the ECSA (**Figure 14a**) for each composition indicates that $\text{ZnPd}_x\text{Co}_{2-x}\text{O}_4$ ($x=0.08$)@NF NECs exhibits a substantial increase in ECSA, achieving an impressive value of 119.5 cm^2 , compared to the ECSA value of 1.955 cm^2 for the undoped pristine spinel $\text{ZnCo}_2\text{O}_4@\text{NF}$ electrode. This improvement is attributed to the Pd^{2+} inhibiting the surface oxidation of ZnCo_2O_4 while promoting its reduction.

To investigate the charge-transfer kinetics at the semiconductor-electrolyte interface, the EIS characterization was employed. The EIS measurement was performed by examining the Nyquist curve of the $\text{ZnPd}_x\text{Co}_{2-x}\text{O}_4$ ($0.00 \leq x \leq 0.08$)@NF NECs, which reveals a semicircular arc for both the doped and undoped Pd^{2+} ZnCo_2O_4 , as shown in **Figure 14b**. Notably, the $\text{ZnPd}_x\text{Co}_{2-x}\text{O}_4$ ($x=0.08$)@NF NECs displays a smaller semicircle with a reduced diameter, indicating lower charge-transfer resistance relative to the other evaluated NECs [98]. This suggests a more efficient

charge-transfer across the solid-electrolyte interface, which facilitates the HER [99]. Furthermore, the Tafel slope of the $\text{ZnPd}_x\text{Co}_{2-x}\text{O}_4$ ($x=0.08$)@NF NECs was found to be 54.3 mV/dec as depicted in **Figure 14c**. This value indicates the dominance of the Volmer-Heyrovsky mechanism in the overall HER process. The CP test conducted indicated that the $\text{ZnPd}_x\text{Co}_{2-x}\text{O}_4$ ($x=0.08$)@NF NECs exhibited a stability of 72 h under constant potential at a current density of 20 mA cm^{-2} while suffering minimal degradation as indicated in **Figure 14d**.

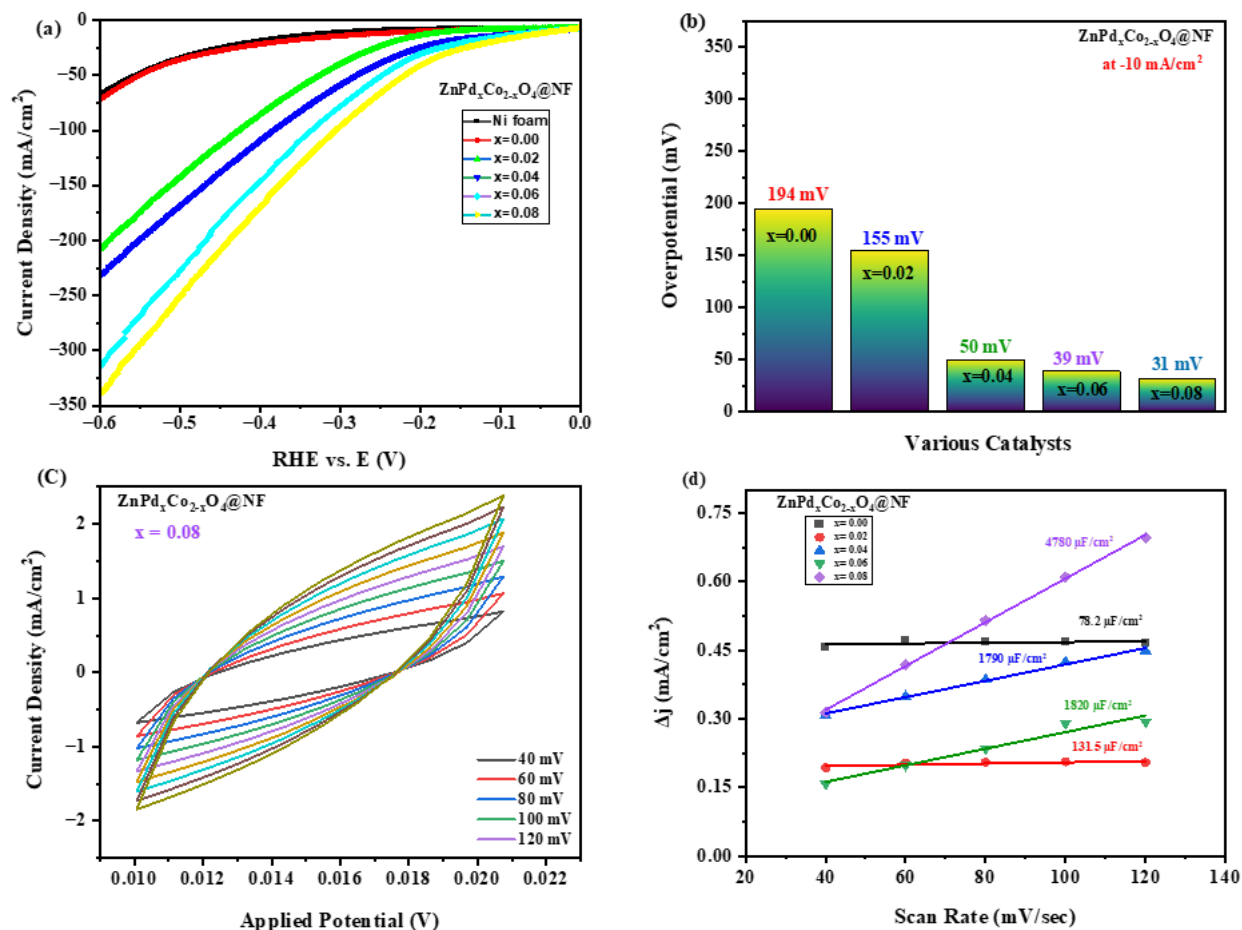


Figure 13:(a) LSV polarization plots; (b) Overpotential (η) histogram; (c) CV curve of $\text{ZnPd}_x\text{Co}_{2-x}\text{O}_4$ ($x=0.08$) NECs; (d) Cdl of $\text{ZnPd}_x\text{Co}_{2-x}\text{O}_4$ electrocatalyst in KOH (1.0 M) solution

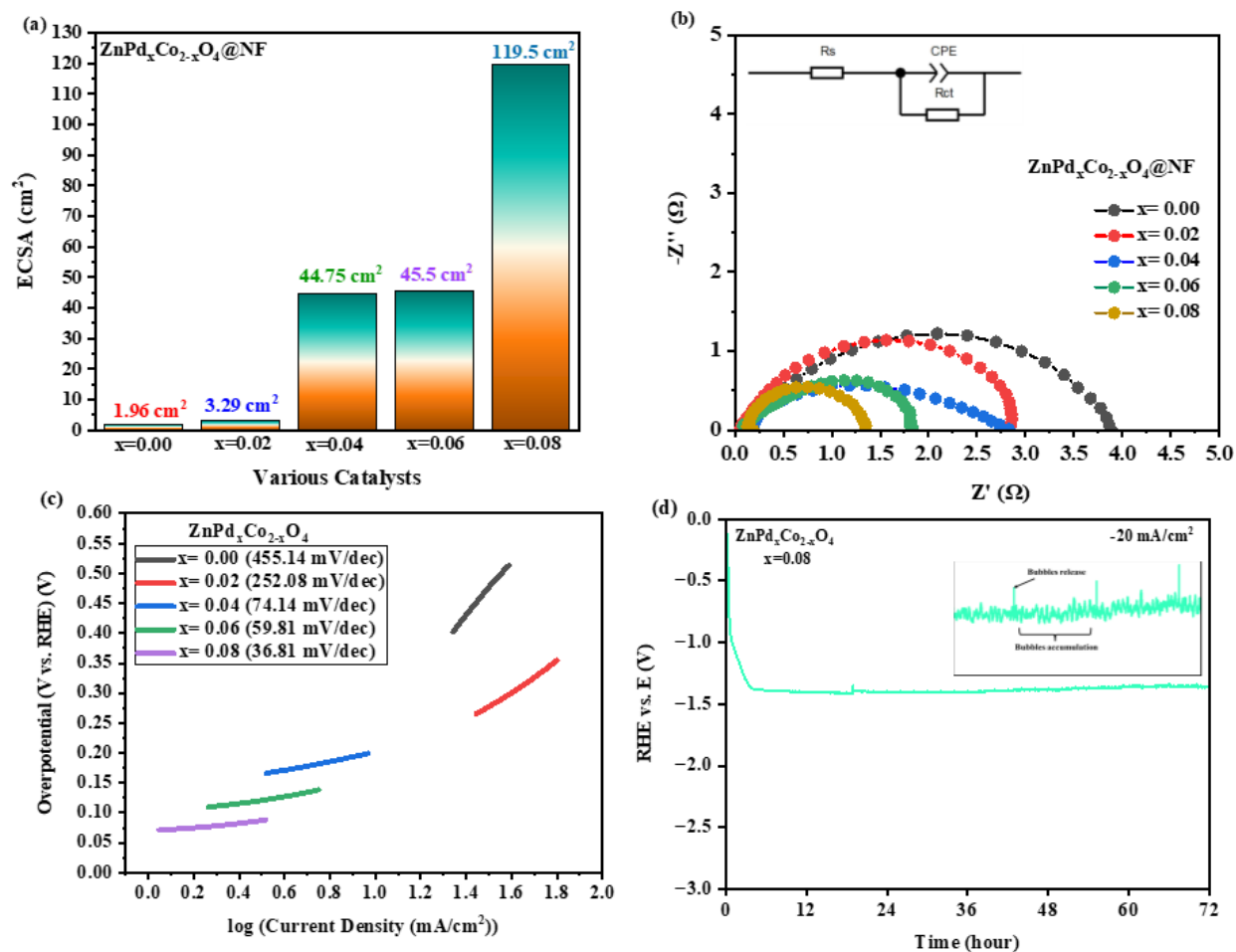


Figure 14: (a) ECSA histogram, (b) EIS spectra, (c) Tafel plots of ZnPd_xCo_{2-x}O₄@NF nanoelectrocatalyst, (d) CP curve of ZnPd_xCo_{2-x}O₄@NF (x = 0.08) nanoelectrocatalyst in KOH (1.0 M) solution

4.3.2 ZnPd_xCo_{2-x}S₄@NF HER performance

For the electrochemical measurement performed for the sulfide catalyst, **Figure 15a** shows that the ratio of x=0.06 of ZnPd_xCo_{2-x}S₄@NF achieved the lowest overpotential around -166 mV at -10 mA/cm² while other ratios of x=0.00, 0.02, and 0.10 are all higher than the best optimized one in which they achieved 281 mV, 185 mV, and 204 mV, respectively as depicted in **Figure 15b**. However, they are all better than bare nickel foam washed with HCl, D.I water, Ethanol, and then DI water that is sonicated for 10 minutes each and then heated at 350°C for 2 h. This good performance is pointed to the existence of Co²⁺ and Co³⁺ couple in the structure, which provides

numerous solid redox species in spinel structure that offer rich catalytically active sites to promote heterogeneous reduction reaction, i.e. HER.

Moreover, the electrochemical double-layer capacitance, C_{dl} , in **Figure 15c** was plotted depending on a non-faradic portion from -0.259 V to -0.249 V at scan rates of (40, 60, 80, 100, 120) mV/s, CV of $ZnPd_xCo_{2-x}S_4@NF$ at ($0.00 \leq x \leq 0.10$). The inset of **Figure 15c** represents the most significant value of ECSA that is concluded from C_{dl} , which indicates that more active sites are exposed during electrocatalysis for $ZnPd_xCo_{2-x}S_4@NF$ of the ratio of $x=0.06$ of a value of 27.0 cm^2 . However, this value is close to the ECSA of the ratio $x=0.00$, 0.02, and 0.10, which they are 8.68 cm^2 , 15.38 cm^2 and 11.75 cm^2 that can be interpreted as the materials that they are fabricated from are similar, so they have close behavior as noticed from the C_{dl} plot, as well as the Tafel slopes presented in **Figure 16a**. Nyquist plots in **Figure 15d** represent the semicircular behavior of low charge transfer resistance that agrees with the performance of the HER process, in which $ZnPd_xCo_{2-x}S_4@NF$ of $x=0.06$ has the smallest value of ~ 1.9 ohms. **Figure 16a** illustrates that the smallest value of Tafel slope for $ZnPd_xCo_{2-x}S_4@NF$ is that of the ratio of $x=0.06$, exhibiting a value of 127.7 mV/dec, explaining its remarkable performance toward the HER process, and displaying the smallest value compared to other ratios that have larger values.

Based on the previous best attitude of $ZnPd_xCo_{2-x}S_4@NF$ of ratio $x=0.06$, it was chosen to be under the stability test of chronopotentiometry (CP). In **Figure 16b**, it was noticed that there was progress in performance toward HER after the stability test for 40 h, as illustrated in **Figure 16b** and it may be due to the gradual activation of the $ZnPd_xCo_{2-x}S_4@NF$ of $x=0.06$ electrocatalyst from the surface to the center, besides the penetration through the big surface cracks in the sample that led to the activation of the active sites below the electrode outer surface. These reliable reasons were introduced by Yihui Wu *et al.* in their work with Ni-S@NF electrocatalyst [100].

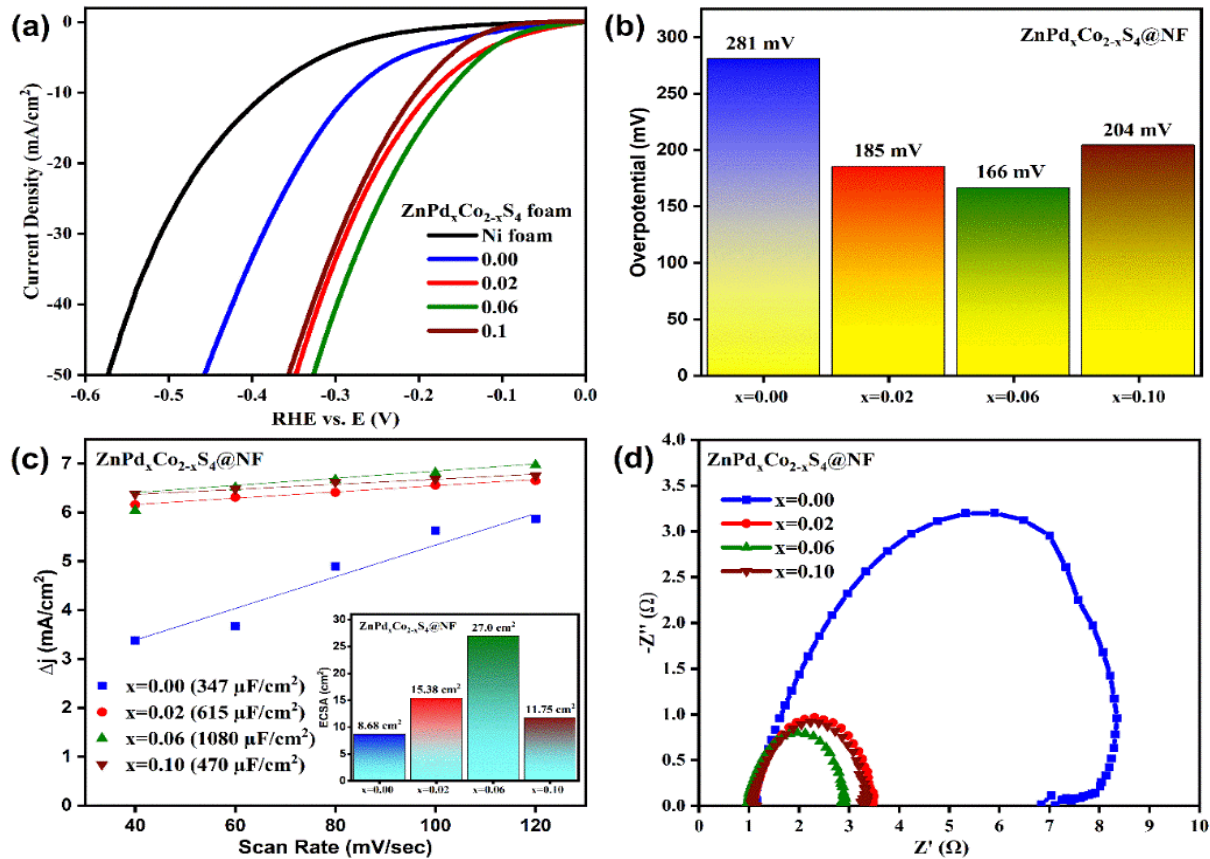


Figure 15: (a) ECSA histogram, (b) EIS spectra, (c) Tafel plots of ZnPd_xCo_{2-x}S₄@NF nanoelectrocatalyst, (d) CP curve of ZnPd_xCo_{2-x}S₄@NF (x = 0.08) nanoelectrocatalyst in KOH (1.0 M) solution

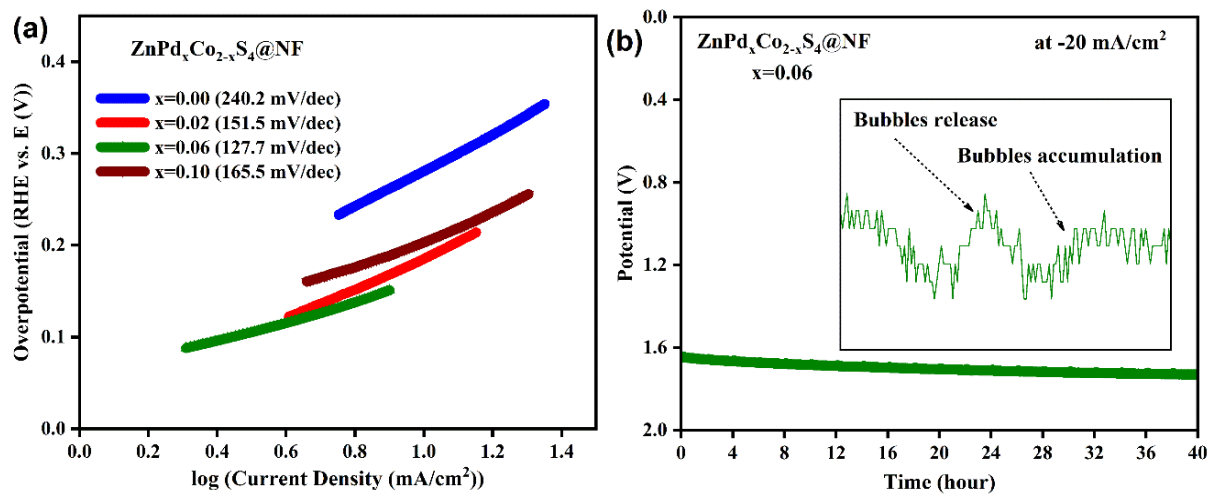


Figure 16: (a) Tafel plots of ZnPd_xCo_{2-x}S₄@NF (0.00 ≤ x ≤ 0.10) nanoelectrocatalyst; (b) Chronopotentiometry curve of ZnPd_xCo_{2-x}S₄@NF (x = 0.06) electrocatalyst in 1M KOH solution.

4.4 Theoretical Investigation of Pd-doped Spinel Oxides

4.4.1 Structural Properties

Firstly, the bulk structures were initially optimized to ensure accurate surface modeling of the electrocatalyst. The $Fd\bar{3}m$ space group, the most commonly observed phase in spinel structures, was obtained from the Materials Project database. Following a series of optimization procedures, the lattice parameter for the ZnCo crystal structure was evaluated to be 8.157 Å. This aligns closely with the experimentally obtained values of 8.13 Å from the XRD powder pattern. To model the ZnPd system, a Pd atom was introduced into the optimized ZnCo structure, resulting in an elongation of the lattice to 8.195 Å. The optimized configurations for both structures are presented in **Figure 17**. The equation of state (E vs V) plot used to determine the equilibrium unit cell volume is presented in **Appendix A(a)**. A comparative summary of the experimental and theoretically calculated lattice parameters is provided in **Table 3**.

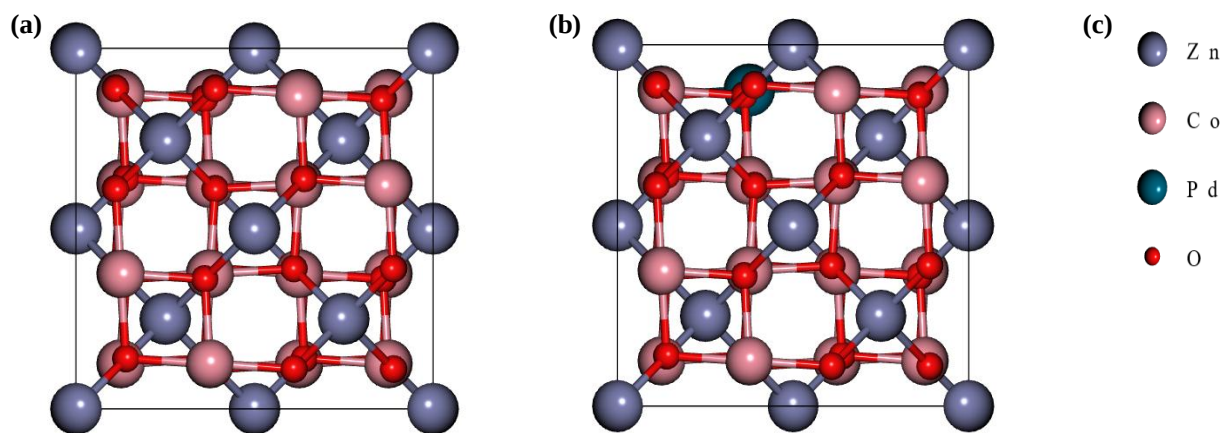


Figure 17: Optimized Bulk Unit Cell of (a) ZnCo_2O_4 (b) $\text{ZnCo}_{2-x}\text{Pd}_x\text{O}_4$

Table 3: Optimized lattice parameter for ZnCo₂O₄ & ZnCo_{2-x}Pd_xO₄ spinel structures

Structure	Experimental		Theoretical	
	a(Å)	V(Å ³)	a(Å)	V(Å ³)
ZnCo ₂ O ₄	8.123	535.890	8.157	542.740
ZnCo _{2-x} Pd _x O ₄	8.130	537.367	8.195	550.360

4.4.2. Catalytic Properties

To investigate the origin of the exceptional performance of the ZnPd electrocatalyst towards HER in comparison to pure ZnCo, the adsorption, and Gibbs free energies ((E_H) & (ΔG_H)) of HER intermediates including H₂O and H were computed by adsorbing these intermediates on a relaxed surface of the optimized bulk unit cells. **Figure 18 (a-f)** displays the relaxed surfaces with hydrogen and water adsorbed on the pristine ZnCo & ZnPd slabs, respectively. These two intermediates are essential in evaluating the performance of electrocatalysts in HER. Sabatier's principle provides a starting procedure for optimizing a two-step reaction involving an adsorbed intermediate, such as the HER [101]. It states that the adsorption energy should neither be too high nor too low for an efficient electrocatalyst. If the adsorption energy is too high (i.e., too positive) the adsorption becomes weak slowing the process, forming the limiting step for the overall reactions. Conversely, if it is too low (i.e., too negative), the hydrogen binds too strongly to the catalyst, hindering its desorption. Hence, the energy for adsorbing hydrogen (H^*) on the two catalysts was first used to screen the active sites on the catalysts. The reaction proceeds as follows:



The adsorption energy (E_H) and Gibbs free energy (ΔG_H) for adsorbed H^* hydrogen atom was determined by adsorbing a hydrogen atom onto the ZnCo and ZnPd surfaces. The (E_H) & (ΔG_H) for the most favorable adsorption height were then calculated. The results indicate that H^* adsorption is more feasible on the Zn sites of both surfaces, with ZnPd having a slight advantage over ZnCo. The calculated E_H & (ΔG_H) values are -0.72 eV, -0.71 eV & -0.48 eV, -0.47 eV for both surfaces respectively. Since we aim to evaluate the role of the Pd atom in improving the HER activity of the ZnPd catalyst, the (E_H) & (ΔG_H) on this site was also determined to be 0.21eV & 0.45 eV respectively. This result suggests that the Zn sites are the active center for hydrogen adsorption on both ZnCo & ZnPd, respectively. The complete table of computed adsorption energies for the HER intermediates is provided in **Tables 4, 5 & 6**.

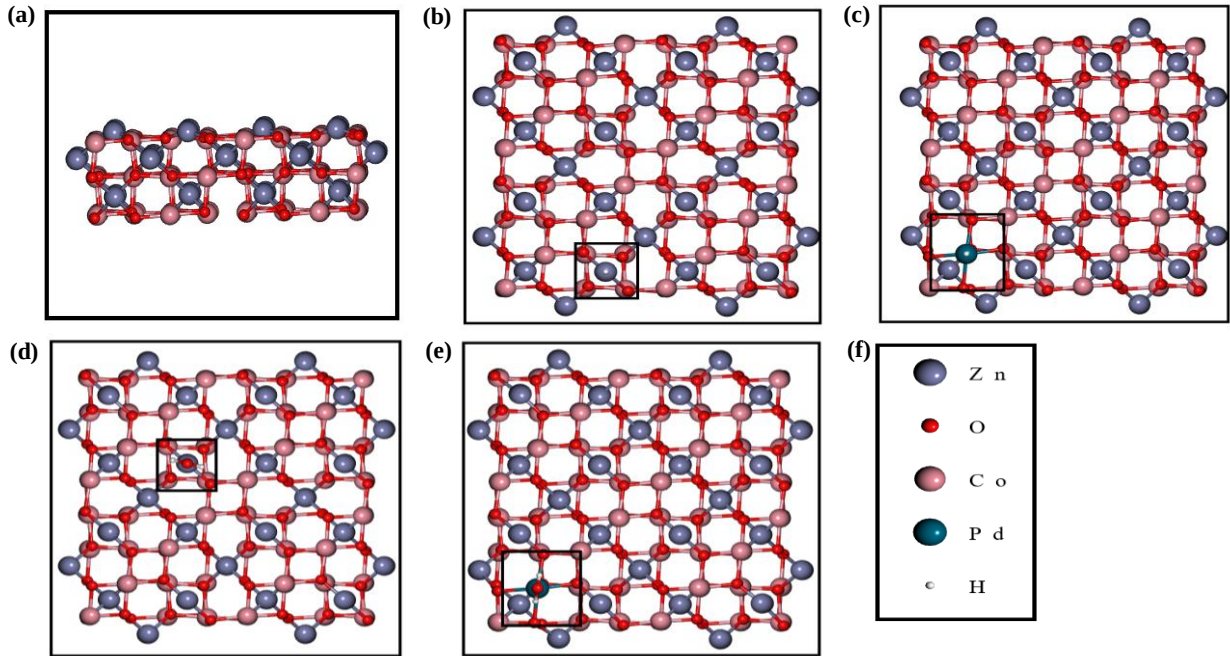
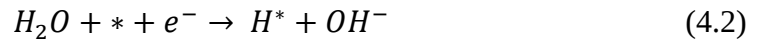


Figure 18: (a) Side view of the pristine ZnCo₂O₄ surface. Top view of the ZnCo₂O₄ surface with a single Hydrogen atom adsorbed on (b) a Zn site (c) a Pd site. Top views of H₂O molecule adsorption on the ZnCo_{2-x}Pd_xO₄ surface at (d) a Zn site (e) a Pd site (f) color legend

Figure 19 (a & b) shows a reaction coordinate representation of the computed values of (ΔG_H) for all active sites on both catalysts. Additionally, **Figure 19(c)**, shows the volcano plots for comparing the activity of the active sites based on their adsorption strength for (H^*) . The volcano plot results from the plot of the rate constant i.e., the $\log(i_0)$ versus the Gibbs free energy for hydrogen adsorption (ΔG_H) [101]. The sites located on the right side of the volcano plot indicate weak adsorption of H^* , while those on the left side represent strong hydrogen adsorption. This analysis confirms that the Zn sites on both catalysts serve as the active sites for H^* adsorption.

Due to the ZnPd and ZnCo catalysts exhibiting similar affinity towards adsorbing H^* we further investigate the adsorption of H_2O molecules on both catalysts because of their impact on catalyst efficiency in alkaline media. The initial step in the HER for most electrocatalysts is the adsorption of a water molecule onto the catalyst surface and its dissociation into adsorbed hydrogen (H^*) and hydroxyl ions (OH^-) [8]. This reaction is represented as:



To evaluate water adsorption energies on the NECs surface, a H_2O molecule (denoted as H_2O^*) was adsorbed on three adsorption sites of interest, these include the Zn site for the ZnCo catalyst labeled as (Zn) and the Zn & Pd on the ZnPd catalyst labeled as (Zn_{Pd} & Pd). The adsorption energy of the water molecule (E_{H_2O}) on the Zn, Zn_{Pd} & Pd sites are -0.19, -0.13 & -0.08 eV respectively, while the Gibbs free energy (ΔG_{H_2O}) for adsorption on these sites respectively are 0.37, 0.43 & 0.48 eV. This result suggests that water binds favorably on the ZnCo catalyst's Zn site and the ZnPd catalyst's Zn & Pd site. Further calculations were performed to calculate the energy barrier from adsorption of a water molecule to adsorption of a hydrogen atom [$(\Delta G_{H_2O}) - (\Delta G_H)$], and the results indicate that the ZnPd catalyst presented a much lower energy barrier of

0.03 eV on the Pd sites which is significantly lower than those of Zn (0.85 eV) and Zn_{Pd} (0.91 eV) respectively as indicated in **Figure 19d**. This result suggests that the H₂O molecule dissociates more easily on the Pd sites, suggesting that the ZnPd catalysts will need the lowest energy to break the bond of HO – H of the H₂O molecule. Hence, the Zn_{Pd} catalyst requires lower energy to generate the H* intermediates necessary for HER. Thus, the reason for its excellent performance towards HER in the alkaline media.

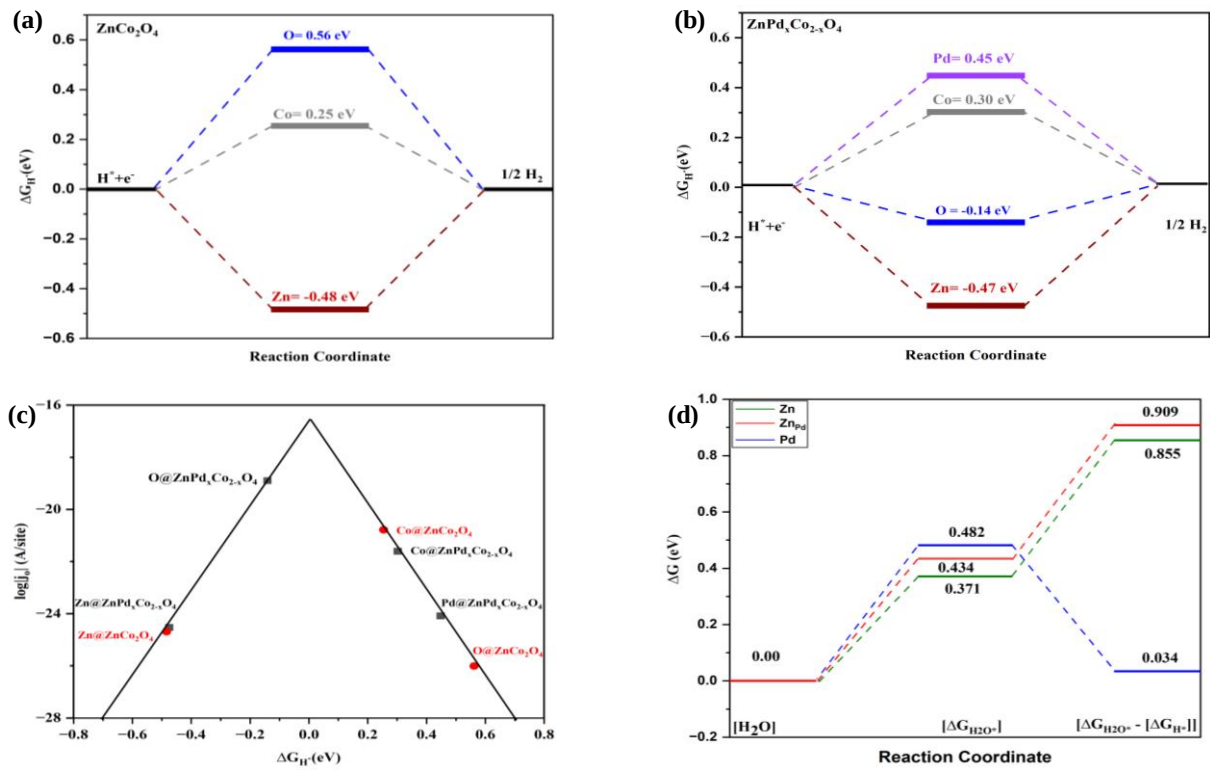


Figure 19: Gibbs free energy diagram for hydrogen adsorption (a) for ZnCo slab (b) for ZnPd slab (c) Volcano plot for active sites (d) Water adsorption/dissociation diagram on Zn, Zn_{Pd} & Pd sites

The Density Functional Theory (DFT) results reveal that H₂O molecules adsorb onto the Pd site and subsequently dissociate into (OH⁻) and (H*) species. The adsorbed hydrogen atom then binds to a nearby Zn atom forming the Volmer reaction step. The reaction then proceeds to form the H₂ molecule either via the Volmer-Heyrovsky routes or the Volmer-Tafel reaction routes. Our model adopts the conventional mechanism of the hydrogen evolution reaction (HER) in alkaline media

[102], this convention assumes that since HER occurs at the cathode, the generated OH^- ions are assumed to desorb from the electrode under a constant potential (eU), while the H^+ adsorbs on the surface, minimizing the impact of the OH^- on the catalytic HER process.

Table 4: Tabulated values of adsorption energy E_A and Gibbs free energy ΔG_H for ZnCo slab.

Adsorption Site	E_A (eV)	ΔG_H	$\log(i_0)$
Zn	-0.72443	-0.48445	-24.688
Co	0.01367	0.25367	-20.785
O	0.32231	0.56231	-26.011

Table 5: Tabulated values of adsorption energy E_A and Gibbs free energy ΔG_H for ZnPd slab

Adsorption Site	E_A (eV)	ΔG_H	$\log(i_0)$
Zn	-0.714	-0.474	-24.524
Co	0.062	0.302	-21.605
Pd	0.208	0.448	-24.083
O	-0.381	-0.141	-43.168

Table 6: Tabulated values of Gibbs free energy ΔG_{H_2O} on selected site on the $ZnCo_{2-x}Pd_xO_4$ slab

Adsorption site	ΔG_{H_2O}	ΔG_H	$[\Delta G_{H_2O} - \Delta G_H]$
Zn	0.371	-0.484	0.854994
Zn _{Pd}	0.434	-0.474	0.908791
Pd	0.485	0.448	0.034172

4.4.3. Electronic Properties

Furthermore, the electronic conductivity of the electrocatalysts plays an essential role in electrochemical water splitting, as it facilitates the essential step in charge carrier transport within the electrocatalyst [103]. Additionally, it is well known that metal doping provides an effective strategy to enhance the electronic conductivity of an electrocatalyst [104]. To further understand

the interplay between Zn and Pd atoms in the ZnPd catalyst and how it improves the material's exceptional catalytic activity for HER, electronic Density of States (DOS) calculations were performed. Notably, the DOS plot for the ZnCo structure indicates a discontinuity in its electronic structure around the Fermi level, a typical behavior of a semiconducting material. Meanwhile, the continuous distribution of the DOS around the proximity of the Fermi level in the ZnPd system, compared to the ZnCo system, indicates that Pd doping enhances the electronic structure of ZnCo, resulting in a metallic state around the Fermi level. Thus, indicating high electrical conductivity and fast charge transfer kinetics for the reduction of adsorbates. **Figures 20(a-d)** present the total DOS for the two structures. To gain a deeper understanding of the contributions of individual atomic components to the electronic DOS, the Projected Density of State (PDOS) was computed and analyzed. The PDOS [103] plot for Zn orbitals displayed in **Figure 20(b)** reveals that the Zn states primarily contribute to the DOS further away from the Fermi level in the region of the valence band (VB), with minimal contributions to the electronic state observed in the further region of the conduction band (CB). The PDOS plot for the Co orbitals, shown in **Figure 20(b)**, reveals that the Co states are highly concentrated near the Fermi level in the ZnCo structure, acting as the primary contributor to electronic transitions from the VB to the CB. Lastly, the O orbitals, as depicted in **Figure 20(b)**, contribute to the electronic DOS both around and beyond the Fermi level in both the CB and VB. For the ZnPd structure, the full PDOS plots are provided in **Figure 20c**, **which** provide insights into the electronic contributions of each atomic component. The PDOS for Zn in **Figure 20(d)** exhibits a similar trend to that of the pristine ZnCo structure. The Co PDOS, presented in **Figure 20 (d)**, also exhibits a similar pattern to the ZnCo structure, with contributions observed far from the Fermi level in both the CB and VB. However, around the Fermi level, additional states were observed; these states were not observed for the Co orbitals in the pristine

ZnCo structure. The PDOS for the Pd orbitals presented in **Figure 20(d)** shows that the dopant contributes majorly to the electronic state in regions closer to the Fermi level in both CB and the VB, with negligible contributions observed further away from the Fermi level. The O PDOS displayed in **Figure 20(d)** exhibits similar trends observed for the Co state, demonstrating the presence of states that were absent for the ZnCo structure around the Fermi level. Moreover, the PDOS plot highlights that the introduction of Pd as a dopant into the ZnCo structure induces a notable shift in the Fermi level toward the conduction band. This shift is attributed to the significant electronic states contributed by the dopant near the Fermi level, along with the Co and O components. The enhanced electronic states around the Fermi level facilitate rapid electron transfer to the adsorbate, thereby improving the HER kinetics. This explains the superior electrocatalytic activity of the Pd-doped ZnCo catalyst. The complete PDOS analysis for each atomic orbital is presented in **Appendices II (Figure S1 & S2)**.

The band diagram displayed in **Figure 21(a)** indicates that the ZnCo and ZnPd electrocatalysts' valence band's maximum and conduction band's minimum lie along the same momentum k-path, indicating their direct band type nature, which facilitates their electron transfer ability without loss of momentum [105]. The band energy dispersion also reveals that the ZnCo catalyst possesses a broader band gap around the Fermi level, reflecting its semimetallic behavior. The introduction of Pd into the ZnCo introduces new energy levels near the Fermi level, while also shifting the Fermi level closer to the conduction band, resulting in a reduced band gap, while also enhancing charge and electron transfer efficiency in ZnPd and significantly improving its electrocatalytic activity [89]. Moreover, the band diagram also reveals a band gap energy (E_g) of 0.84 eV in the ZnCo electronic structure. In contrast, a reduction in the energy gap was induced by the Pd dopant, shifting the Fermi level of the ZnPd closer to the CB as observed in **Figure 21(b)**, confirming its

superior metallic nature to the ZnCo structure. This metallic behavior reduces the energy barrier for electron transfer to H^+ species in the HER intermediates, enhancing its activity towards HER.

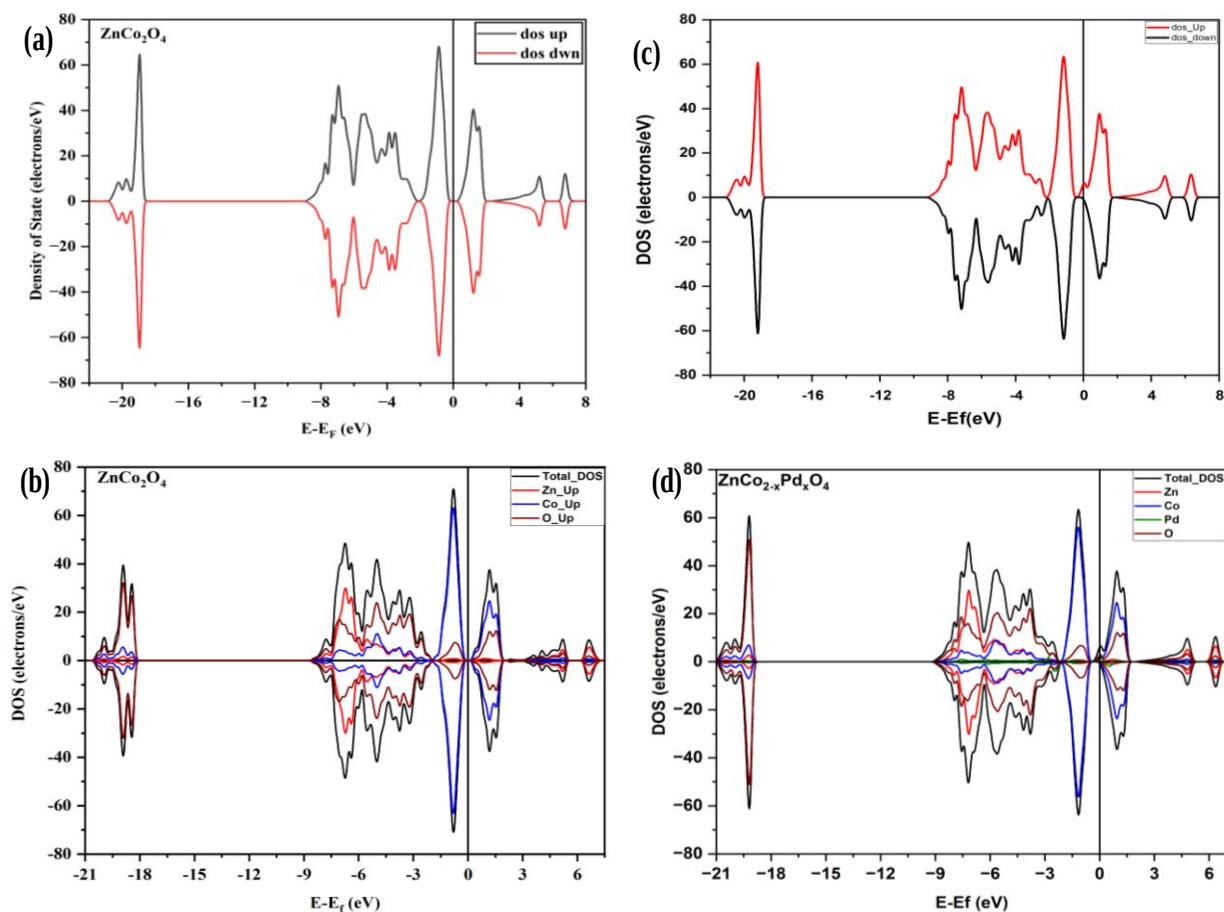


Figure 20: The total DOS plots for (a) ZnCo₂O₄ and (b) ZnCo_{2-x}Pd_xO₄ illustrating the contributions of all components across all energy levels. The Projected DOS (PDOS) plots for ZnCo₂O₄ for (c) ZnCo₂O₄, (d) ZnCo_{2-x}Pd_xO₄ illustrating the elemental contributions

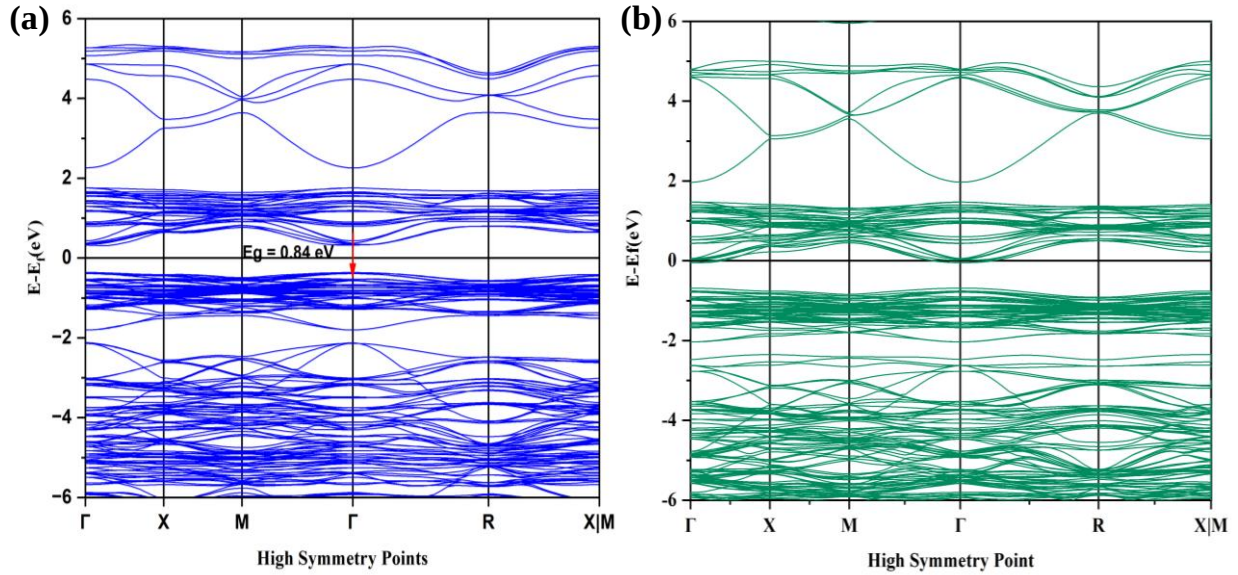


Figure 21: (a) ZnCo₂O₄, showing its electronic energy levels and band gap, and (b) ZnCo_{2-x}Pd_xO₄, illustrating the impact of Pd substitution on the electronic structure.

4.5 Theoretical Investigation of Pd-doped Spinel Sulfides Electrocatalytic Property

4.5.1 Structural Properties

To ensure the DFT calculations accurately model the experimental scenario, geometry optimization of the bulk structures was first performed. The $Fd\bar{3}m$ cubic structure corresponding to the phase of the ZnCo₂S₄ (ZCS) spinel structure observed from the XRD analysis was obtained and optimized. The structure was fully relaxed until the required criteria for accuracy were achieved. After optimization, the lattice parameter for the pristine ZnCo₂S₄ structure was computed as 9.62 Å. The lattice parameter was computed to be 9.67 Å after the structure was relaxed and a Pd atom was introduced to generate the ZnCo_{2-x}Pd_xS₄ (ZCP) system. The elongation in the lattice parameter highlights the structural distortion introduced by the Pd substitution, which is consistent with atomic size effects in the thiospinel framework. **Figure 22(a & b)** displays the

optimized geometries of the two structures. The equation of state (EOS) plot used to determine the equilibrium unit cell volume is presented in **Appendix A(b)**. A comparative summary of the experimental and theoretically calculated lattice parameters is provided in **Table 7**.

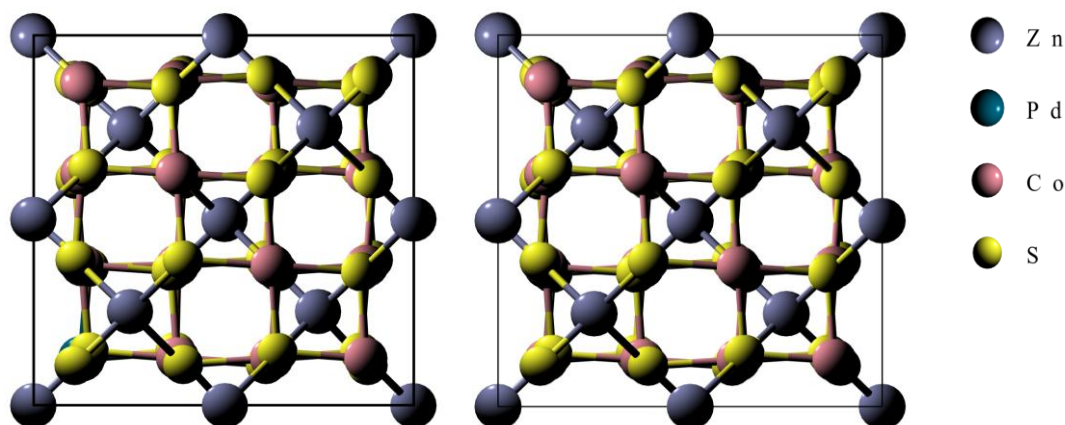


Figure 22: Optimized Bulk Unit Cell of (a) ZnCo_2S_4 (b) $\text{ZnCo}_{2-x}\text{Pd}_x\text{S}_4$

Table 7: Optimized lattice parameter for ZnCo_2O_4 & $\text{ZnCo}_{2-x}\text{Pd}_x\text{S}_4$ spinel structures

Structure	Experimental		Theoretical	
	$a(\text{\AA})$	$V(\text{\AA}^3)$	$a(\text{\AA})$	$V(\text{\AA}^3)$
ZnCo_2S_4	9.316	808.516	9.620	890.277
$\text{ZnCo}_{2-x}\text{Pd}_x\text{S}_4$	9.381	825.558	9.670	904.231

4.5.2 Electronic Properties

To probe the origin of the improved electrocatalytic properties observed in the ZPS catalysts compared to ZCS, their electronic properties were analyzed, as the performance of solid materials is closely related to their electronic structure. **Figure 23** presents the computed Density of State (DOS) and the Partial Density of State (PDOS) for the pristine ZCS and the Pd-doped ZCP

catalysts. The DOS plot for the ZnCo structure displayed in **Figure 23a** shows a discontinuity in its electronic structure around the Fermi level (0 eV), confirming the semiconductor nature of the material. The PDOS plot showing the contributions of the atomic components across various energy levels is displayed in **Figure 23b**. The PDOS plot indicates that the valence band maximum (VBM) near the Fermi level originates from the hybridization of the Co 3d and O 2p states. This suggests that these orbitals are primarily responsible for the excitations of electrons during the electrocatalytic reaction as they populate the Fermi level. Further away from the Fermi level in the valence band (VB) spanning from -3 to -9 eV, the contribution from the Zn 3d states becomes more pronounced, showing hybridization with the S 2p orbitals and minor involvement of Co 3d states. At the furthest part of the VB (~18 to ~21 eV), the predominant contributions arise from the hybridization of the Co 3d and S 2p states. Similarly, the Conduction Band Minimum (CBM) states are mainly derived from Co 3d and S 2p hybridization. The DOS/PDOS analysis highlights the covalent bonding nature between S and the two metals (Zn-S and Co-S) throughout the spinel lattice, as evidenced by the hybridization observed in the DOS plots [106]. Furthermore, the analysis reveals that the Co 3d and S 2p states are the primary contributors to electron excitations during the electrocatalytic reaction, as they dominate the states close to the Fermi level.

The DOS and PDOS plot for the ZCP, shown in **Figure 23(c & d)**, follows a pattern similar to that of the pristine ZCS. The most notable difference is the presence of states at the Fermi level of the ZCP, as indicated by **Figure 23c**, whereas no such states are observed for the ZCS structure. This shows the metallic nature of the ZCP as compared to the semiconducting nature of the ZCS catalyst. The emergence of states at the Fermi level in ZCP is attributed to the introduction of the Pd dopant, whose 4d orbital contributions primarily lie around the Fermi level, hybridizing with Co 3d and S 2p orbitals and thus shifting the Fermi level towards the conduction band. The

presence of electronic states in the Fermi level facilitates electron transfer between the catalyst and the adsorbate, explaining the improved HER characteristics observed for the ZCP catalyst, which aligns with findings from previous studies. Noble metal doping enhances electron transport and increases conductivity by introducing new states around the Fermi level, thereby promoting bonding with the HER adsorbate [107].

The electronic band structures of the electrocatalysts were analyzed to investigate their electronic properties further. The band structure plot for both the pristine and Pd-doped catalysts confirms their direct band gap nature, as the VBM and the CBM occur along the same high-symmetry K-path. This alignment facilitates electron excitations between the bands during the catalytic reaction without any loss of momentum. Additionally, the band structure analysis reveals the band gap for each material. The bandgap for the ZCS was determined to be 0.62 eV, while a reduction in this bandgap value was observed for the ZCP. This reduction is due to the Pd-dopant introducing new states near the Fermi level, shifting it towards the CB. This narrowing of the bandgap enhances the conductivity of the catalyst, resulting in a higher carrier transmission rate, an essential factor for improving the catalytic activity of the electrocatalysts [107], [108]. This reduction in bandgap makes the Pd-doped ZCS spinel catalyst highly suitable for HER applications by providing improved electronic and catalytic performance. **Figure 24(a & b)** presents the band plots for these structures.

Generally, the electronic properties reveal that the improvement in the activity observed for the ZCP catalyst over its ZCS counterpart can be attributed to the electronic states becoming more populated with a significant number of electrons due to the Pd-dopant. This shifted the electron states near the Fermi level to higher energies, thereby enhancing catalytic activity by increasing

the availability of electrons or holes for the reduction or oxidation process closer to the Fermi level [109].

The bandgap value for ZnCo_2S_4 as obtained in this study was computed to be 0.62 eV. This value differs significantly from the experimentally reported bandgap range of 1.60 and 2.8 eV, as cited in references [110], [111]. This discrepancy between the theoretically computed and experimentally obtained values can be attributed to the inherent limitations of the PBE-GGA exchange functional in accurately predicting the bandgap of metal sulfides.

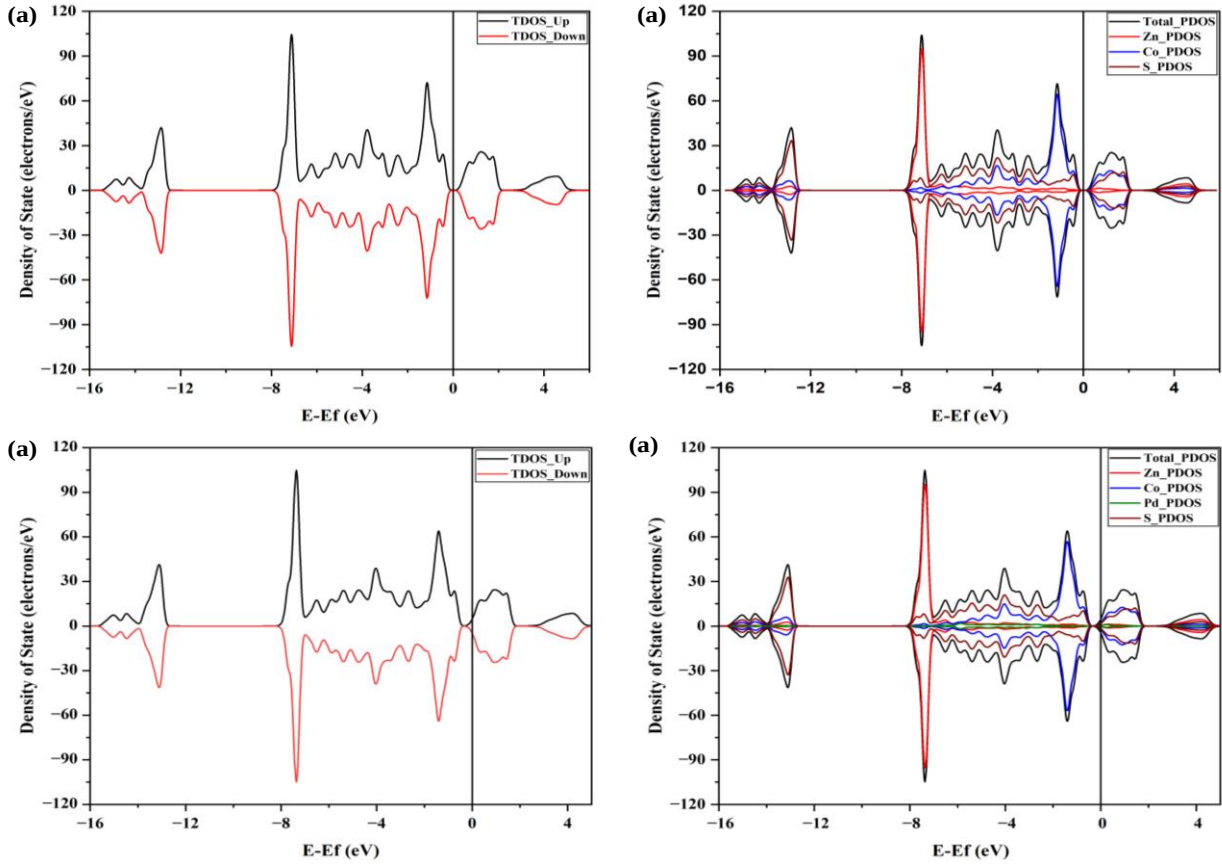


Figure 23: (a) The total DOS plots for ZnCo_2O_4 , (b) The Projected DOS (PDOS) plots for ZnCo_2O_4 , (c) The total DOS plots for $\text{ZnCo}_{2-x}\text{Pd}_x\text{O}_4$ (d) The plot for $\text{ZnCo}_{2-x}\text{Pd}_x\text{O}_4$ illustrating the contributions of all components across all energy levels (d) The Projected DOS

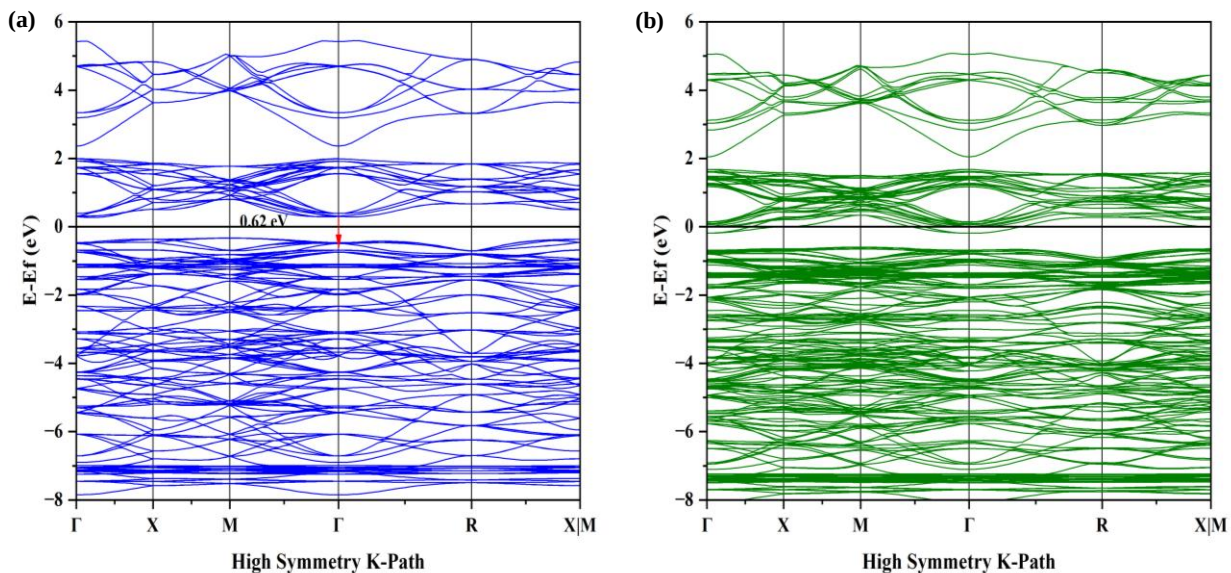


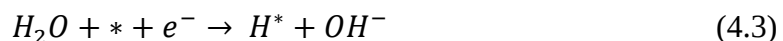
Figure 24: Band structure Plots for (a) ZnCo_2S_4 , showing its electronic energy levels and band gap, and (b) $\text{ZnCo}_{2-x}\text{Pd}_x\text{S}_4$, illustrating the impact of Pd substitution on the electronic structure

4.5.3 Electrocatalytic Activity Evaluation

Following the geometry optimization of the ZCS and ZCP structure, the catalytic properties of these catalysts were investigated. The slabs of both catalysts were modeled and relaxed to generate the optimized configurations. The relaxed slabs were subsequently used to study the adsorption of H^* at different sites of the catalysts. The initial adsorption height was set at 1.5 Å on all other sites apart from the O sites which was set at 1.0 Å, and the systems were further relaxed to obtain the optimized configurations of the slab-adsorbate systems. The corresponding adsorption energies (E_{H^*}) and Gibbs free energies (ΔG_{H^*}) of H^* were computed. **Figure 25(a-f)** illustrates the relaxed surfaces with H^* and H_2O^* adsorbed. The Thermodynamic reaction coordinate profiles based on ΔG_{H^*} were plotted for the respective adsorption sites to assess the activity of each sites towards binding of H^* base on the Sabatier principle [101]. It suggests that an efficient electrocatalyst should exhibit moderate adsorption towards hydrogen binding. The ΔG_{H^*} thermodynamic profiles

for the ZCS catalyst displayed in **Figure 26a** indicate that the Zn site support spontaneous adsorption of H^* , while the Co and O sites exhibit non-spontaneous adsorption towards H^* binding. In contrast, the energy profiles for the ZCP catalyst shown in **Figure 26b** demonstrate that H^* can spontaneously adsorb on all the available sites exothermically. Hence, this result indicates the significant role of the Pd dopants in enhancing the ZCS catalyst by enabling all sites to actively bind H^* towards their surface and improves its overall electrocatalytic performance. The volcano plot in **Figure 26c** supports this result.

By comparing the ΔG_{H^*} thermodynamic profiles of the active sites for the ZCS and ZCP catalysts, it is evident that anomalously, the ZCS slab exhibits the closest binding energy to thermoneutrality. This alignment with Sabatier's principle suggests that the ZCS should demonstrate the highest activity towards HER which contradicts the experimentally observed electrochemical polarization data. This contradicting trend to the experimentally obtained result prompted the investigation of the H_2O adsorption kinetics on the slabs as the experimental analysis was conducted in an alkaline medium (i.e., alkaline electrolyte). For an alkaline media, the initial step in the HER for most electrocatalysts is the adsorption of a water molecule onto the catalyst surface and its subsequent dissociations into adsorbed hydrogen (H^*) and hydroxyl (OH^-) ions [8]. This reaction is represented as:



To investigate the H_2O adsorption kinetics three adsorption sites of interest were selected from the two slabs, these include the Zn sites (Zn) on the ZNC catalyst, and the Zn and Pd sites (Zn_{Pd} & Pd) on the ZNP catalyst. The structural configurations for H_2O adsorption on the Zn & Pd sites are displayed in **Figure 25 (d & e)** respectively. The reaction coordinate for these sites shown in

Figure 3d, indicate that the Zn_{Pd} and Pd sites with ΔG values of -0.59 eV and -0.78 respectively bind H_2O molecules to their surface spontaneously. Meanwhile, the Zn sites with ΔG values of 0.51 eV, bind H_2O molecule non-spontaneously. Further calculations were performed to determine the energy barrier for the reaction kinetics to proceed from the adsorption of H_2O molecule to adsorption of H^* $[(\Delta G_{\text{H}_2\text{O}}) - (\Delta G_{\text{H}^*})]$ at the respective sites. The results indicate that the Zn_{Pd} catalyst presented a much lower energy barrier of -0.12 eV on the Pd sites which is lower than those of Zn (0.66 eV) and Zn_{Pd} (0.50 eV) respectively. The complete results are summarized in **Table 8, 9 & 10**.

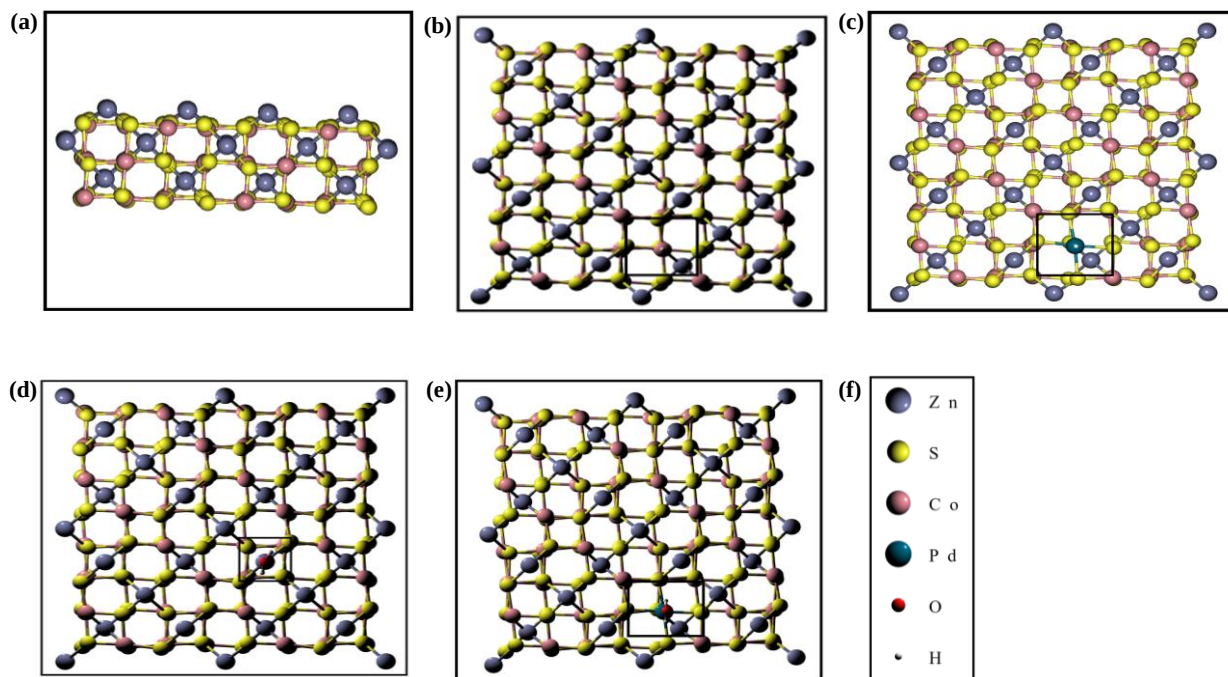


Figure 25: (a) Side view of the pristine ZnCo_2S_4 surface. Top view of the ZnCo_2S_4 surface with a single Hydrogen atom adsorbed on (b) a Co site (c) a Pd site. Top views of H_2O molecule adsorption on the $\text{ZnCo}_{2-x}\text{Pd}_x\text{S}_4$ surface at (d) Zn site (e) Pd site

This result suggests that the H_2O dissociation energetics are more thermodynamically favorable on the ZCP catalyst. Hence, the Zn_{Pd} catalyst requires lower energy to generate the H^* intermediates necessary for HER. This result corroborates the experimental findings. **Figure 26d**,

therefore, demonstrates that the water dissociation energetics are more favorable on the ZCP than on the ZCS catalysts. Additionally, **Figure 26d** suggests that water dissociation is largely the rate-limiting step in the HER for alkaline media.

Table 8: Tabulated values of adsorption energy E_A and Gibbs free energy ΔG_H for ZNC slab

Adsorption Site	E_A (eV)	ΔG_H	$\log(i_0)$
Zn	-0.399	-0.158	-19.29
Co	0.160	0.400	-23.73
S	0.231	0.472	-26.011

Table 9: Tabulated values of adsorption energy E_A and Gibbs free energy ΔG_H for ZCP slab

Adsorption Site	E_A (eV)	ΔG_H	$\log(i_0)$
Zn	-1.33	-1.09	-36.22
Co	-0.93	-0.69	-28.98
Pd	-0.900	-0.66	-28.44
S	-0.850	-0.61	-27.53

Table 10: Tabulated values of Gibbs free energy ΔG_{H_2O} on selected site on $ZnCo_{2-x}Pd_xS_4$ slab

Adsorption site	ΔG_{H_2O}	ΔG_H	$[\Delta G_{H_2O} - \Delta G_H]$
Zn	0.505	-0.484	0.854994
Zn_{Pd}	-0.594	-0.474	0.908791
Pd	0.485	0.448	0.034172

The DFT calculations reveal the kinetics of the HER on the ZCS and ZCP catalyst, which can be explained as follows: For ZCS, the H_2O molecules adsorb favorably onto the Zn site and subsequently dissociate into (OH^-) and (H^*) species. The adsorbed hydrogen atom then binds to the Zn atom forming the Volmer reaction step. The reaction then proceeds to H_2 molecule formation either through the Volmer-Heyrovsky or the Volmer-Tafel reaction pathways on the

same sites. In contrast, for the ZCP, the HER kinetics involve multiple active sites, where all sites act as favorable adsorption sites for the HER intermediates. This synergistic effect among the active sites contributes towards enhancing the efficiency of the HER on the ZCP catalyst [102]. The model adopts the conventional mechanism of the HER in alkaline media this convention assumes that since HER occurs at the cathode, the generated OH^- ions are assumed to desorb from the electrode under a constant potential (eU), while the H^+ adsorbs on the surface, minimizing the impact of the OH^- on the catalytic HER process. The reaction coordinates are presented in **Figure 26**.

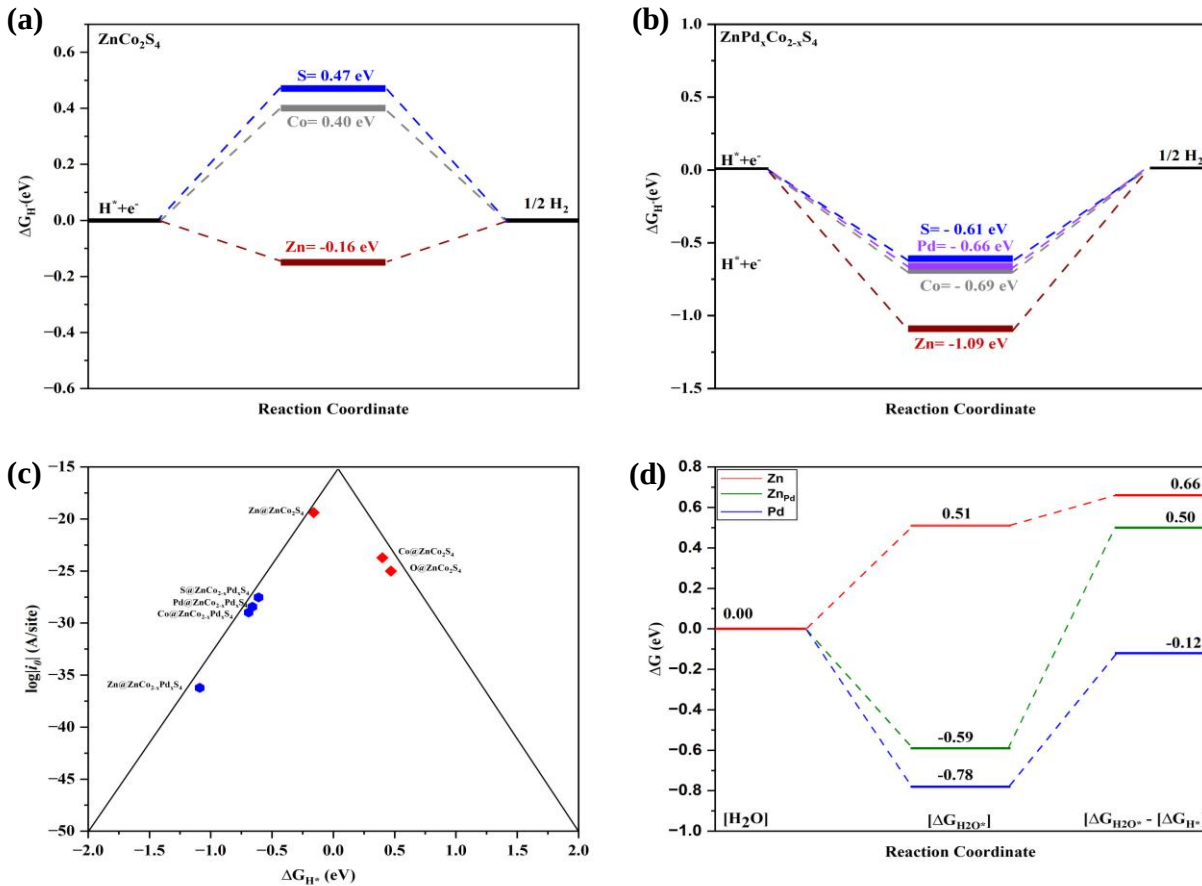


Figure 26: Gibbs free energy diagram for adsorbed hydrogen on (a) ZnCo₂S₄ surface, (b) Gibbs ZnCo_{2-x}Pd_xS₄ surface (c) Volcano plot depicting the activity of adsorption sites for HER, (d) Gibbs free energy diagram for water adsorption and dissociation on Zn, Zn_{pd} & Pd sites

4.5.4 Mechanistic Insight into Electrocatalytic Performance

Although both Pd-doped ZnCo_2O_4 and ZnCo_2S_4 exhibit improved activity compared to their pristine forms, the oxide-based catalyst demonstrates superior HER performance. This enhancement is not primarily due to a reduced band gap or higher density of states at the Fermi level, but rather arises from the nature of the Pd–anion interaction. DFT calculations reveal that Pd forms a more favorable orbital coupling with oxygen than sulfur. This enhanced hybridization leads to more favorable binding energies for reaction intermediates and facilitates improved electron transfer kinetics. The higher electronegativity of oxygen (3.44) relative to sulfur (2.58) results in a more polar covalent Pd–O bond, which promotes stronger electronic coupling between palladium dopants and the oxygen ligands. This increased polarity facilitates effective charge redistribution at the catalytic sites, thereby improving overall catalytic turnover. These findings are consistent with the observations of Cuyacot et al., who highlighted that relativistic spin–orbit coupling at heavy atoms (HA) can significantly influence the chemical bonding characteristics with lighter atoms (LA) [112]. In particular, spin-orbit-induced electronegativity, arising from the relativistic effects in heavy atoms such as Pd, enhances their ability to withdraw electron density from neighboring ligands. This modulation of electron density not only stabilizes key reaction intermediates but also contributes to the superior catalytic performance observed in Pd–O systems compared to Pd–S counterparts.

Furthermore, **Table 11** presents a comparative table consolidating the key electrochemical parameters, including overpotential, Tafel slope, exchange current density, and charge transfer resistance, used to evaluate and compare the catalytic performance of pristine and Pd-doped Zn-Co oxide and sulfide electrocatalysts.

Table 11: Comparison of key kinetic parameters for evaluation of electrocatalyst efficiency

Electrocatalyst	Overpotential (mV)	Tafel Slope (mV/dec)	ECSA (cm^2)	R_{ct} (Ω)	ΔG_{H20} (eV)	Band Gap (eV)	η_{theo} (eV)
$ZnCo_2O_4$	194	455.14	1.95	1.3	0.855	0.84	0.855
$ZnCo_{2-x}Pd_xO_4$	31	36.81	119.5	3.9	0.034	—	0.034
$ZnCo_2S_4$	281	240.1	13.80	6.8	0.66	0.62	0.660
$ZnCo_{2-x}Pd_xS_4$	166	165.5	89.25	1.9	-0.12	—	0.12

CHAPTER FIVE

SUMMARY, CONCLUSION, AND RECOMMENDATION

5.1 Summary

This thesis presents a comprehensive investigation into rational engineering and tuning of zinc cobalt-based spinel electrocatalysts for efficient HER through water splitting. This study is supported by both experimental analyses and DFT calculations. By systemically doping Pd into ZnCo_2O_4 and ZnCo_2S_4 spinels, a significant enhancement in the electrochemical activity of the ZnCo-based spinel electrocatalyst was achieved, indicating the pivotal role of Pd in modulating the physicochemical and electronic properties of the pristine ZnCo_2X_4 ($\text{X} = \text{O}, \text{S}$) spinel structures.

To investigate the structural and morphological characteristics of the synthesized spinel electrocatalyst, structural and morphological characterization techniques, including XRD, SEM, TEM, and HR-TEM analysis, were performed. The results of these characterization analyses confirmed the formation of a well-defined spinel structure. Meanwhile, XPS analysis was performed to gain insight into the oxidation states and surface composition.

The HER activity for various compositions of the synthesized ZnCo-based spinel catalyst revealed that the optimized composition for the oxide catalyst is the $\text{ZnPd}_x\text{Co}_{2-x}\text{O}_4$ ($x=0.08$)@NF, while for the sulfide counterpart is $\text{ZnPd}_x\text{Co}_{2-x}\text{S}_4$ ($x=0.06$) @NF. These compositions attain a lower overpotential of ~31 mV and ~166 mV and exhibit a favorable Tafel slope of ~54.36 and 127.7 mV/dec, respectively, confirming an improvement in their charge transfer and reaction kinetics under alkaline conditions. These results also indicate the superiority of the activity of the oxide catalyst over its sulfide counterpart. Furthermore, EIS and Cdl measurements revealed enhanced active surface area (ECSA) and reduced charge transfer resistance upon Pd incorporation.

Chronopotentiometry (CP) analysis was further employed to confirm the long-term stability of the electrocatalysts. The results revealed that the optimized $\text{ZnPd}_x\text{Co}_{2-x}\text{O}_4$ ($x=0.06$) @NF and $\text{ZnPd}_x\text{Co}_{2-x}\text{O}_4$ ($x=0.06$) @NF retain their activity over a long period with minimal fluctuations of 72 hours and 40 hours, respectively. This further validates their practical sustainability for industrial applications.

Additionally, DFT calculations were performed to support the theoretical analysis, providing critical insights into the enhanced HER performance of Pd-doped ZnCo_2O_4 and ZnCo_2S_4 spinel catalysts by revealing how Pd incorporation tunes their electronic and catalytic properties. In ZnCo_2O_4 , Pd doping improves the electrocatalytic activity by lowering the energy barrier for water dissociation to a nearly thermoneutral energy of 0.03 eV, increasing the DOS near the Fermi level, thereby reducing the observable 0.84 eV bandgap, and promoting faster charge transfer and reaction kinetics. Similarly, for ZnCo_2S_4 , Pd enhanced the activity of the pristine catalyst by improving its conductivity by lowering the energy barrier for water dissociation to a value of -0.12 eV, introducing new electronic states, thereby reducing the observable 0.68 eV. These results indicate the Pd dopant optimized hydrogen binding on the electrocatalyst, improving reaction and charge transfer kinetics, confirming its role in accelerating HER activity through improved electron transfer and active site energy.

In conclusion, this study demonstrates that Pd doping is an effective strategy for tuning and engineering the electrocatalytic properties of spinel structures. The experimental analysis, supported by theoretical studies, provides critical insight into the structure-activity relationship of spinel structures, offering a promising pathway for the development of the next-generation, cost-effective, and efficient hydrogen evolution catalysts for sustainable energy applications.

5.2 Conclusion

From the analysis and results obtained from this work, we can conclude the following:

1. Palladium (Pd) doping has been demonstrated as an effective strategy to enhance the electrocatalytic performance of ZnCo-based spinel catalysts. The incorporation of Pd significantly improves their activity, presenting a viable alternative to conventional noble-metal-based catalysts for water splitting applications, thereby offering a cost-effective and scalable solution.
2. Electrochemical characterization, including linear sweep voltammetry (LSV), cyclic voltammetry (CV), and electrochemical impedance spectroscopy (EIS), revealed that the Pd-doped oxide spinel (ZnCo_2O_4) exhibits superior electrocatalytic activity compared to its sulfide counterpart (ZnCo_2S_4). This enhancement is attributed to improved charge transfer kinetics and a higher electrochemically active surface area.
3. Density Functional Theory (DFT) calculations provided atomic-level insights into the influence of Pd doping on the electronic structure and catalytic behavior of the spinel frameworks. The theoretical findings corroborate the experimental results, confirming the role of Pd in modulating the electronic density near the Fermi level and reducing the energy barriers for hydrogen evolution.
4. Furthermore, DFT analysis elucidates the origin of the enhanced catalytic activity observed in the oxide-based spinel. The stronger Pd–O interaction, coupled with favorable orbital overlap and higher electronegativity of oxygen compared to sulfur, contributes to improved adsorption and desorption kinetics during the hydrogen evolution reaction (HER), thereby explaining the superior performance of the oxide catalyst relative to its sulfide counterpart.

5.3 Recommendations

Based on the outcome of this research, the following suggestions and recommendations will be made:

1. Evaluation of the Electrocatalytic Activity of Pd-Functionalized ZnCo_2Se_4

To comprehensively understand the effect of anion substitution on spinel electrocatalyst performance, it is recommended to investigate the electrocatalytic activity of Pd-functionalized ZnCo_2Se_4 . This evaluation will provide critical insight into how selenium substitution influences the electronic structure, surface reactivity, and overall catalytic behavior in comparison to oxide and sulfide analogues.

2. Anion-Pd Interaction Study

To deepen the understanding of anion substitution effects in ZnCo-based spinel catalysts, it is recommended to investigate the interaction between palladium (Pd) and individual anions (O^{2-} & S^{2-}). Such a study would provide valuable insight into the role of anion electronegativity and orbital hybridization in modulating Pd–anion coupling and overall catalytic performance.

3. Extension to Oxygen Evolution Reaction (OER)

It is essential to evaluate the catalytic performance of Pd-modified ZnCo_2O_4 and ZnCo_2S_4 in the oxygen evolution reaction (OER). This will help determine their potential as bifunctional electrocatalysts for overall water splitting, enabling their application at both the anode and cathode in integrated electrolyzer systems.

4. Catalyst Engineering Strategies

Advanced material engineering strategies such as defect (vacancy) engineering and heterostructure or composite layer formation should be explored to further enhance the

intrinsic activity, conductivity, and stability of ZnCo-based spinel electrocatalysts in water splitting applications.

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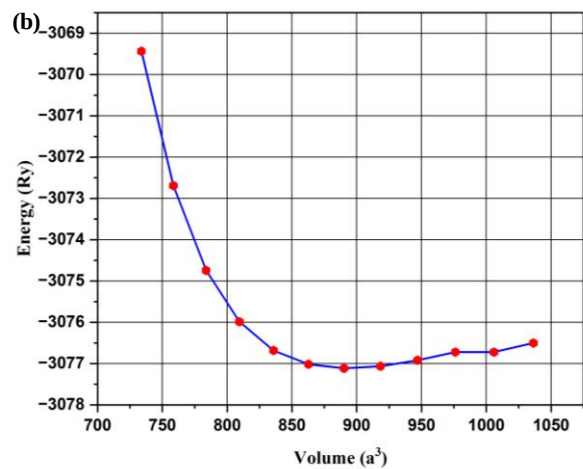
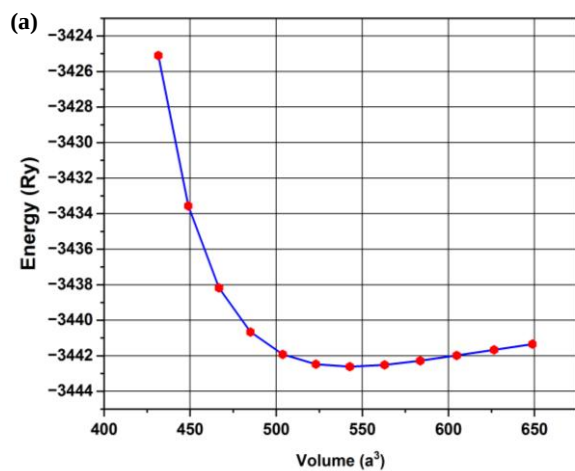
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APPENDIX

Appendix A: Equation of state plot for (a) ZnCo_2O_4 (b) ZnCo_2S_4 bulk structures.



Appendix B: Electronic Density of State (DOS) plots for the ZnCo_2O_4 bulk structure.

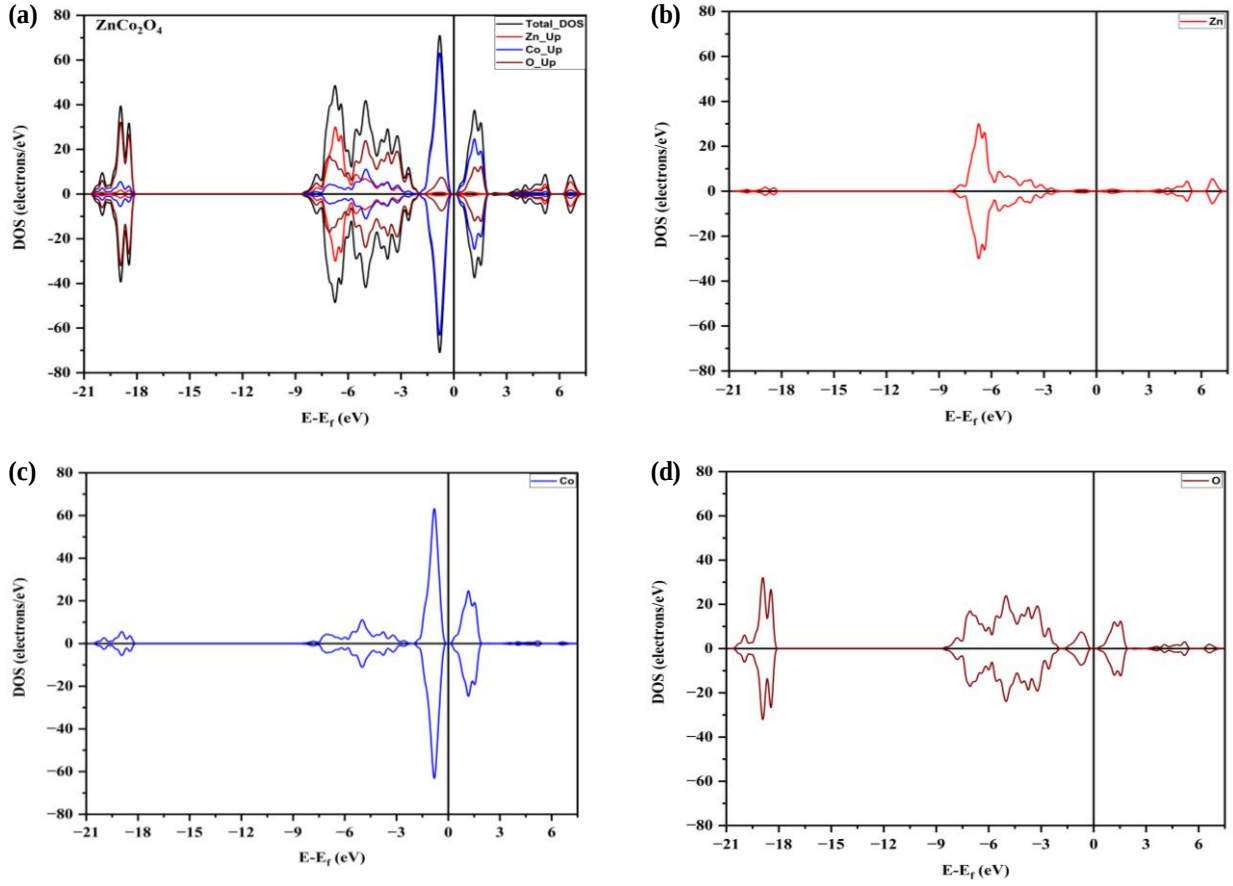


Figure I: Electronic Density of State (DOS) plots for the ZnCo_2O_4 bulk structure. (a) The total DOS plots illustrating the overall electronic states across various energy levels. (b) Projected Density of state (DOS) highlighting the contributions of the atoms to the electronic states, including their specific orbital characteristics for (b) Co (c) Zn & (d) O orbitals.

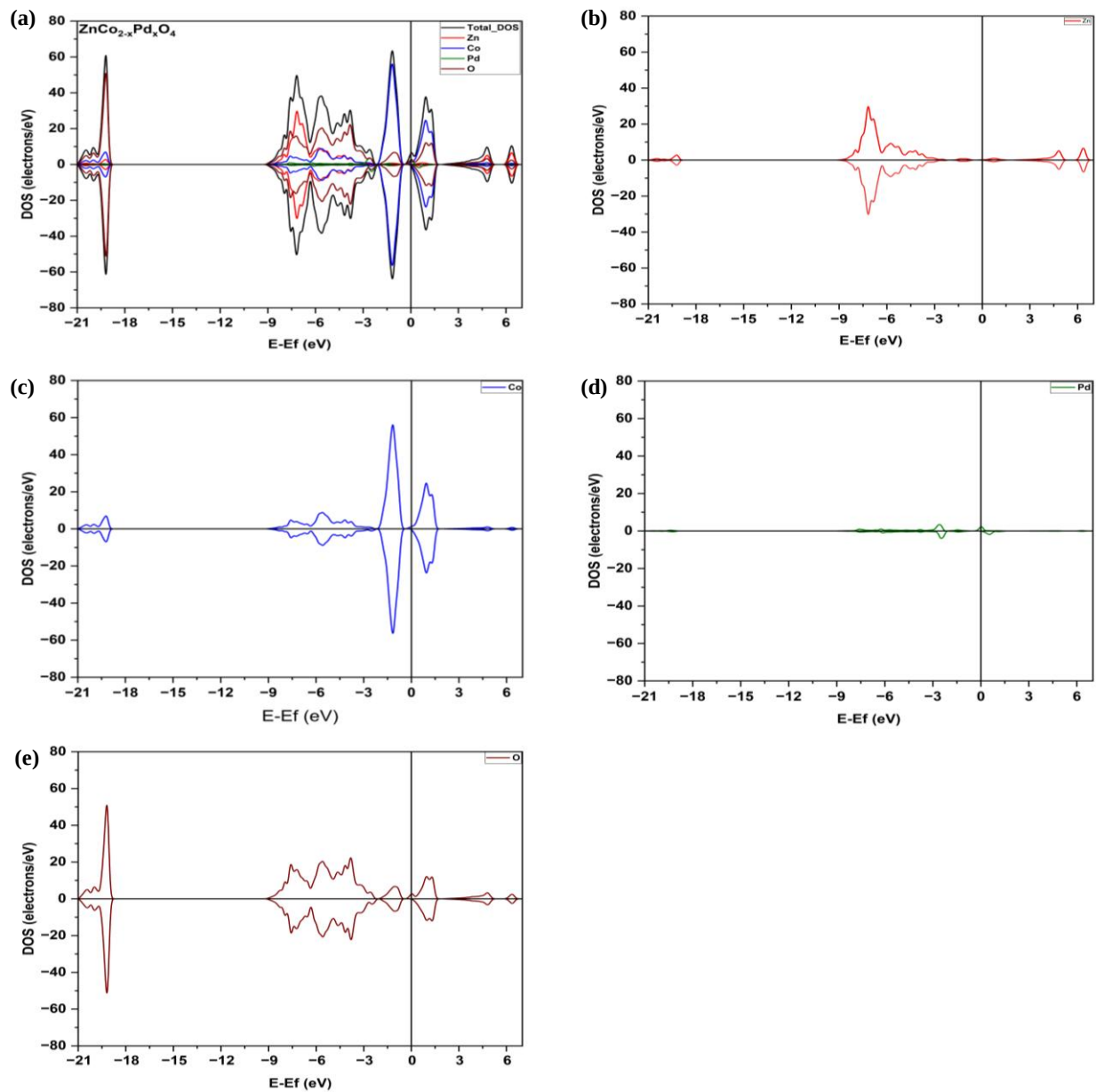


Figure II: Electronic Density of State (DOS) plots for $\text{ZnCo}_{2-x}\text{Pd}_x\text{O}_4$ bulk structure. (a) The total DOS detailing the overall electronic states across various energy levels. Projected Density of state (DOS) for (b) Co (c) Zn (d) O (e) Pd orbitals illustrating their distinct contributions and their influence on the overall electronic properties of the material.

VITAE

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Academic Background : I am a graduate of Physics and Materials science and Engineering with a first-class honor and distinction in both degrees. with a strong background in both academic and research experience. With interest in team work to achieve set goals and objectives, skillful in simulation and modelling of atomic phenomena. With research experience in computational materials design for renewable energy devices, synthesis and characterization of nanomaterials for electrochemical applications. |

INSTITUTION	DATES	QUALIFICATION
King Fahd University of Petroleum and Minerals, KSA	2023-2025	MSc Materials Science and Engineering
Bayero University, Kano, Nigeria	2015 – 2019	B.Sc. Physics
Muslim Community College	2006 - 2012	SSCE Certificate
Annur International School	2001 - 2006	Primary certificate

PROFESSIONAL MEMBERSHIPS & CERTIFICATIONS

- Nigerian Institutes of Physics (Member)
- The Electrochemical Society (Student member)
- National Association of Physics Students (NAPS)

- Diploma in Statistical Data Analysis (SPSS)

RESEARCH EXPERIENCE

Research Assistant: Department of Materials Science and Engineering and Interdisciplinary Research Center for Hydrogen Technologies and Carbon Management (IRC-HTCM), King Fahd University of Petroleum & Minerals **2022-present**

Advisor: Dr. AbdulJabar Alsayoud

CoAdvisor: Prof. Muhammad Ashraf Gondal

I developed a highly active and efficient spinel electrocatalyst for water splitting.

- Synthesis of Zn-Co spinel nanoparticles structure using sol-gel and hydrothermal synthesis method.
- Characterization of Zn-Co spinel structures using XRD, SEM, TEM, EDX, LSV, and ECSA characterization techniques.
- Analysis of electrochemical polarization curves for evaluation and identification of efficient catalysts
- Characterized the materials using BET, XRD, SEM, TEM, FT-IR, TGA, DMA, LOI, DSC, Raman scattering, and TA
- Density Functional Theory (DFT) for computation of structural, electronic properties.
- Evaluation of reaction kinetics and determination of energy barrier for electrochemical reactions using DFT

Undergraduate research: Department of Physics and Electronics, Bayero University, Kano. 2018-2019

Supervisor: Dr. Idris Ahmad

- Research Project: Computation of Nuclear Fusion Reaction Cross-section for Helium-Induced Reactions.

SKILLS

Materials Engineering & Modelling: I have mastered the skills of the detailed synthesis procedure, design, and simulation.

Technical Skills: Microsoft suites, Data analysis and visualization software, Python, DFT, Molecular Dynamics (MD), MATLAB, Generative AI.

Lab skills: XRD analysis, SEM, Polarization Curve Analysis, Electrochemical Impedance Spectroscopy (EIS). Nanomaterial synthesis methods (Sol-gel, Co-precipitation, and Hydrothermal method).

Publications

Refah S. Alkhalidi, **Mubarak A. Adebunmi**, Muhammad A. Gondal, Muneerah A. Almessiere and Abduljabar Alsayoud. Exceptional Pt⁴⁺ Ion Substituted Zinc Cobaltite Spinel Oxides for Enhanced Electrochemical Hydrogen Performance Supported by DFT. **Feb 2025**

Mubarak A. Adebunmi, Refah S. Alkhalidi, Muhammad A. Gondal, Muneerah A. Almessiere and Abduljabar Alsayoud. Ni Foam Supported Pd-Doped Zinc Spinel Oxide Nano-Electrocatalyst for Efficient Hydrogen Production Supported by DFT Study as Well Validated with Experimental Data. **April 2025.**

Mubarak A. Adebunmi, Refah S. Alkhalidi, Muhammad A. Gondal, Muneerah A. Almessiere and Abduljabar Alsayoud (2025). Palladium-Doped Bimetallic Sulphide Spinel Nano-Electrocatalyst Grown on Nickel Foam for Efficient Green Hydrogen Production Validated by First-Principles DFT Study. **(Under review).**

Refah S. Alkhalidi, **Mubarak A. Adebunmi**, Muhammad A. Gondal, Muneerah A. Almessiere and Abduljabar Alsayoud (2025). Synergistic Effect of Dual Metal Ion Doping in Zinc Spinel for Enhanced Hydrogen Evolution via Methanol Oxidation-Assisted Water Electrolysis: A DFT and Experimental Study. **(Under review)**