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IMPROVEMENTS OF ELECTROCHEMICAL WATER SPLITTING
EFFICIENCY BY USING ECONOMICALLY VIABLE
Co/CoPs/TiO₂/NiF ELECTROCATALYSTS

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Academic integrity declaration

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Abstract

The drive for sustainable energy solutions has led to the search for efficient and cost-effective electrocatalysts for green hydrogen production via electrochemical water splitting (EWS). This study addresses the limitations of precious metal-based catalysts by investigating alternative, earth-abundant materials. This research introduces a novel Co/CoPs(240)/TiO₂/NiF electrocatalyst, synthesized using deep eutectic solvent (DES)-mediated electrodeposition of Co and cobalt phosphides (CoPs) on TiO₂-coated nickel foam (NiF) substrate.

Electrophoretic deposition of TiO₂ nanoparticles was successfully applied to NiF, resulting in a smooth and even surface. On this TiO₂-coated substrate, subsequent Co/CoPs deposition produced unique hexagonal and cauliflower-like structures with a uniform distribution of Co and P. Energy dispersive X-ray spectroscopy (EDX), scanning electron microscopy (SEM), and X-ray diffraction (XRD) were used to confirm these features. Optimizing the Co/CoPs deposition times significantly reduced the hydrogen evolution reaction (HER) overpotential to 34.42 ± 4.2 mV at 10 mA cm^{-2} in 1 M KOH. Remarkably, the Co/CoPs(240)/TiO₂/NiF catalyst required only 27.43 mV with a Tafel slope of 48.35 mV dec⁻¹. Stability tests demonstrated minimal performance degradation after 5000 cycles and 40 hours of operation, demonstrating excellent durability. This optimized catalyst outperformed Co/CoPs(240)/NiF, commercial 10% Pt/C electrodes, and other reported catalysts.

The oxygen evolution reaction (OER) performance also highlighted the catalyst's efficiency, with an overpotential of 331.70 mV at 10 mA cm^{-2} in 1 M KOH and a Tafel slope of 73.96 mV dec⁻¹. Stability tests revealed minimal performance degradation after 1000 cycles. Furthermore, a full water electrolyser system using Co/CoP(240)/TiO₂/NiF electrodes achieved a total voltage of 1.612 V at 10 mA cm^{-2} , indicating the practical viability of the optimized electrodes for water splitting applications.

The remarkable performance of the Co/CoPs(240)/TiO₂/NiF electrode is primarily due to the presence of the TiO₂ layer, which enhances the surface area and acts

as a catalyst promoter through synergistic effects and enhanced charge transfer kinetics. This research suggests that incorporating an intermediate TiO_2 layer can promote the catalytic activity of other catalysts as well.

In conclusion, this study presents an effective and economical alternative to noble metal-based electrocatalysts for water splitting. By integrating TiO_2 with Co/CoPs on a NiF substrate, the research advances the development of high-performance, low-cost catalysts and contributes to the sustainable production of green hydrogen.

Keywords:

Deep eutectic solvent-mediated electrodeposition, Electrophoretic deposition of TiO_2 , High-performance electrocatalysts

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List of Abbreviations

η_A	Anodic overpotential
$E_{(\text{applied})}$	Applied electrical potential
CCS	Carbon capture and storage
η_c	Cathodic overpotential
CA	Chronoamperometry
CP	Chronopotentiometry
CoPs	Cobalt phosphides
i	Current
CV	Cyclic voltammetry
DES	Deep eutactic solvent
C_{dl}	Double-layer capacitance
EIS	Electrochemical impedance spectroscopy
ECSA	Electrochemical surface area
EWS	Electrochemical water splitting
EPD	Electrophoretic deposition
EDX	Energy dispersive X-ray spectroscopy
E_{exp}	Experimental potential
FE	Faradaic efficiency
FTIR	Fourier-transform infrared spectroscopy
GC	Gas chromatography
ΔG	Gibbs free energy
$\Delta G_{O^*} - \Delta G_{HO^*}$	Gibbs free energy difference between S-O and S-OOH
Co-H*	Hydrogen adsorbed cobalt
S—H _{ads}	Hydrogen adsorbed on metal
HER	Hydrogen evolution reaction
IL	Ionic liquid
LSV	Linear sweep voltammetry
η	Overpotential
η_{OER}	Overpotential of oxygen evolution reaction

η_5	Overpotential required to achieve current density of 5 mA cm ⁻²
η_{10}	Overpotential required to achieve current density of 10 mA cm ⁻²
η_{20}	Overpotential required to achieve current density of 20 mA cm ⁻²
η_{50}	Overpotential required to achieve current density of 50 mA cm ⁻²
iR	Ohmic losses
OER	Oxygen evolution reaction
V	Potential
RDS	Rate-determining step
RHE	Reversible hydrogen electrode
RF	Roughness factor
C _s	Specific capacitance
E°	Standard cell potential
ΔG°	Standard Gibbs free energy
ΔG _{H*}	Standard Gibbs free energy of hydrogen adsorption
ΔG° _{H₂O}	Standard Gibbs free energy of water dissociation
SMR	Steam methane reforming
TMPs	Transition metal phosphides
TEM	Transmission electron microscopy
TOF	Turnover frequency
WS	Water splitting
WSR	Water splitting reaction
XRD	X-ray diffraction

1 Introduction

1.1 Introduction

To mitigate climate change, promote sustainability, and address the impending energy crisis made worse by the finite supply of fossil fuels, a global shift from fossil fuels to renewable energy sources is imperative. Through the Paris Agreement in 2016, most countries committed to limiting increases in global temperature and lowering greenhouse gas (GHG) emissions [1]. Although there are many renewable energy sources, such as solar and wind, that can be used as alternative energy suppliers to accomplish this goal, their uneven distribution throughout the world and unpredictable supply present significant challenges that underscore the urgent need for effective energy transformation, storage, and transportation technologies [2], [3]. Since hydrogen can successfully fulfil all three of these criteria, it has become a front-runner in this situation. It is appropriate for a range of application scenarios due to its high energy density, flexible, clean, carbon-free, and readily available nature [3]. One of the main, proven techniques for producing green hydrogen is EWS powered by the renewable energy.

EWS breaks down water into molecular hydrogen and molecular oxygen by immersing two electrodes in a water-containing electrolyte solution and applying external electrical energy [4]. This process comprises two reactions: the HER at the negative electrode (cathode) and the OER at the positive electrode (anode) [4]. Theoretically, at least 1.23 V difference between the two electrode is required to proceed EWS to produce hydrogen [4]. However, in practice, the kinetics of these reactions are sluggish at the electrodes, necessitating an excess potential known as overpotential to facilitate the reactions effectively. High-performance electrocatalysts are required to minimize the minimize overpotential, input of energy, and accomplish effective water splitting.

The best functioning catalysts for these reactions now are made of precious metals like iridium (Ir), ruthenium (Ru), and platinum (Pt) [5]. Despite the exceptional catalytic performance of these materials, their scarcity, inadequate stability and exorbitant cost prohibit their commercial use. high cost and poor

stability prevent their commercial application, even when energy savings from lower overpotential barriers are realized [5]. Extensive research has been conducted to find more economical and efficient alternative catalytic materials in response to these difficulties [6]. The emphasis now lies on catalysts made from inexpensive, readily available non-noble metals [6]. Although significant advancements have been made in this field, more work is still required to develop appropriate catalysts that have low overpotential requirements, high catalytic activity, and long-term durability to realize large-scale electrochemical water splitting.

Among the various non-noble metal-based alternatives, cobalt (Co) and cobalt phosphides (CoPs) have emerged as promising candidates due to their abundant availability, lower cost, and excellent catalytic activity in EWR [7], [8]. Research has further revealed that the interaction between titanium dioxide (TiO_2) and metal or metal-based catalysts can significantly modify the electronic states of the catalysts, allowing for fine-tuning of their donor-acceptor properties [9], [10], [11]. This modification enhances the overall catalytic activity, making the process more efficient. Additionally, TiO_2 improves the catalyst's ability to adsorb water molecules due to its increased wettability, which in turn accelerates the reaction kinetics. When catalysts are coated onto nanoparticles like TiO_2 , the exposed surface area is significantly increased, allowing for higher catalyst loading and improved catalytic performance [61].

This research aims to make a significant contribution to the field of electrochemical water-splitting by focusing on the development of cost-effective and efficient catalysts. The goal is to advance the production of hydrogen as a sustainable energy source by improving the affordability and efficiency of the catalysts used.

1.2 Scope of the study

This study is centred on the synthesis and optimization of electrocatalysts based on Co/CoPs for water splitting applications. Although there has been extensive research into low-cost alternative electrocatalysts, this work specifically targets the enhancement of Co/CoPs catalysts activity by employing titanium dioxide

(TiO₂) nanoparticles coated onto NiF as the supporting electrode. The goal is to improve the catalyst's performance by increasing the surface area of the NiF support and enhancing the loading of Co and CoPs.

A significant aspect of this work is understanding the deposition of TiO₂ nanoparticles onto the NiF support. The research investigates how this TiO₂ coating impacts on electrochemical surface area of final catalyst and the performance. While the study does not explore the effect of TiO₂ coating thickness on catalytic efficiency, it does focus on the use of a thin TiO₂ layer.

Catalyst optimization is performed based on the HER overpotential. The optimized Co/CoPs catalyst is then evaluated for its performance as an OER catalyst to investigate its bifunctional catalytic activity. Additionally, the study explores the applicability of the optimized catalyst in overall WS reaction,

1.3 Aim:

This work aimed to investigate low-cost catalytic electrodes composed of earth-abundant transition metals—nickel, cobalt, and titanium—that could compete with rare-earth metal-based catalysts in water splitting reactions, including the OER and HER. The study seeks to develop catalysts that are low-cost, highly efficient, and durable, making electrolysis a viable method of producing hydrogen on a commercial scale. By integrating these inexpensive, high-performance, and stable catalysts, this research aims to support the achievement of net-zero energy targets and advance sustainable energy solutions.

1.4 Objectives

This research project is structured around several key objectives, each corresponding to an important step in the research process, to accomplish the aim outlined above. These objectives guide the investigation from the synthesis and characterization of the catalysts to their performance assessment and the exploration of mechanisms underlying their efficiency. The following four objectives detail the specific steps and methodologies employed to ensure a successful synthesis and characterisation of the developed catalysts.

Objective 1: To design and synthesize novel, economically viable Co/CoPs/TiO₂/NiF electrocatalysts modified with TiO₂ using established electrophoretic and electrodeposition techniques, and to confirm the successful synthesis through characterization methods, including SEM, EDX, and XRD).

Objective 2: To optimise the catalyst for HER performance and assess the efficiency, kinetic mechanisms, and stability of the catalysts in promoting both the HER and OER, which are critical for determining their practical application, through electrochemical characterizations using linear sweep voltammetry (LSV), cyclic voltammetry (CV), chronopotentiometry (CP), and gas chromatography (GC). Additionally, to compare the efficiency of the electrodes with state-of-the-art catalysts.

Objective 3: To investigate the reasons of efficiency improvement using electrochemical surface area (ECSA) measurements through CV and electrochemical impedance spectroscopy (EIS), as well as SEM.

Objective 4: To draw conclusions, and propose directions based on the outcomes to enhance the performance of the developed catalyst even more.

1.5 Research questions

Question 1: How can novel, economically viable Co/CoPs electrocatalysts modified with TiO₂ be designed and synthesized using established electrophoretic and electrodeposition techniques, and how can the successful synthesis of Co/CoPs/TiO₂ electrocatalysts be confirmed through characterization methods such as SEM, EDX, and XRD?

Question 2: How can the catalyst be optimized for HER performance, and how can the efficiency, kinetic mechanisms, and stability of the catalysts in promoting both HER and OER be assessed through electrochemical characterizations such as LSV, CV and CP, Additionally, how does the efficiency of the electrodes compare with state-of-the-art catalysts?

Question 3: What are the reasons for the efficiency improvement of the catalysts, as determined through ECSA measurements CV and EIS, as well as SEM?

Question 4: How can the conclusions drawn to propose directions that enhance the performance of the developed catalyst even further?

1.6 Thesis structure

This thesis comprises seven chapters, each addressing a key aspect of the research. The chapters are organized as follows:

Chapter 1 provides an overview of the research topic, its significance, and the aims and objectives of the study. Chapter 2 of this thesis introduces the thermodynamic, kinetic, and mechanistic aspects of the reactions studied. It provides a thorough overview of the criteria used to evaluate electrocatalysts and discusses the development of catalysts from readily available materials, with a particular focus on CoPs and recent advancements in this area. Additionally, it explains the rationale behind selecting specific materials and synthesis techniques for the development of TiO₂-modified CoPs electrocatalysts. Chapter 3 details the experimental procedures, including the preparation of materials, characterization techniques, and electrochemical performance evaluations. The results of these experiments are presented in Chapter 4, accompanied by a detailed analysis. In Chapter 5, conclusions are drawn from the research findings, limitations, and suggestions are made for future studies aimed at further enhancing the performance of the developed catalysts. Additionally, this chapter outlines the contributions to knowledge derived from this research. The final chapter, Chapter 7, lists all the references that support the research presented throughout the thesis.

2 Literature review

2.1 Hydrogen energy in the global energy transition

The global energy crisis, driven by increasing energy demand and the overreliance on fossil fuels, has escalated concerns over environmental pollution and climate change. Global warming and air pollution are caused by the massive emissions of greenhouse gases that result from the production of energy through the extensive use of fossil-based fuels including coal, oil, and natural gas [3], [12], [13]. The shift to a low-carbon future is thought to depend heavily on hydrogen, one of the sustainable energy alternatives that has sparked a growing interest in these days. Hydrogen, as an energy carrier, presents a promising solution to tackle these challenges by offering a clean and adaptable energy option, particularly for hard-to-decarbonize sectors like heavy industry and transportation. When used as a fuel, hydrogen provides a net-zero emissions option at the point of use, producing only water vapor during energy generation. However, substantial GHG emissions may still be linked to its production and distribution, depending on the production methods and the energy sources utilized in these processes [12], [13].

Based on the processes used in production and the corresponding carbon emissions, hydrogen is divided into several categories, the principal ones being Gray, Blue, and Green hydrogen [3]. Gray hydrogen is produced from natural gas through steam methane reforming (SMR), which releases significant amounts of CO₂ and CO into the atmosphere [3]. The majority of hydrogen produced today comes from it, and even though it is profitable, it adds to the ongoing dependency on fossil fuels, and carbon emissions [3]. Blue hydrogen is a lower-carbon alternative since it uses SMR but also uses carbon capture and storage (CCS) technologies to cut carbon emissions [3]. However, CCS is not entirely efficient, and some emissions are still released into the atmosphere. Further the produced H₂ in these methods needs to be separated and purified for storage and applications [3]. On the other hand, hydrogen can be produced through water electrolysis. Once the process that uses renewable energy sources to split water into hydrogen and oxygen without emitting any carbon [3], [12], [14]. Therefore,

this H_2 produce using this method is named as Green hydrogen [3]. Countries with surplus renewable energy can convert that excess into hydrogen through this method, which can then be exported or transported to other regions globally. The H_2 produce using this method can easily be collected as it produces only at the cathode of the electrolysis process while other only by product is formed at the anode. Therefore, an additional separation and purification steps are not needed for the process. Although it is thought to be the most sustainable form of hydrogen, the challenge lies in the high cost of production, primarily due to the energy-intensive nature of electrolysis, high production and material cost of catalytic electrodes and the current price of renewable energy [3]. Despite its sustainability advantages, green hydrogen is not yet widely deployed on a large scale due to economic constraints and the need for substantial infrastructure development to support renewable energy and electrolysis [3].

Hydrogen production methods, aside from water electrolysis, result in significant greenhouse gas emissions, making them environmentally unsustainable [12], [13]. Additionally, the reliance on fossil fuels for hydrogen production perpetuates dependency on countries rich in these resources and fails to offer a long-term solution, as fossil fuels are finite and contribute to environmental degradation [13]. In contrast, hydrogen produced through water electrolysis, powered by renewable energy sources like wind, solar, and hydroelectric power, is both environmentally friendly and sustainable [13]. These renewable energy sources are widely available across the globe, though their availability can vary by region due to factors such as climate and geography, and their intermittent nature poses challenges. However, renewable energy, when available, can be harnessed to produce hydrogen, which can then be stored for later use, providing a reliable energy solution during periods when renewable energy generation is insufficient. This makes hydrogen produced via electrolysis a promising alternative for reducing both emissions and energy dependence.

2.2 Hydrogen production by electrochemical water splitting

The water splitting reaction (WSR) involves the formation of molecular hydrogen and molecular oxygen through the dissociation of water molecules, as illustrated

in Equation 2-1 [15], [16]. This reaction is energetically unfavourable, necessitating a minimum thermodynamic input of 237.14 kJ mol⁻¹, the Gibbs free energy of water ($\Delta G^{\circ}_{\text{H}_2\text{O}}$), under standard temperature and pressure conditions [17], [18]. To facilitate this reaction, the requisite energy must be supplied. When this required energy is provided in the form of external electrical energy, the process is known as EWS and the Gibbs free energy (ΔG°) and standard cell potential (E°) shows a relationship given by the Equation 2-2 [19].



$$\Delta G^{\circ} \rightarrow -nF \times E^{\circ} \quad (2-2)$$

Here, n represents the stoichiometric number of electrons in the balanced chemical equation required to disassociate one mole of water molecule, while F denotes the Faraday constant, which is 96,485 C/mol [18], [19]. This reveals that the minimum thermodynamic electrical potential energy of 1.23 V per electron necessitates to generate hydrogen from EWS at 297 K [18], [20], [21], [22].

This electrolysis is performed in an electrolysis setup where the cathode and anode are immersed in an electrolyte solution containing water, which can be either acidic or basic, as illustrated in Figure 1 [16], [18]. When a sufficient external electrical potential is applied between the two electrodes, water molecules or hydroxide ions in the electrolyte interact with the positive electrode (anode) to produce molecular oxygen, while water molecules or protons in the electrolyte interact with the negative electrode (cathode) to produce molecular hydrogen [16]. The processes occurring at the anode are referred to as the anodic half-reaction or OER, while the reactions at the cathode are known as the cathodic half-reaction or HER [16]. Both reactions are influenced by electrolyte bath pH level [16].

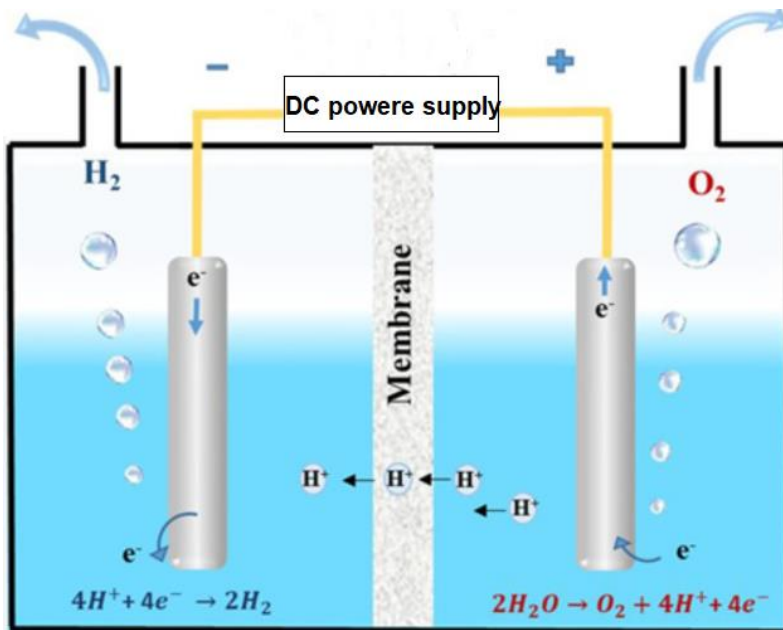


Figure 1 A schematic diagram of a typical electrochemical water electrolysis setup. Figure adapted from reference [23]

The HER process is expressed in Equation 1-3 for an acidic or neutral electrolyte and Equation 2-5 for an alkaline electrolyte requiring a minimum electrical potential energy of 0.00 V reference to reversible hydrogen electrode potential (vs. RHE) [16], [18]. Conversely, the OER process is expressed in Equation 2-4 for an acidic electrolyte and Equation 1-6 for an alkaline electrolyte and requires a minimum electrical potential of -1.23 V (vs. RHE) [16]. This reaction is referred to as the oxidation reaction [7], [16].

Cathodic half-reaction (acidic electrolyte):



Anodic half-reaction (acidic electrolyte):



Cathodic half-reaction (alkaline electrolyte):



Anodic half-reaction (alkaline electrolyte):



When this electrical energy for EWS is sourced from renewables, the process yields green hydrogen with zero carbon emissions throughout the cycle. This approach presents a viable method for storing sustainable energy as chemical fuel, addressing the challenges of intermittent supply and uneven distribution of renewable energy sources.

However, to fully leverage EWS with renewable energy, several challenges must be overcome. These include addressing the kinetic energy barriers of OER and HER, enhancing hydrogen production efficiency, and reducing the cost of electrode materials. To meet these challenges, developing efficient electrocatalysts is essential.

2.2.1 Energy barriers of EWS reaction

Any chemical reaction involves thermodynamic and kinetic energy barriers, which can be understood by analysing the reaction profile. The energy profile of the WSR, illustrated in Figure 2(a), shows that the thermodynamic energy is the difference between the energy of the reactants (water) and the sum of the energies of the products (hydrogen and oxygen). This value, calculated under standard conditions, is positive at 237 kJ/mol ($\Delta G^{\circ}_{\text{H}_2\text{O}}$) [24]. Consequently, external energy must be supplied for the reaction to proceed, as it cannot occur without at least this minimum energy. In electrochemical water splitting using an ideal electrode, the minimum electrical potential energy difference between the cathode and anode equivalent to this energy is 1.23 V, as shown by the potential gap between the two vertical lines in the schematic current (i) vs. potential (V) diagram in Figure 2(b) [24].

However, real water splitting systems require significantly higher electrical potential than the theoretical 1.23 V due to additional energy barriers known as kinetic energy barriers and the resistance across the electrolyte between the anode and cathode. The kinetic energy barrier is associated with the activated

states of the reaction and is determined by both anodic and cathodic reaction pathways [24]. In electrochemistry, the energy barrier associated with the cathodic reaction is called the cathodic overpotential (η_c) or HER overpotential (η_{HER}), while the barrier associated with the anodic reaction is called the anodic overpotential (η_a) or OER overpotential (η_{OER}) [24]. These are depicted in the blue current-potential (I-V) curve in Figure 2(b) [24]. Since the activated states energy are determined by the reaction pathway, changing the reaction pathway can tune the required overpotential.

Considering the reaction mechanisms of the anodic and cathodic reactions, the only way to modify each reaction mechanism is by using electro catalyst for the anode and cathode, which will be discussed in detail in the Chapter 2.1.2 and 2.1.3). When electrocatalyst is used, the required overpotential can be reduced as illustrated in the black I-V curve in Figure 2(b) [24].

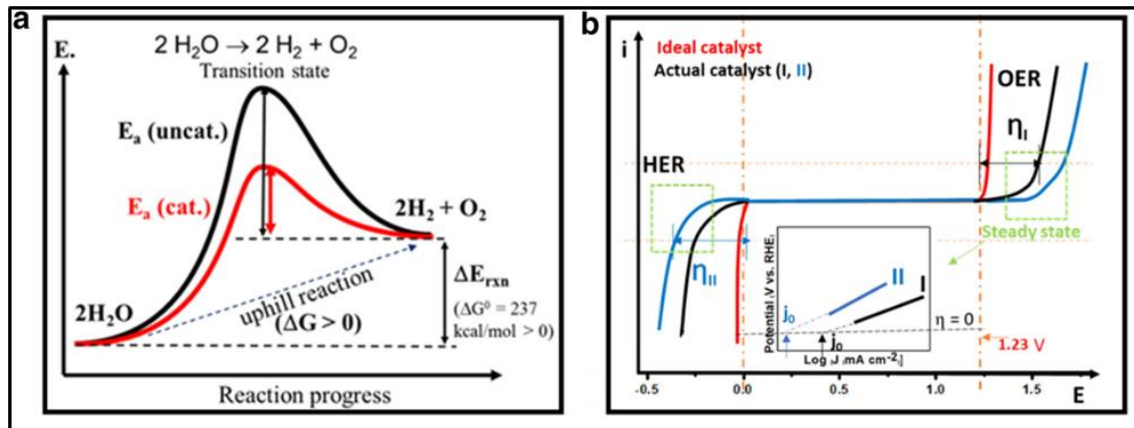


Figure 2: (a) Schematic illustration of the catalyst's role in lowering the activation energy barrier; (b) activity in terms of overpotential, Tafel slope, and exchange current density. Figure adapted from [24].

Another energy barrier due to resistance across the electrolyte is known as Ohmic losses, which can be minimized by appropriate electrolytic cell design. Therefore, in summary, as shown in Equation 6, a real electrochemical water splitting system requires an applied electrical potential ($E_{applied}$) greater than the thermodynamic energy (1.23 V) due to additional energy considerations: kinetic energy barriers ($\eta = \eta_a + \eta_c$) and Ohmic losses (iR) due to solution resistant in the electrolyte [16], [25].

$$E_{applied} \rightarrow 1.23 V + \eta_A + \eta_C + iR \quad (2-7)$$

Numerous studies have identified Pt as the best-performing electrode material for the HER and RuO₂ and IrO₂ as the best for the OER [16]. However, the high cost of these materials, due to their low abundance, makes their use in large-scale water electrolysis prohibitive. The current challenge in EWS research is to find efficient, low-cost electrode materials that can perform HER and OER at low overpotential with high reaction rates and long-term durability. OER Mechanism in EWS

2.3 Mechanism of OER in EWS

In EWS, the OER is the most unfavourable reaction due to its high thermodynamic and kinetic energy barriers, as discussed in the previous Chapter (2.1). The OER is strongly dependent on the acidity or basicity of the electrolyte solution; in basic and acidic media, the initial reactant differs. In a basic medium, hydroxyl ions are the source of oxygen, while in an acidic medium, water molecules serve this role, as outlined in Equations 2-4 and 2-6. This section details the OER pathway at the anode of the electrochemical cell.

In a basic medium, under the influence of the electromotive force provided by the external circuit, the electron-bearing oxygen end of the hydroxyl ion is attracted to the anode. In an acidic medium, the oxygen atom, with its net electronegative side, of the water molecule is drawn to the anode. This process is known as the mass transfer step, and it is influenced by the solution resistant.

In the subsequent step, these oxygen ends of different species are adsorbed onto the electroactive sites denoted as "S" on the anode surface, forming adsorbed hydroxyl intermediates (S—OH) as shown in Equations 2-8 and 2-9. This step involves the transfer of the first electron in OER and is referred to as the Volmer step [26], [27], [28].

In a basic electrolyte:

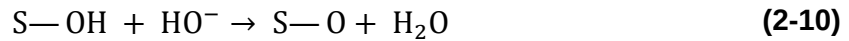


In an acidic electrolyte:

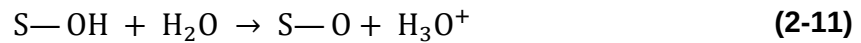


In the next step, the adsorbed OH interacts with another hydroxyl ion in a basic electrolyte or water molecule in an acidic electrolyte to form an adsorbed oxygen (S—O) intermediate, as shown in Equations 2-10 and 2-11. This step involves the second electron transfer and is known as the second electron transfer step of OER [26], [27], [28].

In a basic electrolyte:

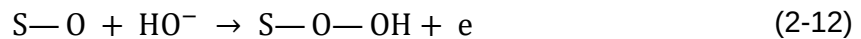


In an acidic electrolyte:

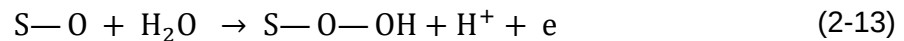


Following this, the third electron transfer step occurs when another hydroxyl ion in basic electrolyte or water molecule in protonated electrolyte interacts to form an adsorbed peroxy (S—O—OH) intermediate, as shown in Equation 2-12 and 2-13 [26], [27], [28].

In a basic electrolyte:

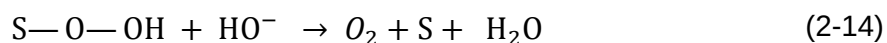


In an acidic electrolyte:

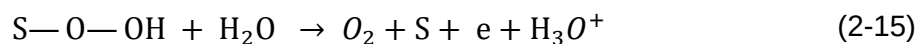


There are two possible routes in the OER process to form molecular oxygen after these steps. In the first route, the adsorbed peroxy intermediate transforms into an oxygen molecule, regenerating the electroactive site of the electrode and releasing the fourth electron at the anode, as shown in Equations 2-14 and 2-15 [26], [27], [28].

In a basic electrolyte:



In an acidic electrolyte:



In the other possible route, two adsorbed nearby oxygen species (S—O) react to liberate O₂, as shown in Equation 2-16.



During OER, the steps detailed in Equations 2-8 to 2-15 occur at the interface of the electrode and electrolyte, involving four electron transfer reactions to produce one molecule of oxygen. These steps are called intermediate steps of OER as they occur along the pathway of generating O₂ in any electrochemical OER.

The Tafel slope offers valuable insights into the rate determining step (RDS) of the OER, influencing the overall reaction mechanism. Chapter 2.2.2 will cover how to calculate the Tafel slope in detail. In Tafel analysis, 120 mV dec⁻¹ Tafel slope indicates that the first step in the OER mechanism is the RDS [17]. When the RDS involves the conversion of M—OH to M—O, the Tafel slope typically measures around 60 mV dec⁻¹ [17]. In cases where the RDS includes the combined transfer of electrons and protons, such as the transformation from M—OH to M—O, the Tafel slope can drop to 40 mV dec⁻¹, indicating that both proton and electron transfers are rate-limiting [17]. Smaller imply that the reaction is more favourable to reduce the overpotential, enhancing catalytic efficiency [17]. Therefore, understanding the relationship between the RDS and the Tafel slope is crucial for designing more effective catalysts for the OER, as it helps identify mechanisms that lower energy barriers and improve overall performance of electrode [17].

Eventhough the oxygen evolution process is not important in H₂ production by EWS, this OER is mandatory as it require to complete the water splitting process.

In Overall, OER involves four steps in which four-electrons exchange between electrode and reactant and hence it involves high thermodynamic barrier (1.23 V) and high overpotential energy due to inferior kinetics and remain as one of the major bottlenecks of EWS [26], [27], [28].

The intermediate step which has highest Gibbs free energy difference (ΔG°) in OER is govern the overall standard ΔG° for the OER. Examining the connection between the η_{OER} on various catalyst surfaces and the ΔG° between OER intermediates produced a volcano shaped plot. Consequently, It was revealed that there exists a clear proportionality between the η_{OER} overpotential and ΔG° between S-O and S-OOH ($\Delta G^\circ_{\text{O}^*} - \Delta G^\circ_{\text{HO}^*}$) as shown in the Figure 3 [7]. This along with the Sabatier principle points that an efficient catalyst should react with the reactant in a way that makes it easy to detach in order to guarantee maximum performance with the least amount of overpotential for the OER [7]. According to this information, a minimum η_{OER} of 0.25 to 0.5 V could be achieved, with RuO_2 catalyst having the lowest value and sitting atop the most effective electrocatalysts for OER. Therefore, this catalyst has become a benchmark electrocatalyst for OER [16]. However, Ru is a rare earth element and hence expensive, discouraging its extensive use in commercial applications for WS. Therefore, extensive investigations have been carried out to search for alternative catalysts that require low overpotential, exhibit higher kinetics, and offer long-term durability.

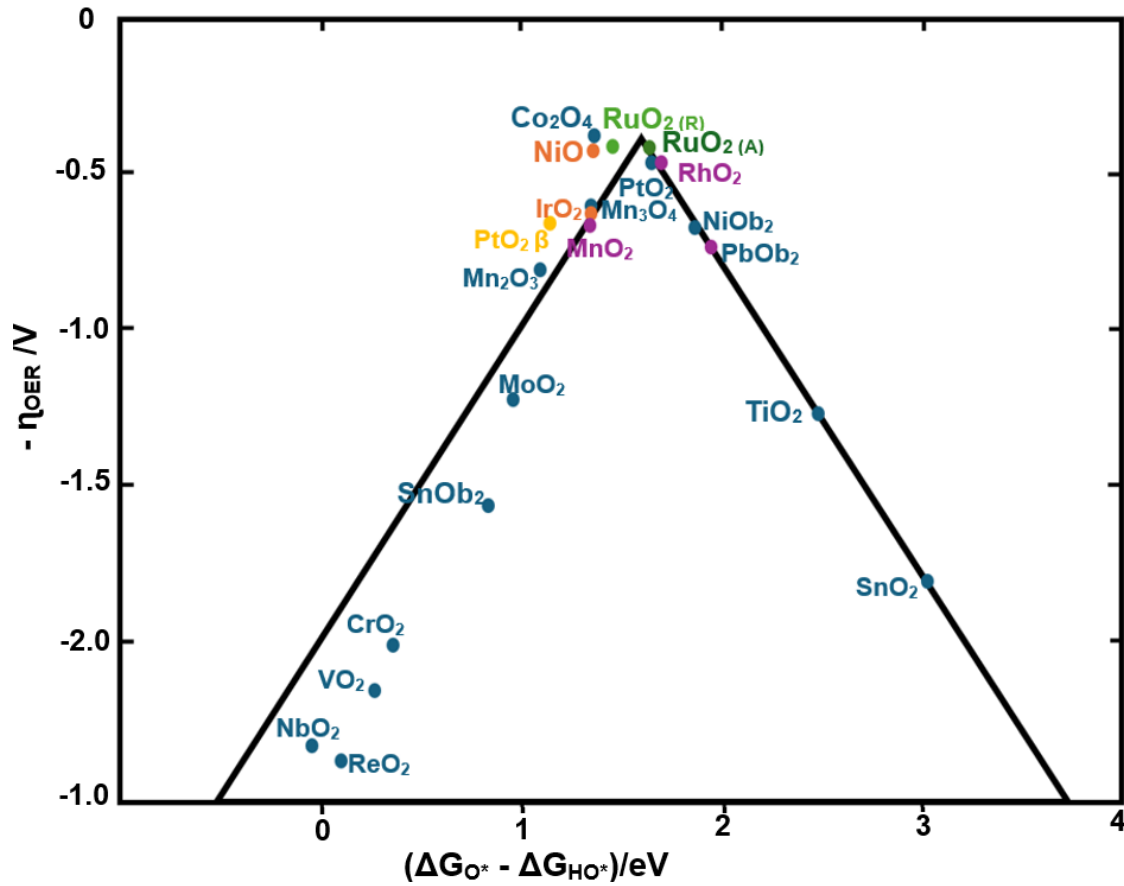


Figure 3 Volcano plot $-\eta_{\text{OER}}$ Vs $\Delta G_{O^*} - \Delta G_{HO^*}$ for OER on metal oxides [7]

2.3.1 Mechanism of HER in EWS

Similar to the OER, the electrochemical HER is significantly affected by the proton concentration in the electrolyte solution. In acidic environments, protons act as the primary reactants and serve as the hydrogen source. In contrast, in alkaline environments, where protons are absent, hydrogen atoms from water molecules provide the necessary hydrogen [16]. This section will delve into the underlying HER pathway at the cathode of the electrochemical cell.

In an acidic medium, under the influence of electromotive force from the external circuit, positively charged protons are attracted to the negatively charged cathode. In a basic medium, the partially positive hydrogen atoms of water molecules are similarly attracted to the cathode. This initial movement of species towards the electrode is referred to as the mass transfer step in HER [29].

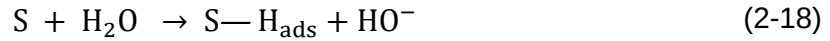
Following this mass transfer step, the HER process occurs at the electrode-electrolyte interface through electrochemical adsorption of reactant on electrode, followed by desorption of product through either electrochemical or chemical process. The HER mechanism in both acidic and alkaline media differs slightly as the reactions described by Equations 2-17 to 2-21 [26], [27], [28].

Step 1: Electrochemical adsorption (Volmer reaction)

- In acidic medium:



- In alkaline medium:

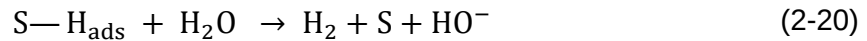


Step 2: Electrochemical desorption (Heyrovsky reaction)

- In acidic electrolyte:



- In alkaline electrolyte:



Chemical desorption (Tafel reaction)

- In both electrolytes:



Regardless of the electrolyte pH, the first step in the HER mechanism always accompanied electrochemical adsorption of reactant on electrode surface. In acidic media, protons are electrochemically adsorbed onto the electroactive site “S” on the cathode surface with an electron transfer from the cathode, forming adsorbed hydrogen on metal ($S-H_{ads}$), an intermediate, as shown in Equation 2-17 [16]. In alkaline media, where water molecules are the sole source of

hydrogen, an additional water dissociation transition step is required to generate protons for forming the $S-H_{ads}$ intermediate as illustrated in Equation 2-18 [16]. During this step, the interaction of the water molecule with "S" and the water dissociation occur simultaneously through different transition states [30], [31]. This initial step in the HER mechanism in both media is known as the Volmer reaction [18], [26], [27], [28], [32].

In the subsequent step of the HER, there are two possible pathways: electrochemical desorption and chemical desorption, applicable to both media. In electrochemical desorption, another proton (in acidic HER, as illustrated in Equation 2-19) or the hydrogen end of a water molecule (in alkaline HER, as shown in Equation 2-20) couples with the $S-H_{ads}$ with an electron transfer process to form molecular hydrogen. This step is referred to as the Heyrovsky reaction [26], [27], [28].

In the chemical desorption pathway, known as the Tafel reaction, two adjacent $S-H_{ads}$ intermediates, which are close enough to interact, combine to generate molecular hydrogen without involving an electron transfer process, as depicted in Equation 2-21[33]. This reaction pathway contrasts with the Heyrovsky reaction, which involves an electron transfer and does not require the $S-H_{ads}$ intermediates to be in neighbouring positions [26], [27], [28].

The presence of two $S-H_{ads}$ at neighbouring positions is crucial for the Tafel reaction to occur. Therefore, the Tafel reaction requires sufficient surface coverage of H_{ads} and the availability of neighbouring metal atoms to facilitate their interaction. Surface coverage depends on the rate of formation of $S-H_{ads}$ and the rate of desorption of H_2 . If the desorption process favours the Heyrovsky reaction, which does not require adjacent $S-H_{ads}$, the surface coverage might be lower for the Tafel reaction. However, if the Heyrovsky reaction is slow, the Tafel reaction might become more competitive. Both reactions compete with each other, and their transition state energies play a crucial role in determining which pathway is more favourable under given conditions.

All these factors are closely related to the properties of the electrode, such as its material type, surface structure, and electrochemical characteristics. The

electrode's properties influence the kinetics of the formation of $S-H_{ads}$ and molecular hydrogen desorption, the distribution of active sites, and the transition states energy of the reaction intermediate pathways. Understanding and optimizing these factors are essential for enhancing the efficiency of the HER, whether it proceeds predominantly through the Tafel reaction, the Heyrovsky reaction, or a combination of both. Given the same reactants and conditions, the exact mechanism and the RDS of HER is thus, correlated with the cathode electrode material [26], [28] and can be predicted using Tafel slope [26].

As discussed in OER, the RDS for HER can be identified by analysing the Tafel plot. Tafel slopes of 30 mV dec^{-1} are expected when the Volmer reaction is rapid and the Tafel reaction occurs slowly, indicating the Tafel reaction is the RDS [34]. If the RDS is a Heyrovsky reaction, a Tafel slope of 40 mV dec^{-1} is anticipated [34]. Conversely, a Tafel slope of 120 mV dec^{-1} is observed if the Volmer step is the RDS while either the Heyrovsky or Tafel reaction proceeds rapidly [34]. These values may slightly deviate from the theoretical values in practical scenarios.

In considering the mechanism of HER, the intermediate $S-H_{ads}$ bond strength is important in determining the efficiency of molecular hydrogen generation. According to the Sabatier principle, achieving a higher yield of molecular hydrogen necessitates optimizing the $S-H_{ads}$ bond strength. For an efficient catalytic site, the $S-H_{ads}$ bond strength should be moderate so that effective binding of H with the catalyst and releasing H_2 from the catalyst [6], [35]. For a range of HER catalysts, Trasatti discovered a volcano-shaped correlation between the logarithm of exchange current density ($\log(j_0)$) and the $S-H_{ads}$ bond strength in 1970 [36], as shown in the Figure 4 [6], [35], [37]. Trasatti's findings indicated that the $\log(j_0)$ increases with $S-H_{ads}$ bond strength up to a certain point, after which it decreases with further bond strengthening. With Pt being nearest to the volcano plot's peak, this suggests the existence of an ideal $S-H_{ads}$ strength. Platinum has thus been identified as the best HER electrocatalyst and has become the benchmark for HER catalyst [17].

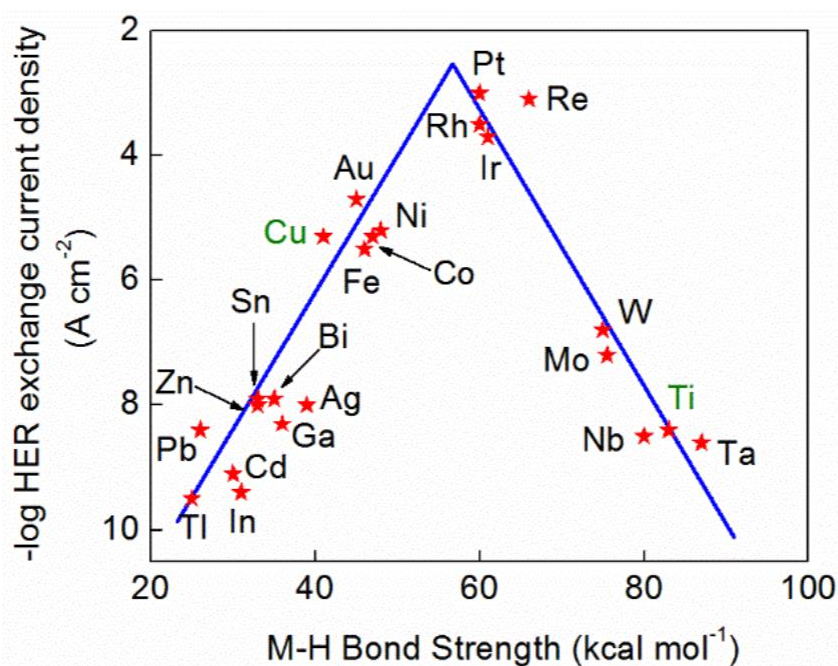


Figure 4: Trasatti's HER Volcano plot, the y axis plots the exchange current densities for HER and the energy of the intermediate metal-hydrogen bond formed between adsorbed H and the electrode surface on the x axis. The figure adapted from reference [36]

2.4 Key electrochemical metrics for assessing HER and OER catalyst performance

2.4.1 Onset potential and overpotential

Onset Potential

The potential at which an observable current starts to flow in an electrochemical reaction, signifying the beginning of the reaction, is known as the onset potential. For HER and OER, it represents the potential where these reactions begin to occur, and it is determined by LSV or CV experiment.

In an ideal scenario with perfect electrodes, HER and OER would occur exactly at their respective equilibrium potentials. However, in practical applications, real-world electrodes require a more negative potential for HER and a more positive potential for OER compared to their standard equilibrium potentials. This discrepancy is due to various factors, including electrode material properties, surface conditions, and reaction kinetics. However, the onset potential is not

precisely defined because there is no exact current value universally accepted as the starting point. Typically, it is the potential required to achieve a small, measurable current, generally between 2 to 0.5 current density in mA cm^{-2} .

Overpotential

The term "overpotential" (η) refers to the difference between the standard thermodynamic equilibrium (E°) for a given reaction (for H_2 and O_2 evolution, this is 0.0 mV (Vs. RHE) and 1230 mV (Vs. RHE), respectively, at 25 °C) and the actual potential or experimental potential (E_{exp}) at which a defined current density is observed. As an illustration, consider the overpotential needed to reach current densities of 5 mA cm^{-2} (η_5), 10 mA cm^{-2} (η_{10}), and 100 mA cm^{-2} (η_{100}). However, because a green hydrogen production system using solar energy that runs at 12.3% efficiency typically produces a current density of 10 mA cm^{-2} , the overpotential parameter that is most frequently reported as η_{10} [27], [33].

The actual potential (vs. RHE) required to achieve different current densities can be experimentally determined using LSV, CV, or CP methods. However, solution resistance may affect the potential measured by these techniques. Therefore, to produce an iR -compensated polarization curve, the potential drop caused by solution resistance is compensated, as shown in Equation 2-22, and the current density is plotted against the iR -compensated potential, as illustrated in Figure 5. The solution resistance can be accurately determined through an EIS experiment, as described by Colic et al. (2015) [38]. From this plot, the actual potential required to achieve the desired current density is determined. The overpotential then quantifies the additional potential (Vs. RHE) that needs to trigger the electrochemical reaction at a given current density, as described by Equation 2-23 [39], [40].

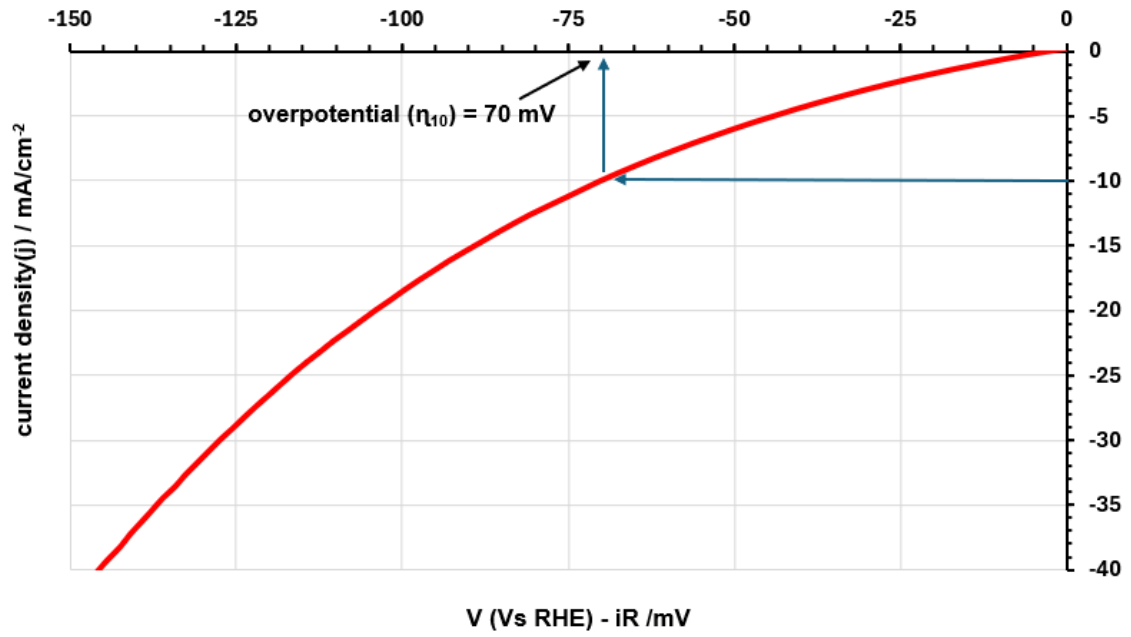


Figure 5: Schematic diagram illustrating the determination of overpotential using an iR-compensated polarization curve obtained from LSV data.

$$E = E \text{ (Vs. RHE)} - iR \quad (2-22)$$

$$\eta = E - E^\circ \quad (2-23)$$

2.4.2 Tafel slope and exchange current density

In the 1920s, an important theory relating current and voltage in electrochemical reactions was introduced by a group of scientists including Valentine Butler, Tibor Erdey-Grúz, and Max Volmer [41]. This theory was later developed into the Butler-Volmer equation, which describes the kinetics of multi-step electron transfer reactions [41].

The Butler-Volmer equation for a multi-step electron transfer reaction is expressed as Equation 23 [27], [42]:

$$j = j_0 e^{\alpha F \eta / RT} \quad (2-24)$$

where J is the current density, α is the transfer coefficient, j_0 is the exchange current density, F is the Faraday constant, R is the gas constant, and T is the absolute temperature [42]. By taking the logarithm of both sides and rearranging,

a linear dependence of overpotential on the Log (current density) may be obtained, expressed as Equation 2-24:

$$\log j = \log j_0 + \frac{2.303\alpha F}{RT} \times \eta \quad (2-25)$$

This equation can be further simplified to a well-known form called the Tafel Equation 2-25 [42]:

$$\eta = a + b \times \log j \quad (2-26)$$

where a is a constant and b is the Tafel slope, defined as $b = 2.303RT/\alpha F$. Since the b inversely proportional to the α , b is also indicating the rate at which current density changes with overpotential and is a critical parameter for evaluating electrocatalysts [42].

For a given electrochemical reaction, a lower Tafel slope denotes faster kinetics and greater Tafel slope denotes slower kinetics [27]. Therefore, when comparing two different electrode materials under identical reaction conditions, the electrode with the smaller Tafel slope demonstrates better catalytic performance [27].

The intercept “ a ” in the Tafel plot corresponds to the logarithm of j_0 , an innate property of the electrode that gauges the rate of electron transfer between the electrode and reactant. Since it transfers electrons more quickly, an electrode with a higher j_0 is regarded as a better electrocatalyst.

Under steady-state conditions, using iR -compensated current-voltage data obtained from techniques such as LSV performed at very low scan rates, chronoamperometry, or chronopotentiometry, a plot of η versus $\log j$ can be constructed. From this plot, the parameters a and b can be determined through linear fitting beyond the onset potential, as illustrated in Figure 6 [40], [42].

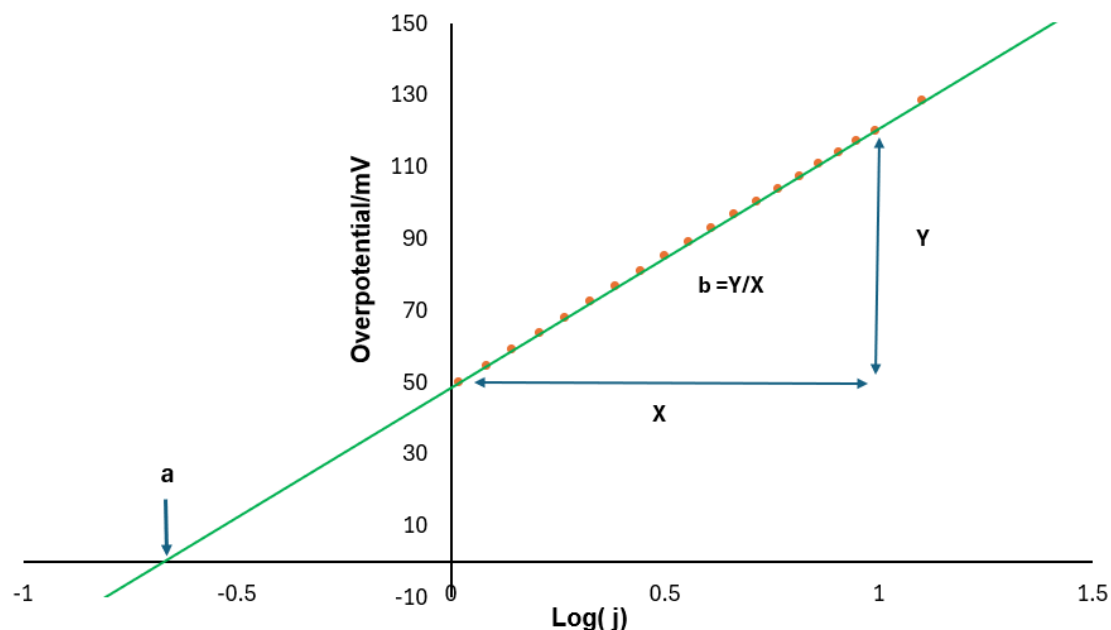


Figure 6: Schematic diagram of overpotential vs. $\log(j)$, where the orange dots represent experimentally obtained overpotential values corresponding to $\log(j)$, and the green line represents the linear fit to the experimental data.

2.4.3 Stability

To use electrocatalysts in practical water splitting applications, long-term stability is a crucial criterion. This stability is evaluated using two primary methods: CA or CP.

In the CV method, stability is assessed by comparing the cyclic voltammograms before and after conducting more than 1000 CV scans in a specific electrolyte. If the voltammograms remain identical, it indicates that the catalyst has not degraded, detached from the supporting electrode, or undergone any changes during the experiment.

In the CA or CP methods, stability is determined by monitoring changes in current or potential over time while running the experiment at a constant potential or current. These tests are typically conducted for more than 10 hours. A fixed amount current is employed in the case of the CP method, while for the CA method, a fixed potential is maintained for longer time period typically more than 12 hours [7], [40]. If the results remain stable throughout the experiment, it

indicates that the catalyst has not degraded or detached from the supporting electrode and has good long-term stability [7].

2.4.4 Faradaic efficiency (FE)

In electrochemistry FE is defined as the percentage of charge converted to yield of a particular electrochemical reaction [7], [43], [44]. This reveals if the reaction under electrochemical reaction under study consumes all the charge supplied and efficiency of the process. FE is measured by taking the percentage ratio of the amount of product (in moles) generated ($n_{\text{effective}}$) through electrochemical process to the amount of product (in moles) theoretically generated ($n_{\text{theoretical}}$) during the reaction as in the following Equation 26 [7], [43], [44].

$$FE = \frac{n_{\text{effective}}}{n_{\text{theoretical}}} \times 100\% \quad (2-27)$$

The $n_{\text{theoretical}}$ is calculated applying faradaic law using the amount of charge supplied (Q), number of electrons needed to convert one mole of product (Z) and the Faraday constant (F), as given in the following Equation 27.

$$n_{\text{theoretical}} = \frac{Q}{ZF} \quad (2-28)$$

In water electrolysis, to determine the actual amount ($n_{\text{effective}}$) of gas (hydrogen or oxygen) produced requires a reliable and accurate quantitative method. while most of the time, the separately collected gas volume is converted to amount of moles using real gas equation (assuming H_2 and O_2 are real gas and collected gas are pure) GC is better choice for separating and quantifying the gases.

2.4.5 Turnover frequency (TOF)

TOF of electrocatalysts is rate of the product generated by an active site of catalyst involving the reaction at a particular overpotential and hence Higher the TOF better the catalyst. This is calculated by taking the ratio of the amount of product (H_2 or O_2 in water splitting) generated per unit time to the total electroactive sites on the catalyst. In heterogeneous catalytic reaction, only the surface-active site of the catalyst is participated as reactant molecule cannot access to the catalyst which are not in the surface and hence, they are inactive.

2.4.6 Geometric activity, mass activity, and electrochemical surface area

Geometric activity

The activity of an electrode can be assessed by the amount of current produced per unit of its geometric surface area, known as the geometric activity. This measurement, typically expressed in mA cm^{-2} , reflects the electrode's capability to produce current at a particular voltage per unit area of the electrode material. This approach is suitable for smooth or flat electrodes where the geometric surface area closely approximates the actual surface area. However, for rough or three-dimensional electrodes, this method can yield inaccurate interpretations due to the significant discrepancy between the geometric and actual surface areas.

Mass activity

To address the limitations of geometric activity, especially for electrodes with complex structures, the activity is often normalized by the catalyst mass loading. This measure, known as mass activity, is expressed in mA g^{-1} of catalyst. While mass activity provides a more meaningful evaluation of catalyst performance, it operates under the assumption that all the loaded catalyst participates in the electrochemical reaction, which is not always the case. Not all the bulk material interacts with the reactants, leading to an underestimation of the catalyst's effectiveness [7].

Electrochemical surface area and specific activity

Given the limitations of geometric and mass activities, determining the actual surface area of a catalyst is crucial for accurately assessing electrode activity. It is typically much higher than their geometric surface area, varying significantly among different electrodes [45]. By normalizing the real surface area with the geometric surface area, the roughness factor (RF) can be determined [45]. This factor is essential for comparing catalytic activities across different electrodes and assessing catalyst durability by measuring the real surface area before and after electrochemical reactions [46].

Several methods exist for determining the real surface area of an electrocatalyst, with the ECSA being a prominent one [46], [47]. ECSA is often determined using the electrochemical double-layer capacitance (C_{dl}) method, which involves CV measurements in the non-faradaic region, where no oxidation reduction couple, of the electrode material under investigation [46]. By conducting several CV scans at different low scan speeds and drawing the j_0 against the scan speed, the gradient of this plot gives the C_{dl} of the electrode. The ECSA can be obtained by taking the ratio of the C_{dl} to the specific capacitance (C_s) of the electrode material, as illustrated in Equation 2-28 [46]. This method, as developed by Trasatti and Petrii [47], provides a reliable in situ measurement of the electrode's active surface area, which is crucial for a more accurate evaluation of electrocatalyst [46].

$$ECSA = \frac{C_{dl}}{C_s} \quad (2-29)$$

2.4.7 Earth-abundant materials as functional catalysts for water splitting

Water splitting reactions at the anode and cathode require energy surpassing their thermodynamic barriers due to intermediate reactions at the electrode-electrolyte interface. Current catalysts like Pt for HER and RuO_2 for OER are highly efficient due to their optimal adsorption and desorption energies for reaction intermediates. However, their high cost and scarcity hinder large-scale commercial applications [17]. Research efforts are thus directed towards earth-abundant materials to mitigate these limitations.

Efficient electrocatalysts should exhibit high recyclability, intrinsic activity for HER and OER, durability, chemical and thermal stability. TMs like Fe, Co and Ni fulfil these criteria due to their electronic configurations (presence of unpaired and empty orbitals in the d orbital), which facilitate the adsorption-desorption process of reactive intermediates [48].

Further, the relative abundance of these materials is 5.63% for Fe, $2.5 \times 10^{-3}\%$ for Co, and $8.4 \times 10^{-3}\%$ for Ni, resulting in market prices of \$120, \$33,420, and

\$18,440 per ton, respectively, which significantly impacts their suitability for commercial applications compared to non-noble elements like Pt at \$28,800,000 and Ru at \$14,400,000 per ton [49]. Although Fe is cheaper, its instability in basic media limits its use as a standalone catalyst [48]. Cobalt and nickel, has gained attention due to its optimal hydrogen binding energy, making it an excellent candidate for HER, despite its instability in harsh media [50]. Modifying this with robust materials can enhance its stability and catalytic activity [50]. These TMs, existing in various compounds such as oxides, selenides, phosphides, and sulphides, have shown promising catalytic activity and durability in water splitting applications [48]. Among these, transition metal phosphides (TMPs) are appealing electro catalysts for HER. Proton is accepted by the phosphorous (P) end of TMPs during water electrolysis, and hydride is accepted by TMs. This promotes hydrogen generation by weakening the metal-hydrogen interaction. Furthermore, d-orbital stabilization by phosphorus via ligand formation facilitates the electron transfer process from Metal (M) to phosphorus atom, enhancing HER performance [8].

2.4.8 Cobalt phosphides (CoPs) as catalysts.

CoPs are a subclass of TMPs with excellent catalytic properties due to their unique electronic structures, which facilitate both HER and OER. The introduction of phosphorus into Co tunes the electronic environment, creating partial positive and negative charges on Co and phosphorus sites, respectively, enhancing water molecule adsorption and accelerating HER and OER [51], [52]. With more unpaired d electrons in Co, CoPs have the potential to be extremely favourable HER electrocatalysts. These electrons contribute easily to the formation of hydrogen adsorbed cobalt (Co-H^{*}). Furthermore, phosphorus takes electrons away from Co-H^{*}, weakening the Co-H^{*} bond and encouraging hydrogen desorption. Standard free energy of hydrogen adsorption (ΔG_{H^*}) is thus adjusted to the ideal level for the HER process [8]. Further Co and P-containing catalysts are also used as OER catalysts (e.g. [8], [53]) and as bifunctional catalysts (e.g. [54]). During the OER process, these materials tend to convert to their oxide/hydroxy form while partially dissociating the Co-P bond [8]. The oxide form

acts as the true OER centre, while Co-P provides conductive sites [8]. Formation of the peroxy (O-O) bond is crucial for the OER process, and the fast movement of H^+ in Co-P and oxide/hydroxy forms is beneficial for the formation of peroxy bonds, leading to the release of oxygen in the next step [8]. Based on these understanding it can be infer that CoPs catalysts can be used as both OER and HER and therefore act as a bifunctional catalyst.

2.4.9 Synthesis methods for CoPs and advantages of electrodeposition method.

Su et al. (2017) [55] have contributed valuable insights with their review "Synthesis and Application of Transition Metal Phosphides as Electrocatalysts for Water Splitting," which offers comprehensive information on TMPs catalysts for water splitting reactions. Additionally, Deng et al. (2024) [8] have published an excellent review titled "Recent Advances in Cobalt Phosphide-Based Materials for Electrocatalytic Water Splitting: From Catalytic Mechanism and Synthesis Method to Optimization Design," providing in-depth knowledge about CoPs catalysts synthesis and their application for WSR. In summary, CoPs can be synthesized through various methods such as thermal decomposition, solvothermal processes, and electrodeposition [8], [55]. Thermal decomposition involves heating metal and phosphorus precursors under inert conditions to control morphology [55], yet it demands high energy input, involve toxic organic precursors and may release toxic gases like phosphine [55]. Solvothermal synthesis, conducted in closed vessels under pressure with organic solvents, offers versatility in producing nanostructured materials [55] but requires stringent safety precautions due to the flammable and corrosive nature of solvents [55] .

In contrast, electrodeposition emerges as a favourable method, particularly in aqueous or ionic liquid media, for its mild reaction conditions and precise control over composition and morphology [56]. Ionic liquid media, in electrodeposition, provide several advantages over aqueous media by eliminating bubble formation during deposition, ensuring different morphologies and more uniform coatings essential for high-performance electrocatalysts [57]. Moreover, electrodeposition enables binder-free electrode preparation [55], distinguishing it from other

methods that often require binders to adhere the synthesized material to substrates. This feature not only simplifies the fabrication process but also enhances the stability and efficiency of the electrodes, making electrodeposition particularly suitable for developing advanced catalysts and electrochemical devices. Overall, electrodeposition stands out as an environmentally friendly and efficient technique for synthesizing cobalt phosphides, offering superior control and performance in EWS applications.

2.4.10 CoPs catalyst preparation by electrodeposition method and use of supporting electrode.

Electrodeposition is a popular method for developing CoPs-based catalysts due to its ease of use, controllability, and ability to produce uniform coatings with a range of dimensions, shapes, and different nano structures. This binder-free method is cost-effective and results in robust, high electrically conductive materials [8]. For example, Jiang et al. (2015) used electrodeposition to prepare Co-P on a Cu film, achieving low overpotential and high kinetic activity for both HER and OER [58]. The catalyst exhibited low η_{10} for HER (94 mV) and for OER (345 mV), with 42 mV dec⁻¹ and 47 mV dec⁻¹ Tafel slopes, respectively. SEM images revealed complete coverage of CoP particles on the Cu film, highlighting the effectiveness of the electrodeposition technique. The HER overpotential improvement compared to other electrodes is noteworthy, indicating high catalytic efficiency. The low Tafel slopes suggest excellent kinetic activity. Further enhancement could be achieved through the use of porous electrodes and the development of high-porosity 3D catalyst structures to optimize efficiency.

Similarly, Bai et al. (2016) electrodeposited Co/CoP on nickel foam, resulting in high catalyst loading and low overpotential [59]. catalyst that exhibited remarkable performance for HER in an alkaline solution, achieving η_{10} with only 35 mV and a Tafel slope of 71 mV dec⁻¹ [59]. This catalyst was directly electrodeposited onto high surface area nickel foam, resulting in high catalyst loading and rough 3D nanoparticles, which contributed to a high ECSA. The binder-free electrodeposition technique enhanced internal contact between the catalyst nanoparticles and the electrode, reducing internal resistance. However,

the aqueous medium used in electrodeposition caused hydrogen evolution during deposition, disrupting the catalyst coating and preventing uniform architecture formation. Additionally, the Ni foam substrate's surface remained relatively smooth, suggesting that increasing its roughness through acid etching or growing additional nanoarchitectures could further improve surface area and catalyst performance. Despite these challenges, the study represents a significant advancement, achieving lower overpotential and better kinetics than Pt/C catalysts [59]. In another study, CoP catalyst prepared on a carbon membrane derived from biomass carbonization evaluated for both HER and OER [60]. The CoP catalyst achieved a 10 mA cm^{-2} with an overpotential of 140 mV for HER and 1.48 V for OER, and respective Tafel slopes of $109.30 \text{ mV dec}^{-1}$ and $137.59 \text{ mV dec}^{-1}$ [60]. Further the CoP electrolyser, composed with this catalyst for both anode and cathode, outperformed traditional Pt/C//RuO₂/C systems by requiring a lower cell voltage of 1.56 V to achieve 10 mA cm^{-2} [60]. Through a series of experiments, this study identified that high phosphorus content negatively impacted internal electrode conductivity and weakened the cobalt-phosphorus interaction [60], indicating a need for optimization. The porous structure and high interaction between CoP and the supporting membrane facilitated electron movement and active site accessibility, highlighting CoP/C catalysts potential as an efficient and sustainable alternative to noble metal-based catalysts. The use of biomass offers a greener, cost-effective technology, and the carbon membrane's porous architecture increases catalyst loading and effective surface area. Despite these advancements, the HER overpotential remains high compared to other electrodes, suggesting that utilizing high surface area, high conductivity, and catalytically active supporting electrodes could further enhance activity.

In evaluating the efficiency of CoPs catalysts prepared via electrodeposition, the choice of supporting electrode plays a critical role, as illustrated by above studies and according to the discussed examples NiF seems to be highly desirable according to low HER overpotential given by the Co/CoP on nickel foam catalyst [59]. Further, it has been demonstrated that using NiF as a supporting electrode significantly enhances the performance of any catalysts, particularly in

applications such as the water WS process and therefore it is a choice of most researchers. This superior performance can be attributed to two main factors: firstly, the high surface area provided by the foam-like structure of NiF, which facilitates greater loading of catalyst; secondly, the intrinsic catalytic activity of nickel itself. In a related study, Mass et al. (2016) synthesized a catalyst containing both cobalt and cobalt phosphide by thermally treating a precursor compound, dichlorobis(triphenylphosphine)cobalt (II) [61]. This catalyst was evaluated for the OER after being coated onto two different supporting electrodes: NiF and glassy carbon (C). The results showed that the NiF-supported catalyst exhibited a 30 mV lower overpotential compared to the C-supported electrode, achieving a current density of 10 mA cm⁻² in a basic medium [61]. This outcome underscores the synergistic effect between CoP and Ni, where the presence of nickel significantly enhances the OER activity of the catalyst system.

2.4.11 Ionic liquid (IL) medium and deep eutectic solvent (DES) medium electrodeposition.

While electrodeposition is typically conducted in aqueous media, using IL and DES offers several advantages for achieving uniform coatings of electrocatalysts. As previously mentioned, this method is preferable over aqueous medium deposition because it avoids interference from HER side reactions, resulting in more robust and durable electrodes. Chiu et al. [62] discovered that the deposition potential significantly affected the morphology, elemental ratios, and crystallinity of CoP and Co when deposited using butyl-1-methylpyrrolidine dicyanamide ionic liquid combined with Co ions and phosphate precursors. This IL exhibited enhanced deposition efficiency relative to aqueous solutions and effectively suppressed the HER side reaction [62]. Srivastava et al. (2012) demonstrated these advantages by synthesizing Ni and Co coatings on brass substrates, comparing the quality of coatings deposited from IL and aqueous media [57]. The morphology of the coatings differed significantly: dense nodular and fine equiaxed crystals were observed for Ni and Co coatings, respectively, in IL media, whereas polyhedral crystals and acicular flakes were observed in aqueous media [57]. The study also reported a reduction in charge transfer

resistance from 600 ohms and 28 ohms for Ni and Co coatings in aqueous media to 457 ohms and 7 ohms in IL media, respectively [57]. The improved morphology, characterized by a higher catalytic surface area and beneficial crystal phases, along with reduced charge transfer resistance, enhances the catalytic activity for water splitting reactions. Additionally, electrodes deposited in IL media displayed higher corrosion resistance compared to those from aqueous media [57], which is an advantage for the long-term durability of WS catalysts. However, DESs offer several advantages over ILs in electrodeposition. They are more cost-effective and less toxic. Additionally, electrodeposition using DESs is typically conducted at elevated temperatures, which results in final structures that are more crystalline compared to those obtained through low-temperature deposition methods [8]. Co oxides and phosphides deposited at varying potentials using Ethaline-based DESs exhibited diverse shapes and sizes of structures [8]. Additionally, research by Kang et al. (2020) demonstrated that CoP deposited using DESs displayed superior catalytic activity in oxidation of hydroxy methyl furfural compared to CoPs deposited using aqueous electrolytes [63]. However, research on CoP catalysts deposited in DESs for water splitting reactions is limited and requires further investigation, as highlighted in a recent review article by Deng et al. (2024) [8].

2.4.12 TiO₂ as a catalytic promotor.

Several investigations have reported that TiO₂ interaction with other metal or metal-based catalysts optimizes catalyst-H adsorption energy, thereby lowering the activation barrier of the HER by modifying the catalysts' electronic states [9], [10], [11]. It can increase water adsorption, thereby enhancing the overall water splitting reaction. TiO₂ also provides a stable base layer that can improve the adhesion and distribution of CoP on the electrode surface, further enhancing the catalytic activity and durability of the electrode. TiO₂ is a corrosion-resistant material, and when catalysts are supported on this substrate, the catalytic durability increases while maintaining or enhancing catalytic activity, with TiO₂ acting as a co-catalyst [64]. Furthermore, when catalysts are coated on nano-level

particles, the electrode-electrolyte interface surface area and the space for product formation increase three-dimensionally [64]. Such coating results in a final catalyst with high porosity, which enhances mass transfer and facilitates the release of gaseous products [64]. Additionally, this approach increases the ECSA and reduces catalytic particle agglomeration [64]. However, the electrical conductivity of TiO_2 is low due to its semiconductor nature [64], [65], [66]. If the TiO_2 coating is not appropriately applied, the electrical conductivity decreases significantly, leading to diminished catalytic activity [64]. By utilizing TiO_2 in nanoparticle form, this constraint on electrical conductivity can be minimized, thereby maintaining the efficiency of the catalyst [64]. Additionally, the use of an interconnected network of TiO_2 and other conductive catalysts can further improve the conductivity of the electrode [67]. In the investigation by Emran et al., the Nd-Gd-Pt-TNTA catalysts exhibited a reduced band gap in TiO_2 nanotubes and enhanced conductivity due to the doping with Nd, Gd, and Pt, leading to improved catalytic activity compared to their individual forms [66]. The study suggests incorporating other catalysts into TiO_2 to further improve conductivity and catalytic activity [66]. Pandian Ganesan et al. (2018) investigated TiO_2 -coated CoS_2 as a hybrid catalyst for both the HER and the OER. Their results showed that the catalyst required η_{10} of 198 mV and 231 mV, respectively, for HER and OER. These values are lower than the overpotentials required by individual TiO_2 and CoS_2 catalysts, revealing a synergistic effect between TiO_2 and CoS_2 . The study demonstrated that the reduction of the electrochemical bandgap is a significant factor contributing to the enhanced activity for both OER and HER (Ganesan et al., 2018). Yuan et al. synthesized a series of catalysts by coating TiO_2 on Co_3O_4 , $\text{Co}(\text{OH})_2$, and CoS_2 catalysts, and investigated their HER activity in alkaline electrolyte [9]. According to the results, all the TiO_2 -incorporated catalysts showed lower overpotentials than the individual Co-based catalysts, highlighting the advantage of TiO_2 modification [9]. Among these catalysts, TiO_2 -modified Co_3O_4 exhibited the lowest HER overpotential (49 mV) and Tafel slope (79 mV dec^{-1}) [9]. This investigation concludes that the efficiency enhancement is attributed to the synergistic effect between the Co catalyst and TiO_2 , as well as to defects in the catalysts [9]. The

improved catalytic efficiency motivates further investigation into the effects of TiO_2 incorporation into other catalysts.

2.5 Research gap

The potential of CoPs electrocatalysts for HER and OER in EWS is well documented. However, a significant research gap exists in the synthesis and optimization of CoP electrocatalysts using electrodeposition techniques in DESs. Existing studies predominantly focus on traditional preparation methods, overlooking the potential advantages offered by DESs, such as their morphology tenable properties, environmental friendliness, and cost-effectiveness.

Furthermore, while TiO_2 has been shown to enhance the catalytic activity of CoPs when incorporated through mixing or surface treatments, the specific method of using TiO_2 nanoparticles as a coating to improve the morphology and electrochemical surface area of CoPs on substrates has not been explored. This unexplored strategy presents a promising opportunity to enhance electrocatalytic performance by leveraging the synergetic effects of TiO_2 and CoPs.

Addressing this gap, the proposed research will focus on synthesizing Co/CoPs catalysts via low-cost DES-mediated electrodeposition on TiO_2 -coated NiF substrates. The hypothesis is that TiO_2 coating will enhance the electrochemical surface area and distribution of CoPs, thereby improving the EWS performance through synergetic effects of CoPs and TiO_2 . Systematic studies of the HER and OER activities of these novel electrocatalysts will be conducted to evaluate their overall water splitting (OWS) efficiency. This research aims to advance the development of more efficient and cost-effective catalysts, significantly contributing to the field of sustainable energy applications.

3 Experimental methods and characterisations

This research aims to investigate bifunctional electrocatalysts based on low-cost, earth-abundant transition metals, metal oxide and metal phosphide—Ni, TiO₂, Co and CoPs as alternatives to the high-cost, scarce Pt and Ru based electrocatalysts. This methodology section outlines the experimental procedures, characterization techniques, optimization strategies, and performance evaluation methods used throughout the study, explaining why these methods were chosen and how they were implemented.

3.1 Material synthesis

The following chemicals and materials were used in synthesizing the Co/CoPs/TiO₂/NiF, Co/CoPs/NiF, 10% Pt/C/NiF, and RuO₂/C/NiF electrodes

Titanium (IV) oxide (TiO₂, nanoparticles <21 nm primary particle size, 99.5%, ACS Reagent, Sigma Aldrich), cobalt(II) chloride (anhydrous, ≥98.0%, Sigma Aldrich), absolute ethanol (99.9 %, sigma Aldrich), potassium hydroxide (99.99%, Sigma Aldrich), choline chloride (99%, Acros organics), urea (Fisher Scientific), sodium hypophosphite monohydrate (NaH₂PO₂·H₂O, >99%, Sigma Aldrich), nickel foam (99.5%, 93% porosity, 20 Pores/cm, 0.9 mm thickness, 0.62 g/cm³ Bulk Density), platinum on activated carbon (nano powder, 10%Pt, Themo Scientific, USA), ruthenium(IV) oxide (99.9%, Sigma Aldrich), Nafion (D5, 5%, alcohol based, Fuel cell store)

3.1.1 Co/CoPs/TiO₂/NiF and other electrocatalyst synthesis.

The synthesis of the Co/CoPs/TiO₂/NiF catalyst was conducted in two main stages. Initially, TiO₂ was deposited onto NiF as shown in the Figure 7. In the second stage, Co/CoPs was deposited onto the TiO₂-coated NiF (TiO₂/NiF) as described in the Figure 8. Additionally, several other electrodes, including Co/CoPs/NiF and Co/TiO₂/NiF, were synthesized for comparison purposes. For benchmarking, 20% Pt/C on Ni foam (Pt/C/NiF) and RuO₂ on NiF (RuO₂/NiF) were also prepared. Detailed descriptions of these synthetic routes are provided in the following sections.

3.1.1.1 Synthesis of Co/CoPs/TiO₂/NiF electrocatalyst

Electrophoretic deposition of TiO₂ on NiF supporting electrode (TiO₂/NiF)

TiO₂ nanoparticle suspension was first prepared by mixing TiO₂ nanoparticles (0.1000 ± 0.0001 mg) with absolute ethanol (80.0 ± 0.5 ml) in a Pyrex glass beaker, followed by magnetic stirring for 20 minutes and subsequent ultrasonic horn sonication (10 W, 5 pulse s⁻¹) for 10 minutes. The resulting suspension serves as the electrolyte solution for electrophoretic depositing of TiO₂ nanoparticles on NiF. Prior to deposition, the NiF supporting electrode (2.0 ± 0.1 cm $\times$ 1.0 ± 0.1 cm) was treated with 3 mol dm⁻³ HCl acid for 20 minutes while undergoing sonication in an ultrasonic cleaning bath (power 10, pulse 5). The NiF was then rinsed sequentially with DI water and absolute ethanol to remove trace surface pollutants. In a two-electrode electrodeposition system, the cleaned NiF served as the cathode and platinum plate as the anode, positioned 19.5 ± 0.5 mm apart, TiO₂ film deposition was achieved via constant voltage (30.0 ± 1.0 V), with the active geometric surface area of NiF (1.5 ± 0.1 cm²) masked using a masking tape. To ensure even distribution of TiO₂ on both sides of the NiF, the deposition was carried out on both sides of the NiF for 120 ± 1 s. Following deposition, the masking tape was removed, and the sample were sintered at 450 °C for 30 minutes with a ramping rate of 5 °C s⁻¹, followed by natural cooling. The sample were labelled as TiO₂/NiF.

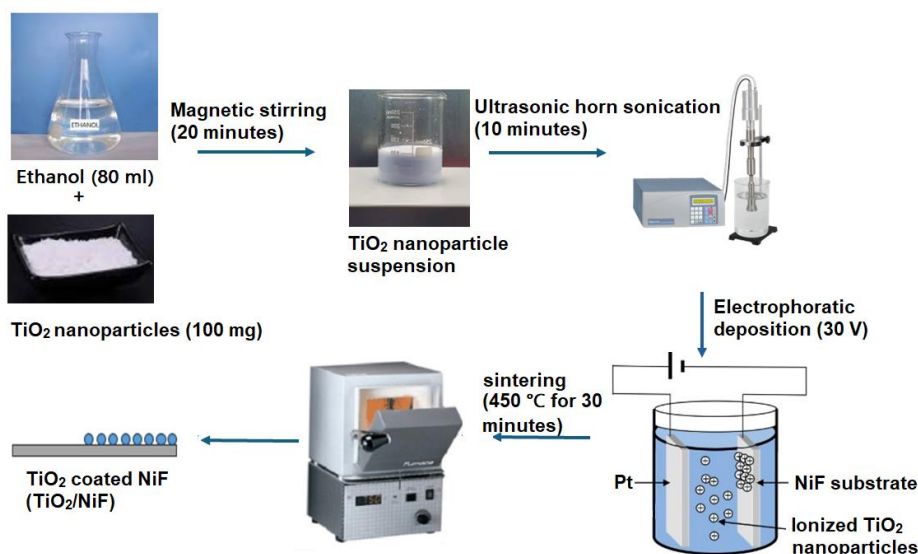


Figure 7: A schematic representation of TiO_2/NiF electrode fabrication process

Deep eutectic solvent mediated Co/CoPs deposition

$\text{CoPs}/\text{TiO}_2/\text{NiF}$ electrode was fabricated through cathodic electrodeposition of CoP on the TiO_2/NiF . A schematic representation of the electrode fabrication process is shown in Figure 8. To prepare the electrolyte, anhydrous CoCl_2 (0.3000 ± 0.0001 g) was mixed with choline chloride (15.0000 ± 0.0001 g) and urea (7.5000 ± 0.0001 g). This mixture was heated at 120 ± 0.5 °C while being magnetically stirred until a clear, transparent solution was formed. Then, NaH_2PO_4 (0.4500 ± 0.0001 g) was added to the solution and stirring continued until all the NaH_2PO_4 dissolved while maintaining the same temperature. The temperature of the solution was then controlled at 90 ± 0.5 °C to be used as the electrolyte. In a two-electrode electrodeposition system, TiO_2/NiF served as the cathode, while a platinum plate acted as the anode, positioned 19.5 ± 0.5 mm apart. CoP film deposition on TiO_2/NiF was conducted under constant current conditions (50.000 ± 0.001 mA), with the active geometric surface area of TiO_2/NiF being 1.0 ± 0.1 cm^2 . To ensure even distribution of CoP, the electrodeposition was carried out on both sides for equal durations. The electrodeposition times were 15, 30, 60 and 120 minutes per side, resulting in total electrodeposition times of 30-, 60-, 120- and 240-minutes total electrodeposition time to achieve various CoP thicknesses on the TiO_2/NiF . According to the total CoP deposition time, the electrodes were named as follows:

Co/CoPs(30)/TiO₂/NiF for electrode prepared with a 30- minutes deposition time, Co/CoPs(60)/TiO₂/NiF for 60 min, Co/CoPs(120)/TiO₂/NiF for 120 min, and Co/CoPs(240)/TiO₂/NiF for 240 min.

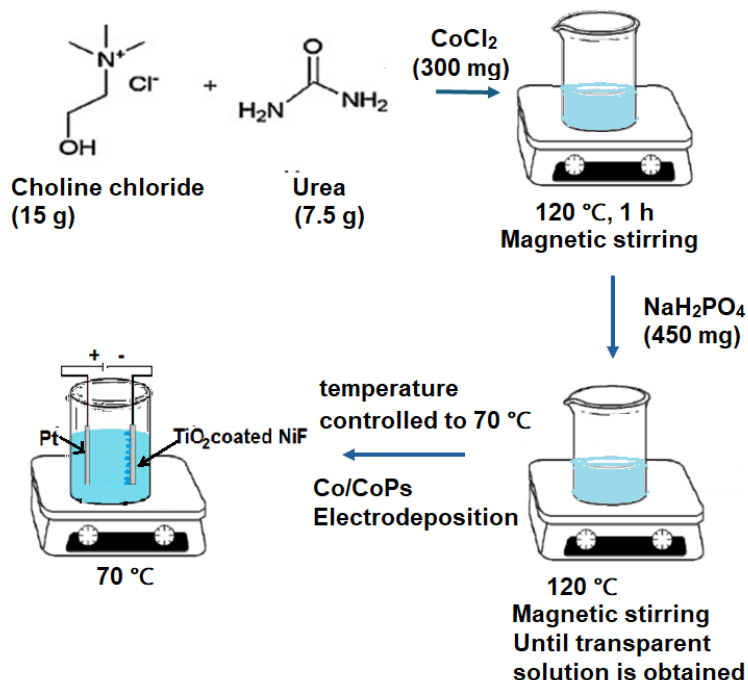


Figure 8: A schematic representation of Co/CoPs/TiO₂/NiF electrode fabrication process

3.1.1.2 Synthesis of Co/CoPs(240)/NiF and Co(240)/TiO₂/NiF catalysts.

To enable a comparative assessment of the activity between the synthesized Co/CoPs(240)/TiO₂/NiF and various other controlled electrodes, different preparations were conducted. The Co/CoPs/NiF electrode was prepared similarly to the Co/CoPs(240)/TiO₂/NiF electrode but using a bare NiF electrode instead of a TiO₂/NiF electrode. The Co/TiO₂/NiF electrode was prepared in a manner similar to the Co/CoPs(240)/TiO₂/NiF electrode, except NaH₂PO₄ adding to the electrolyte. Additionally, the Co/NiF electrode was prepared in the same way as the Co/CoPs(240)/TiO₂/NiF electrode but using a bare NiF electrode and without the addition of NaH₂PO₄ to the electrolyte.

3.1.1.3 Synthesis of Pt/C/NiF and RuO₂/NiF catalysts.

The electrodes were prepared according to the procedure outlined by Yu et al. (2019) [69]. In brief, catalyst ink with commercial Pt/C or RuO₂ catalyst powder (5.0 ± 0.1 mg) was dispersed in a mixture of deionized water (0.550 ± 0.001 ml), ethanol (0.250 ± 0.001 ml), and 5% Nafion (0.200 ± 0.001 ml). This mixture was sonicated for 1 hour. Then, 0.200 ± 0.001 ml of the ink was coated on a 1.0 ± 0.1 cm² area of a NiF electrode (2.0 ± 0.1 cm $\times$ 1.0 ± 0.1 cm) to achieve a catalyst loading of 1 mg cm⁻² on NiF. This was followed by air drying for 24 hours.

3.2 Material characterisations

3.2.1 X-ray diffraction (XRD)

XRD analysis is a non-destructive technique used for characterizing materials by investigating their crystallographic information [36], [70]. X-rays generated by the X-ray source in the diffractometer are directed onto the sample at various incident angles. The diffracted X-ray beams at specific angles are detected by the X-ray detector in the instrument, producing a diffractogram that plots detected intensity of the diffracted X-ray beam against the diffraction angle [36], [70], [71]. In this study, XRD experiments were conducted using X-diffractometer (Bruker D5005 diffractometer, Cu K α radiation ($\lambda = 1.5418$ Å), operated at 40 kV and 40 mA). Diffraction data were collected in the 10 to 90 2 θ range with a step width of 0.02° and scanning speed of 0.04° s⁻¹ to identify crystallographic information of the Co/CoP/TiO₂/NiF. The collected data were plotted using Origin software to generate the diffractogram, and the diffraction peaks were compared with standard data to qualitatively identify the materials present in the synthesized electrode.

3.2.2 Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX)

SEM is a technique used to study the morphology and size of materials [36]. Most SEM instruments are equipped with EDX facilities, which detect the X-rays generated from the sample due to the interaction with high-energy electrons. These X-rays are characteristic of the elements present in the sample, allowing

for the analysis of the composition and distribution of elements in specific areas of the SEM image [36]. In this study, SEM images of the synthesized electrode at different magnifications (300x to 150,000x) were obtained without applying conductive coating on the sample using a Tescan S8000G FEGSEM with Oxford instrument at an accelerating voltage of 20 kV. EDX information was acquired using the integrated EDX facilities (Ultim Max 100 EDS detector), determining the elemental composition and distribution in specific areas of the sample.

3.3 Electrochemical characterization methods

In the field of electrochemistry, particularly in WS research, various techniques are used to characterize and evaluate the performance of electrode materials. The primary techniques employed in this research include CV, LSV, CP, and EIS. In this research, all electrochemical characterizations were carried out using a potentiostat (IviumStat.h, Alvatek, UK), with data acquisition facilitated by IviumSoft (IviumStat.h, Alvatek, UK). The following sub sections briefly discuss these techniques, highlighting how each was conducted, and the specific information extracted to evaluate and characterize the electrocatalysts.

3.3.1 Reference electrode and calibration

Throughout this experiment Ag/AgCl (KCl, 1M) electrode (HCH Instruments, Inc., USA, CHI11P) was used as the reference electrode. Before each electrochemical experiment, the accuracy of the reference electrode was verified through a calibration procedure. The master electrode and the reference electrode intended for use in the experiment were connected to the reference and working electrode cable respectively on the potentiostat. Both electrodes were then immersed in a 1M KCl solution, and the potential difference between them was measured. If the potential difference was less than 20 mV, the reference electrode was deemed accurate and used for the experiment. If the potential difference exceeded 20 mV, the reference electrode was replaced with a new one.

3.3.2 Liner sweep voltammetry (LSV) and cyclic voltammetry (CV)

LSV and CV are important and fundamental electrochemical techniques for characterizing and evaluating electrode materials, particularly in water splitting

research. Both methods involve scanning the potential over a specific range and measuring the resulting current flow, generating potential-current plots known as voltammograms. LSV scans the potential linearly over time in the given potential window (either from lower value to higher value or vice versa). In contrast, CV cycles the potential within a defined range.

Both LSV and CV voltammogram enable the determination of performance of working electrode such as onset potential and overpotential required to achieve a specific current or current density. Additionally, by plotting the overpotential against the logarithm of the current density gives the Tafel plot which gives the information of reaction kinetics of the electrode material and exchange current density. CV voltammogram allows to get enables additional information of redox behaviour and reversible processes to be obtained/gathered. Furthermore, the double-layer capacitance (C_{dl}) can also be determined from CV data by performing scans at different rates in the non-faradaic region and plotting the average of the cathodic and anodic currents against the scan rate. The slope of this curve gives the C_{dl} , which is related to the electrochemically active surface area. The catalyst's stability can be further assessed by conducting numerous CV scans (typically more than 1000) within a given potential range.

Electrochemical setup

Electrochemical experiments were conducted using a typical three-electrode system in a 1 M KOH electrolyte, as depicted in Figure 9. A Pt electrode (1 cm x 1 cm) served as the counter electrode, and an Ag/AgCl (KCl, 1M) electrode (HCH Instruments, Inc., USA, CHI11P) was used as the reference electrode. The synthesized electrodes (immersed surface area 1 cm x 1 cm x 2) were utilized as the working electrode. Before setting up the electrochemical cell for each test, the Pt electrode was thoroughly cleaned with 1 M HCl followed by distilled water, and the working electrode was washed with ethanol and then distilled water. After each electrochemical test, the potential of the reference electrode was checked against a master reference electrode of the same type.

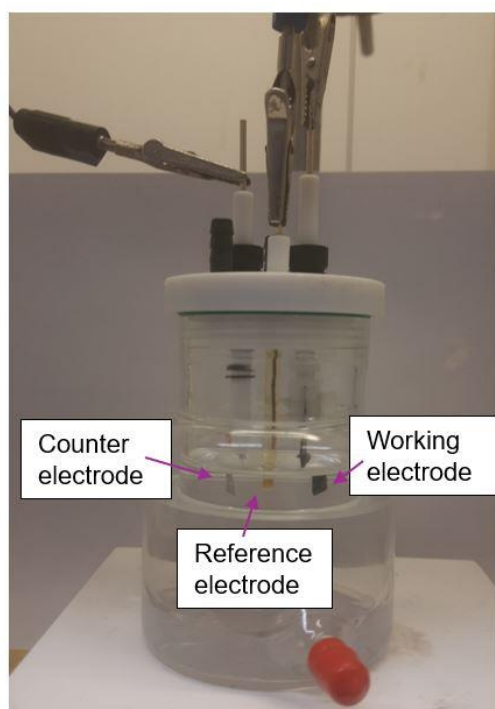


Figure 9: Electrochemical cell with three electrode system.

LSV measurements were conducted using the three-electrode setup at a scan rate of 5 mV s^{-1} . For the HER, the potential range was set from -1.4 V to -0.9 V (vs. standard 1M Ag/AgCl reference electrode). For the OER, the potential range was set from 0.3 V to 0.7 V (vs. standard 1M Ag/AgCl reference electrode). Prior to taking the readings, several CV scans were performed at a scan rate of 150 mV s^{-1} until a stable CV curve was obtained according to established guidelines detailed by Anantharaj and Noda (2022) [40]. Once the stable CV was achieved, LSV tests were conducted. The current -voltage data was used to evaluate the performance of working electrode as follows:

Overpotential and Tafel slop determination

The voltage data were then converted to the RHE reference scale using the Equation 3-1. The potential was then iR -corrected using the Equation 3-2. Finally, the current density, obtained by dividing the current observed at each potential by the geometric surface area of the working electrode, was plotted against the iR -corrected potential (V) using Origin software. From this plot, the overpotential at specific current density was determined by interpolation.

$$E(\text{vs. RHE}) = E(\text{vs. Ag/AgCl}) + 0.222V + 0.059 \times \text{pH} \quad (3-1)$$

$$V = E(\text{vs. RHE}) - iR \quad (3-2)$$

$$\eta = b \log(j) + a \quad (3-3)$$

Next, the current and V data were used to generate a plot of overpotential versus $\log(j)$. The region where overpotential exhibited a linear relationship with $\log(j)$ was identified and fitted to the Tafel Equation 3.3, with a R^2 value of 0.99. In this equation, b represents the Tafel slope, a is a constant related to the electrode, and j denotes the current density. The linear fitting and graph plotting were performed using Origin software to obtain the Tafel plot. The slope (Tafel slope) of this plot was then analysed to determine the RDS of the HER and OER on the working electrode.

CV experiment

In this research CV experiments were utilized for two primary purposes: assessing electrode stability and determining the ECSA.

Electrode stability

To investigate the electrode stability for HER, 5000 CV cycles were performed within a voltage window of -1.4 to -1 V (vs. Ag/AgCl) at a scan rate of 100 mV/s. For OER stability, 1000 CV cycles were conducted within a voltage window of -0.3 to 0.8 V (vs. Ag/AgCl) at a scan rate of 100 mV/s. The initial and final CV curves were compared to determine any significant shifts during the experiments, indicating stability or degradation.

ECSA calculation

For ECSA determination, an initial CV experiment was conducted from -1.4 to 0.6 V (vs. Ag/AgCl) at a scan rate of 1 mV/s to identify the non-faradaic region, where no oxidation-reduction peaks are present. Subsequent CV experiments were then conducted within this non-faradaic region at different scan rates ranging from 5 to 30 mV/s. The average of the cathodic and anodic current densities at the

midpoint of the voltage region was plotted against the scan rate, with a standard error greater than 0.95. The slope of this plot was taken as the C_{dl} of the electrode. The ECSA for each electrode was determined by dividing the C_{dl} by the specific capacitance (C_s) of the NiF electrode. Origin software was used to plot the graphs and calculate the standard errors in this experiment.

3.3.3 Electrochemical Impedance spectroscopy (EIS)

EIS is a powerful and versatile technique used to analyse the electrochemical behaviour of various electrode materials. It is particularly useful for studying electrocatalysts [72], photocatalysts, photo-electrocatalyst, heterojunction solar cells, and battery applications. EIS utilizes alternating current (AC) to differentiate between the resistive and capacitive components at electrode interfaces, providing detailed insights into the electrochemical processes [72].

In this research, EIS was employed to assess the solution resistance between the working electrode and the reference electrode for iR compensation during the electrode performance evaluation, focusing on overpotential and Tafel slope as previously described. Additionally, EIS was utilized to determine the charge transfer resistance (R_{ct}) of the catalyst at the electrode-electrolyte interface.

4 Result and discussion

4.1 Synthesis of Co/CoPs/TiO₂/NiF electrocatalyst and material characterisation.

4.1.1 Synthesis of TiO₂/NiF and characterisation

TiO₂ suspension in absolute ethanol (2.5 g/dm³) was used in the EPD process to achieve a uniform coating of TiO₂ nanoparticles on the struts of nickel foam (NiF). Magnetic stirring ensured the mixing of solid particles in the solution, while ultrasonication provided stability to the suspension through cavitation effects, enhancing solute dissolution and potentially reducing the particle size of TiO₂ by collapsing cavitation bubbles [73]. This process facilitated deagglomeration due to microjets and along with shock waves [73]. During this process, TiO₂ nanoparticles acquired a positive charge. This positive charge generation was reported in the several literatures e.g. [73], [74], [75]. In the EPD, these positively charged nanoparticles migrated towards the cathode and deposited on the struts of NiF. As apparent TiO₂ sedimentation was not seen following the sonication treatment, the solution was utilized straight away for the EPD procedure. The cathodic TiO₂ EPD process required 30 V for 2 minutes due to the low conductivity of the ethanolic TiO₂ suspension in order to achieve a thin and uniform layer of TiO₂ nanocoating on the NiF struts (TiO₂/NiF).

To confirm the TiO₂ deposition on NiF, the obtained TiO₂/NiF was characterized using XRD, and the results were compared with those of pure NiF, as shown in Figure 10. As seen in Figure 10, Pure NiF exhibits three distinct sharp and intense peaks in the X-ray diffractogram 2 θ Bragg's angles at 44.36°, 51.68°, and 76.24°, corresponding to the Ni(111), Ni(200), and Ni(220) FCC lattice planes [76]. Since there are no additional peaks related to any other materials, it can be confirmed that the NiF is free of impurities. The identical NiF-related peaks are also visible in the TiO₂/NiF XRD pattern shown in Figure 10. Additionally, peaks at 25.01°, 37.55°, and 62.41° correspond to the anatase form of TiO₂ (101), (004), and (204) planes, respectively, while peaks at 27.0° and 47.7° correspond to the rutile form of TiO₂ (110) and (200) planes. This confirms the deposition of TiO₂ on NiF [77].

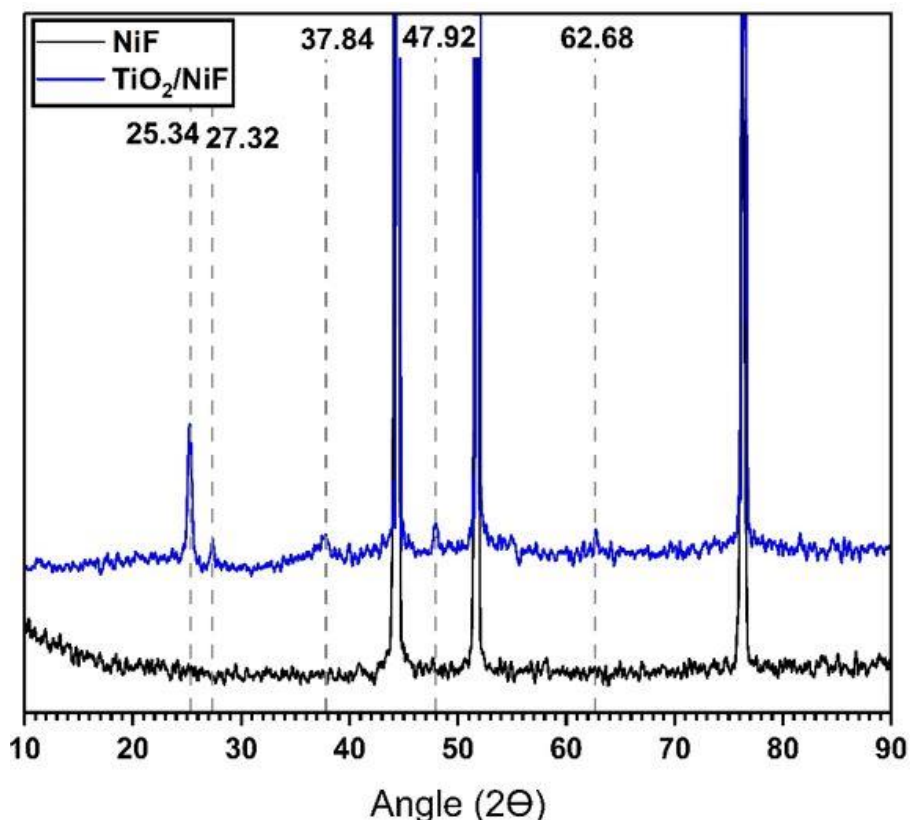


Figure 10: XRD diffractogram of (a) NiF and TiO₂/NiF

The morphological impact of TiO₂ deposition on NiF was investigated by means of SEM image analyses of both NiF and TiO₂/NiF and the images are shown in Figure 11. Figure 11 (a) shows low magnification SEM images of bare NiF. High porosity and high surface area interconnected struts are visible in the images of the NiF. Nevertheless, as seen in Figure 11 (b), the higher magnification analysis of the NiF struts reveals a smooth surface, comparable to other flat materials. On the other hand, coating with spherical TiO₂ nanoparticles results in a notable improvement in the roughness, exposed surface area and an increase in the porosity of the structure, as Figure 11 (b) and (c) illustrates. Therefore, it is clear from comparing the figures that the TiO₂-coated NiF structure in would be more beneficial for developing high surface area with high porosity catalyst on top of these structures. Additionally, as shown in Figure 11 (d), the coated TiO₂ particles are spherical particles in the 20–30 nm range that are coated on NiF without aggregating during the EPD process.

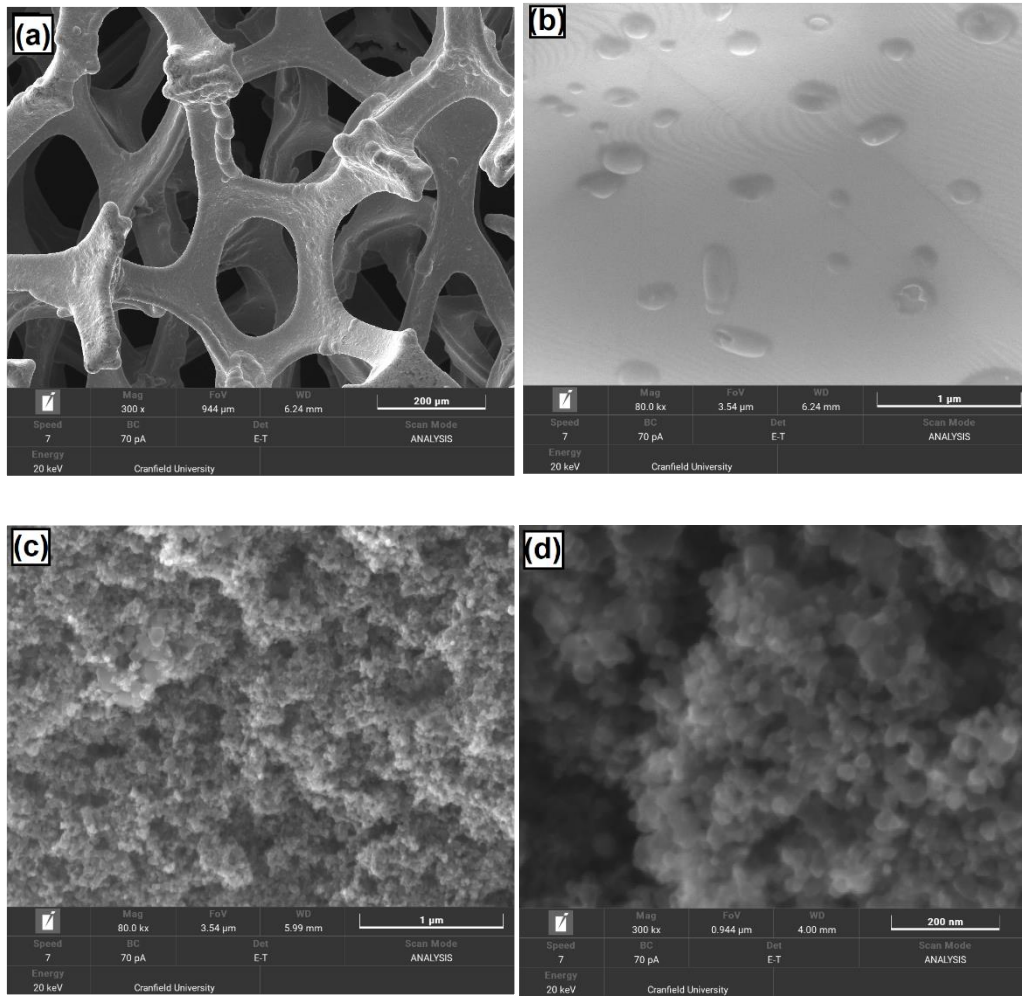


Figure 11: SEM image of (a) bare NiF (low magnification), (b) bare NiF (high magnification) (c) TiO₂/NiF (low magnification) (d) TiO₂/NiF (high magnification)

The reason for choosing the EPD process is to coat TiO₂ nanoparticles with predefined size and shape onto the NiF struts, achieving a high-porosity coating with strong mechanical strength. While dip and spray coating methods are viable alternatives for coating predefined particles, EPD delivers a superior-quality coating with robust adhesion. Although electrodeposition using Ti precursors is also another option, it frequently results in a less porous coating with variable TiO₂ particle sizes after sintering

However, achieving a uniform TiO₂ coating on NiF structures using EPD involves numerous factors that impact the final quality and uniformity of the coating. While the SEM images in Figure 11 (c) confirmed that EPD can produce a relatively consistent TiO₂ layer over the NiF struts, several intrinsic and extrinsic factors

contribute to variations in thickness and uniformity. The TiO_2 suspension in ethanol is a critical in the EPD process. Despite meticulous control over temperature, stirring time, and ultrasonic treatment power and duration, improper charging can still occur. This results in non-uniform particle distribution and varying deposition rates, leading to inconsistent TiO_2 coating thickness across the NiF surface as shown in Figure S1 in the supporting information. These problems show how precise suspension parameter control is necessary to guarantee consistent charging and stable suspension quality.

Further, the surface of the Ni foam, deposition time, and the technique for withdrawing the coated NiF from the solution are also critical factors. In comparison to the flat surfaces, more TiO_2 is deposited at the edges of the Ni foam due to the higher electric charge concentration there. This is because the electric field has a propensity to become stronger at corners and sharp edges, which results in a localized increase in the rates of deposition. To overcome this obstacle and produce a high-quality coating, the electric field distribution must be optimized. Post-deposition, the evaporation of ethanol from the coated sample is highly dependent on environmental conditions, particularly humidity. The integrity of the coating may be undermined if ethanol evaporates quickly or unevenly and causes cracks in the TiO_2 layer. Because it is non-toxic and inhibits bubble formation at the cathode in comparison to aqueous media, ethanol was selected for this investigation. Nevertheless, despite efforts to reduce this issue, the low water content in absolute ethanol and ethanol the reduction of at high direct DC voltage can still result in bubble formation at the cathode. These bubbles have the potential to worsen uniformity problems and lead to coating defects. In order to lessen these effects, controlled evaporation environments and altered solvent compositions might be required.

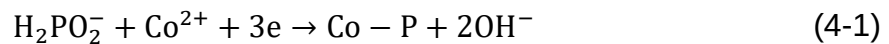
Yet another crucial concern is the mechanical stability of the TiO_2 coating. some of the TiO_2 nanoparticle coating may detach form the coating when the coated NiF is removed from the deposition bath, leaving surface imperfections and uneven thickness. The detachment indicates the necessity of gentle handling and possible enhancement of binding forces during the coating procedure to enhance

adhesion. Even with meticulous control, there are still difficulties with the sintering process. Because the coated samples must be placed on an incinerator disk, some TiO₂ will stick to the disk and may cause partial detachment during sintering. The degree to which this detachment occurs depends on how the sample and disk make contact; this leads to a variation in coating between samples. Clamping the samples on the side where TiO₂ is not coated during sintering is one way to solve this problem, but it has drawbacks of its own and isn't always feasible.

In conclusion, even though there are many variables that interact to affect the final coating's thickness and uniformity, the EPD process for coating TiO₂ on NiF structures produces high-porosity TiO₂ nanoparticles with a predetermined size and high mechanical stability, which is not possible with other coating techniques.

4.1.2 Synthesis of Co/CoPs/TiO₂/NiF and characterisation

The electrodeposition of Co and CoP on the TiO₂/NiF electrode was carried out in an electrolyte bath containing NaH₂PO₄ and CoCl₂. The formation of CoPs during deposition is complex. According to the literature, the direct formation of elemental phosphorus is unlikely; instead, a metal ion-assisted phosphide formation occurs, with the exact stoichiometric reaction not well-defined due to the potential formation of several cobalt phosphide compounds [8], [78], [79]. The possible reaction can be explained by the Equation 4-1 [8]:



In addition to CoPs deposition, Co may also be deposited during the reaction, as shown in the equation 4-2 [57].



Therefore, this electrodeposition process likely results in the deposition of both Co and CoPs. Furthermore, electrodeposition in an IL medium offers cathodic deposition free from side reactions, facilitating the formation of strongly attached Co and CoPs. In contrast, electrodeposition in an aqueous medium can interfere with the HER reaction, leading to poor stability of the deposited materials [8].

To confirm the Co and CoPs deposition on NiF, the obtained Co/CoPs/TiO₂/NiF was characterized using XRD and the result are shown in the Figure 12. As seen in Figure 12, the only additional peak shown in the Co/CoPs/TiO₂/NiF relative to TiO₂/NiF is located at 45.8°, which could be related to CoP (112) [80].

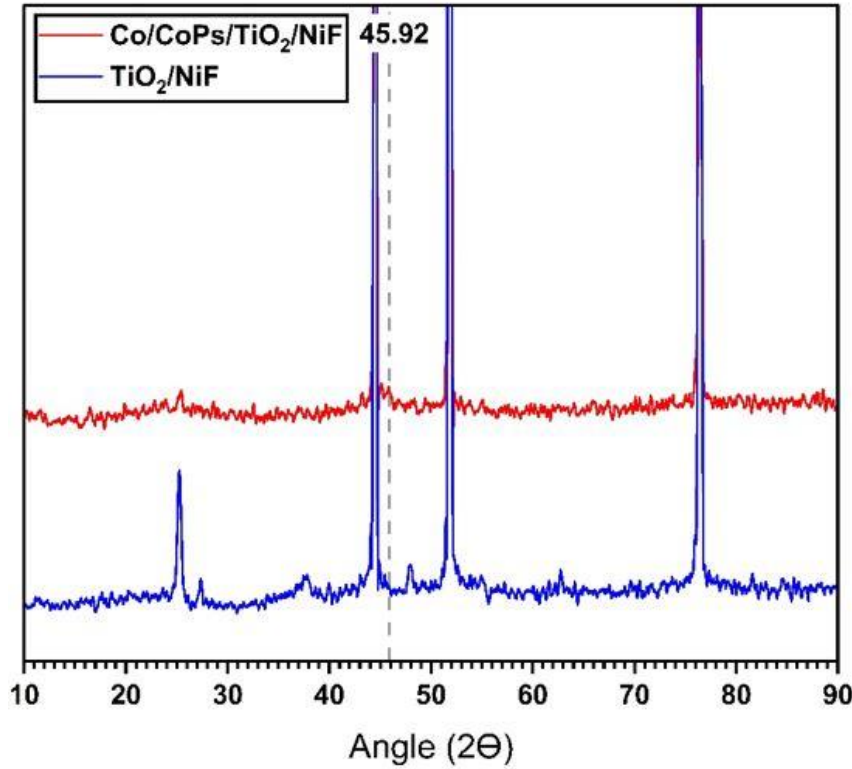


Figure 12: XRD diffractograms of TiO₂/NiF and Co/CoPs/TiO₂/NiF

SEM analysis

To provide a detailed understanding of the microstructure of Co/CoPs/TiO₂/NiF, SEM analyses were conducted, and the resulting images shown in Figure 13. The low magnification SEM micrograph in Figure 13 (a) reveals a highly micro-porous, three-dimensional growth structure. Upon further magnification, Figure 13 (b) displays two distinct types of structural growth: one is interconnected cauliflower-shaped distributed throughout the TiO₂/NiF surface, while the other consists of thick, flat, hexagonal-shaped crystalline structures scattered randomly on the cauliflower-shaped surface. These two morphologies indicate a complex growth mechanism, with the cauliflower-shaped structures providing a rough,

irregular surface and the triangular crystalline structures offering a more defined, geometric surface.

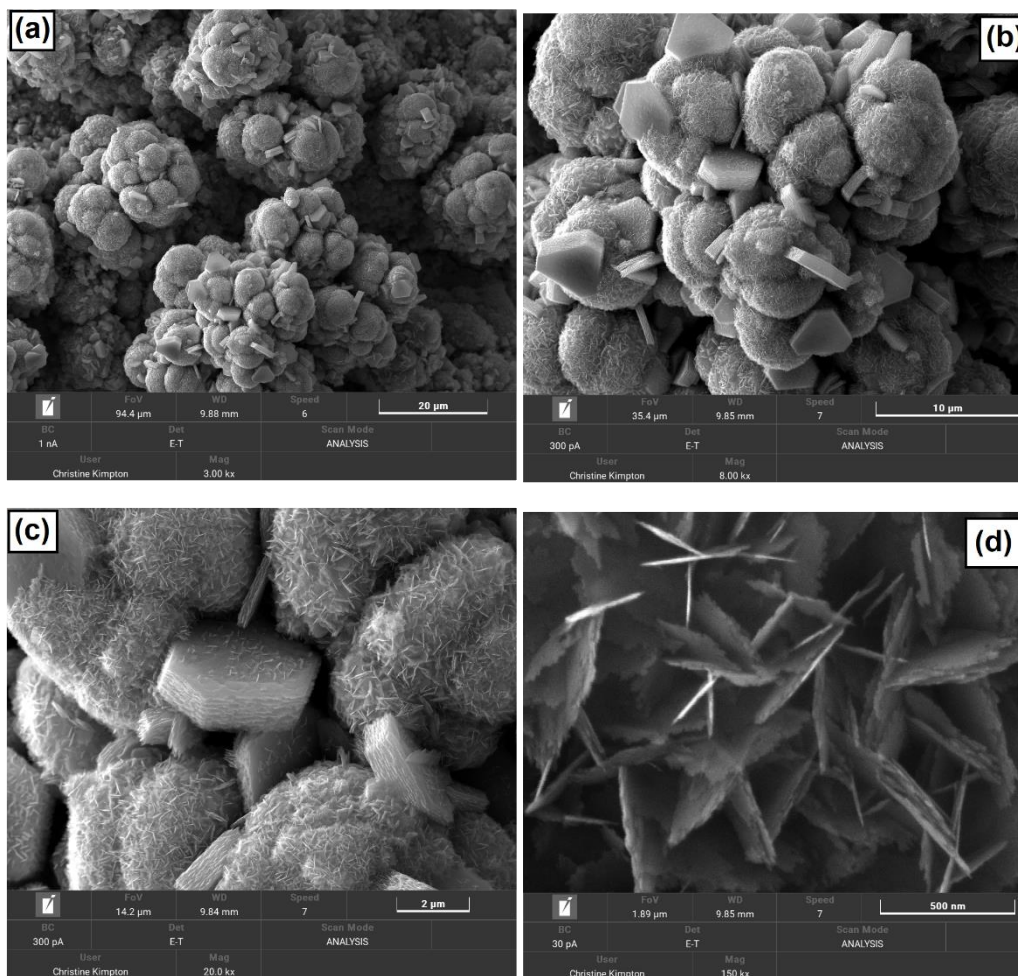


Figure 13 SEM images of Co/CoPs/TiO₂/NiF at (a) 3k magnification, (b) 8k magnification, (c) 20k magnification, and (d) 150k magnification

Further, the high magnified image focusing on the non-porous, hexagonal-shaped structure, shown in Figure 13 (c), reveals that the thick sheets are composed of very thin, orderly arranged nano sheets resembling the structure of graphite. Although this type of structures without porous are not particularly beneficial for surface reactions, the orderly arrangement can enhance electronic conductivity and mechanical stability, both of which are advantageous for catalytic performance. Meanwhile, high magnified image shown in Figure 13 (d) illustrates that the cauliflower-shaped structure is composed of irregularly arranged thin nano-sheets, contributing to high nano-porosity and surface area.

This type of structure is particularly advantageous for surface-participated reactions. The increased surface area allows for a higher amount of exposed-active catalyst, providing more sites for heterogeneous catalytic reactions including HER and OER. Additionally, the porous nature facilitates the movement of reactants and products within the structure, which is essential for efficient catalytic processes such as the HER and OER. The unique surface morphology of Co and CoP catalysts prepared by a deep eutectic electrolyte bath consisting of urea and choline chloride is markedly different from that of catalysts prepared by other techniques, including solid-state reactions (e.g. [81], [82], [83], [84], [85] [61, 62, 63, 64, 65]), solvothermal reactions (e.g. [86], [87], [88]) , and different electrodeposition methods (e.g. [54], [59]). The finer, more homogeneous distributions seen in deep eutectic solvent preparations contrast with the larger, aggregated particles and less uniform surface features frequently produced by solid-state reactions [62], [89], [90], [91], [92]. The electrodeposited Co and CoP catalysts exhibit distinct surface characteristics, particularly when compared to those derived from other deep eutectic solvents (e.g. [62], [89], [90], [91], [92]). This suggests that the electrolyte composition and deposition conditions significantly influence the resulting morphology. Further, the TiO₂ nanospheres may have had an impact on the final Co/CoPs/TiO₂/NiF catalyst's morphology and roughness since they act as a template for the growth of Co and CoPs. The surface area, stability, active site distribution, and reaction pathways of the catalysts are all impacted by these morphological variations, which ultimately affect the catalytic performance of this material.

In order to reveal the surface elemental distribution and the elements composition EDX mapping and quantification were performed, and the results are depicted in the Figure 14. The EDX elemental mapping image of Co/CoPs/TiO₂/NiF, shown in Figure 14 (a) and (b) demonstrates that Co and P are evenly distributed across the TiO₂/NiF surface. In this mapping area as shown in Figure 14 (c), small area of bare Ni is visible, appearing in pink, along with tiny regions of Ti (Figure 14 (d)), appearing in white. The observed bare Ni and Ti (comes from TiO₂) regions may be attributed to the peeling of the catalyst during repeated washing with water and ethanol. Oxygen is probably present because of surface oxidation that

happened in the interim between the SEM analysis and catalyst synthesis. In spite of this, the EDX mapping verifies that TiO_2/NiF has been successfully decorated with Co and P elements. The EDX quantification image in Figure 14 (b) further corroborates the presence of these elements. The quantitative analysis (supporting information Figure S2 and Table S1), reveals that the surface catalyst consists average of 58.87% Co and 1.42% P, indicating the presence of both cobalt and cobalt phosphide species on the catalyst surface.

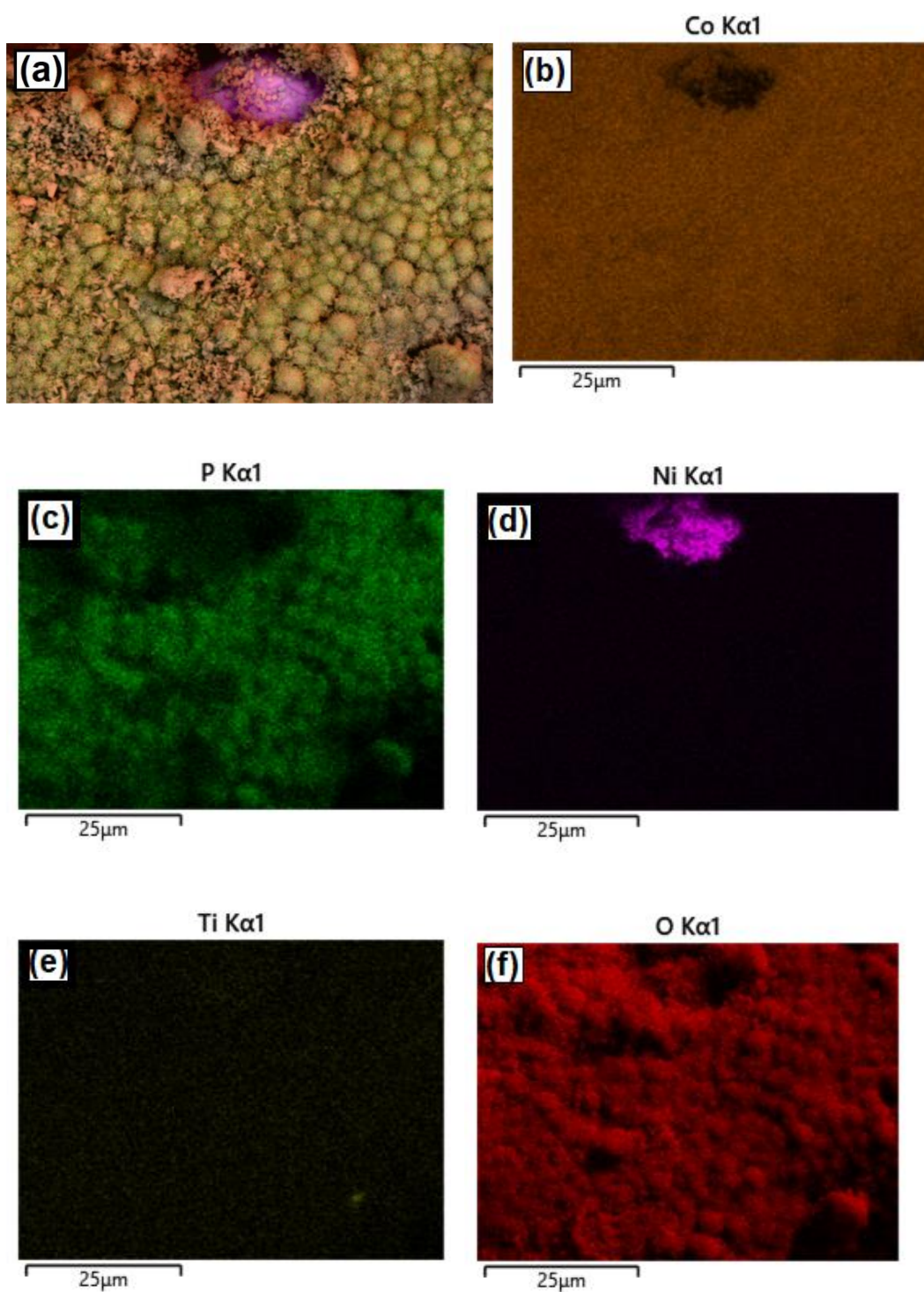


Figure 14: (a) SEM image along with the corresponding elemental mappings for (b) Co, (c) P, (d) Ni, (e) Ti, and (f) O in the Co/CoPs/TiO₂/NiF sample.

4.2 Optimisation of Co/CoPs/TiO₂/NiF and application for electrocatalytic water splitting

4.2.1 Optimisation of Co/CoPs/TiO₂/NiF electrode for HER

To identify the optimal Co/CoPs/TiO₂/NiF electrode for the HER, electrodes were prepared with varying EPD times: 30 min, 60 min, 120 min, and 240 min for the deposition of Co and CoP species on TiO₂/NiF substrates. The objective was to find the optimal deposition time for Co and CoP species while keeping other variables, like temperature and the composition of the Co and P precursors, constant. According to the EPD times, the electrodes were assigned the following labels: Co/CoPs(30)/TiO₂/NiF, Co/CoPs(60)/TiO₂/NiF, Co/CoPs(120)/TiO₂/NiF, and Co/CoPs(240)/TiO₂/NiF. TiO₂ deposition and Co and CoPs deposition significantly affects the Co/CoPs/TiO₂/NiF catalyst performance, as was previously discussed. As a result, several batches of each electrode were made and evaluated for HER using LSV in a typical three-electrode system in 1.0 M KOH solution.

The iR-corrected polarization curves for each Co/CoPs/TiO₂/NiF electrode, prepared from three separate batches with varying Co/CoP deposition times for HER in 1 M KOH, are shown in Figure 15. Figure 16 presents the average of selected overpotential (η) values at η_5 , η_{10} , η_{20} , and η_{50} , with error bars representing the standard error of the mean from the η values obtained from Figure 15 for the different electrodes.

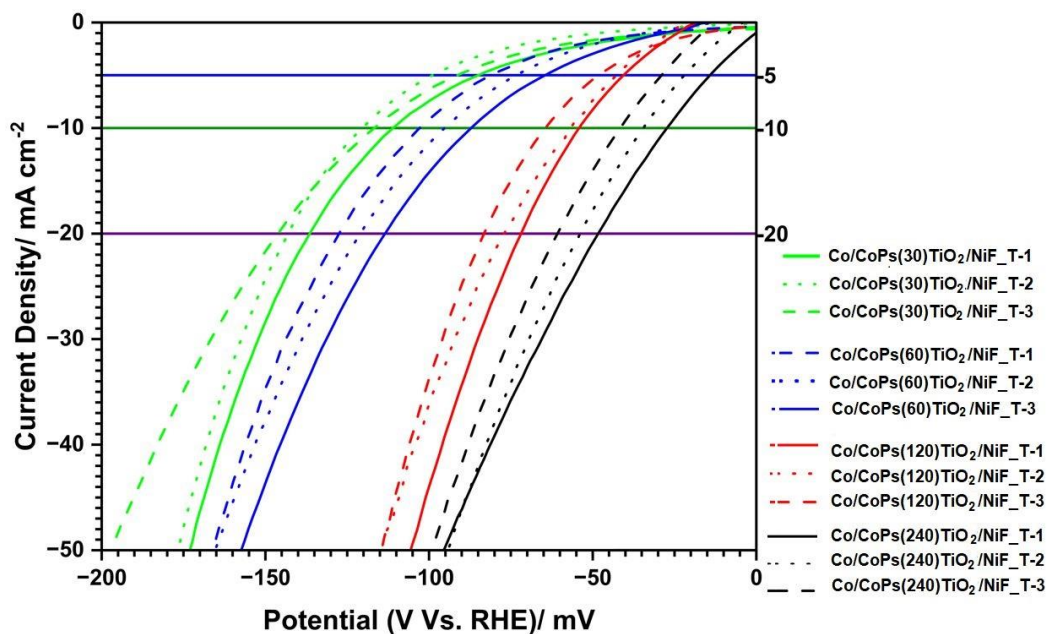


Figure 15: The HER iR-corrected polarization curves for various Co/CoPs/TiO₂/NiF electrodes at a scan rate of 5 mV s⁻¹ in 1 M KOH. Each colour line represents the same type of electrode prepared from three separate batches.

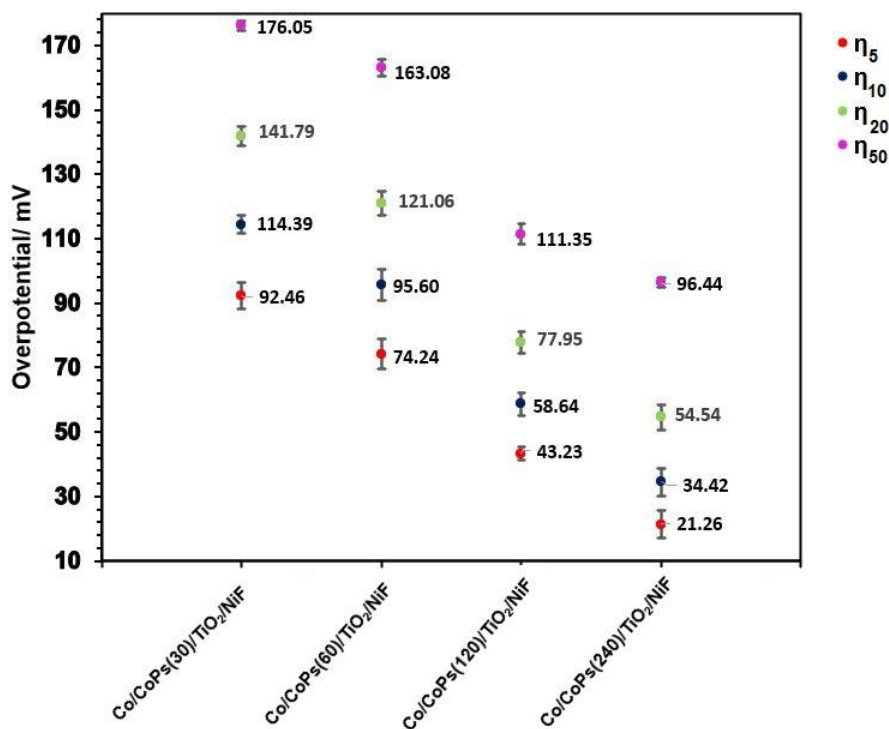


Figure 16: The average HER overpotential values for different Co/CoPs/TiO₂/NiF electrodes, calculated from the HER overpotentials of electrodes prepared from three separate batches.

According to Figure 16, the HER overpotential required to achieve a particular current density varies as follows: Co/CoPs(30)/TiO₂/NiF > Co/CoPs(60)/TiO₂/NiF > Co/CoPs(120)/TiO₂/NiF > Co/CoPs(240)/TiO₂/NiF. This indicates that increasing the loading of Co and CoPs species in the Co/CoPs/TiO₂/NiF catalyst by extending the EPD time lowers the overpotential required for HER at any given current density. However, extending the EPD time for Co and CoPs deposition beyond 240 minutes resulted in the catalyst peeling off and detaching during both the EPD process and HER testing. Therefore, catalysts prepared with EPD times longer than 240 minutes were not evaluated. As mentioned in Chapter 2.2.1, the overpotential of WS catalysts is generally evaluated overpotential required to achieve 10 mA cm⁻² current density (η_{10}). According to the results in the figure, the η_{10} values for Co/CoPs(30)/TiO₂/NiF, Co/CoPs(60)/TiO₂/NiF, Co/CoPs(120)/TiO₂/NiF, and Co/CoPs(240)/TiO₂/NiF are 114.38 ± 2.74 mV, 95.60 ± 4.85 mV, 58.63 ± 3.47 mV, and 34.42 ± 4.21 mV, respectively. Therefore, Co/CoPs(240)/TiO₂/NiF can be described as the optimal electrode for HER in 1 M KOH, with the lowest obtained η_{10} for Co/CoPs(240)/TiO₂/NiF being 27.43 mV. Typically, solution-phase synthesis methods face challenges in reproducibility; however, this catalyst, prepared from three different batches, demonstrates reasonably good reproducibility, as the overpotentials lie within a maximum standard mean error of ±4.86 mV.

4.2.2 Performance evaluation of Co/CoPs/TiO₂/NiF catalysts and benchmarking for HER

In EWS electrode evaluation, the use of average polarization curves could not be seen in the literature, likely because average curves do not represent the true potential-current relationship rather indicate the mean result with probable deviation. However, as demonstrated in Section 4.2.1, the synthesized Co/CoPs/TiO₂/NiF catalyst shows good reproducibility. Therefore, to compare the electrode performance and kinetics of the prepared electrodes, the iR-corrected LSV curves of the best electrode from each Co/CoPs/TiO₂/NiF catalyst, along with those of the bare NiF, TiO₂/NiF, Co/CoPs/NiF, and commercial Pt/C catalysts, are shown in Figure 17.

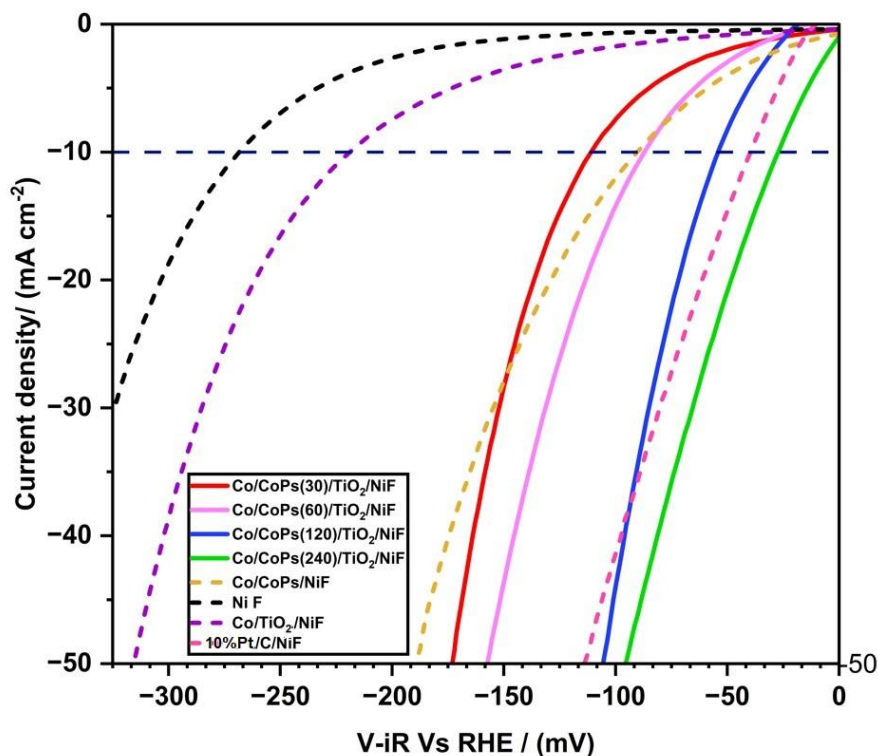


Figure 17: The HER iR-corrected polarization curves for the Co/CoPs(240)/TiO₂/NiF, Co/CoPs/NiF, NiF, Co/TiO₂/NiF, and 10% Pt/C/NiF conducted at a scan rate of 5 mV s⁻¹ in 1 M KOH.

As shown in the Figure 17, the bare NiF and Co/TiO₂/NiF required higher overpotentials of 271.11 mV and 221.57 mV, respectively, to achieve η_{10} , indicating that they are not efficient catalysts for HER. The Co/CoPs(30)/TiO₂/NiF, Co/CoPs(60)/TiO₂/NiF, Co/CoPs(120)/TiO₂/NiF, and Co/CoPs(240)/TiO₂/NiF catalysts required 111.20 mV, 89.75 mV, 53.33 mV, and 27.43 mV overpotentials, respectively, to achieve η_{10} , indicating that the lowest overpotential can be achieved with the Co/CoPs(240)/TiO₂/NiF electrode. This improvement could be attributed to the increased EPD time for Co and CoPs, leading to higher catalytic loading. Furthermore, the overpotential of the Co/CoPs(240)/TiO₂/NiF electrode is 64 mV lower than that of the Co/CoP/NiF ($\eta_{10} = 91.12$ mV), indicating that Co/CoPs(240)/TiO₂/NiF better catalyses the HER reaction than Co/CoPs/NiF. This suggests that the incorporation of TiO₂ has significantly improved the catalytic activity. Additionally, the commercial

10%Pt/C-based electrode required 41.85 mV at η_{10} , which is consistent with various other reported activities of commercial Pt/C on NiF (e.g. [83], [93]). Based on the results, the synthesized Co/CoPs(240)/TiO₂/NiF showed a 14.42 mV lower overpotential at η_{10} than the commercial Pt/C, indicating the superior performance of Co/CoPs(240)/TiO₂/NiF. Furthermore, η_{10} Co/CoPs(240)/TiO₂/NiF catalyst is lower than the Co/CoP-NF (35 mV at η_{10}) catalyst prepared by Bai et al. (2016) using a similar EPD method [59]. It also outperforms all other CoP-based non-noble metal electrocatalysts, as summarized in the recent review article by Deng et al. (2024) for HER in 1 M KOH [8].

As discussed in Chapter 2.1.3, the alkaline HER can proceed through two main mechanisms: Volmer-Heyrovsky and Volmer-Tafel. In the Volmer-Heyrovsky mechanism, water dissociation and hydrogen adsorption (Volmer reaction) are followed by hydrogen gas liberation through the reaction of adsorbed hydrogen with another water molecule in the electrolyte. In the Volmer-Tafel mechanism, the Volmer reaction is followed by the coupling of two adjacent adsorbed hydrogen atoms. Some electrodes may follow both mechanisms to different extents simultaneously. The Tafel slope calculation helps determine the exact mechanism followed during the HER.

The Tafel plot and the calculated Tafel slopes for each electrode and Co/CoPs/NiF are shown in Figure 18. According to the figure, the Tafel slopes of Co/CoPs(30)/TiO₂/NiF, Co/CoPs(60)/TiO₂/NiF, Co/CoPs(120)/TiO₂/NiF, and Co/CoPs(240)/TiO₂/NiF electrodes are 87.15 mV dec⁻¹, 84.36 mV dec⁻¹, 75.34 mV dec⁻¹, and 48.35 mV dec⁻¹, respectively. All these Tafel slopes fall within the range of 40 mV/dec to 120 mV dec⁻¹, indicating that the RDS for HER involves both Volmer and Heyrovsky steps. Additionally, the Tafel slope for Co/CoPs(240)/TiO₂/NiF is lower than that of Co/CoP/NiF (131.43 mV dec⁻¹) suggesting that Co/CoPs(240)/TiO₂/NiF has faster kinetics for HER than Co/CoP/NiF. However, the Tafel slope of Co/CoPs(240)/TiO₂/NiF is slightly higher than that of Pt/C catalyst (30 mV dec⁻¹), indicating that the kinetics of Co/CoPs(240)/TiO₂/NiF are slightly slower than those of the Pt/C catalyst.

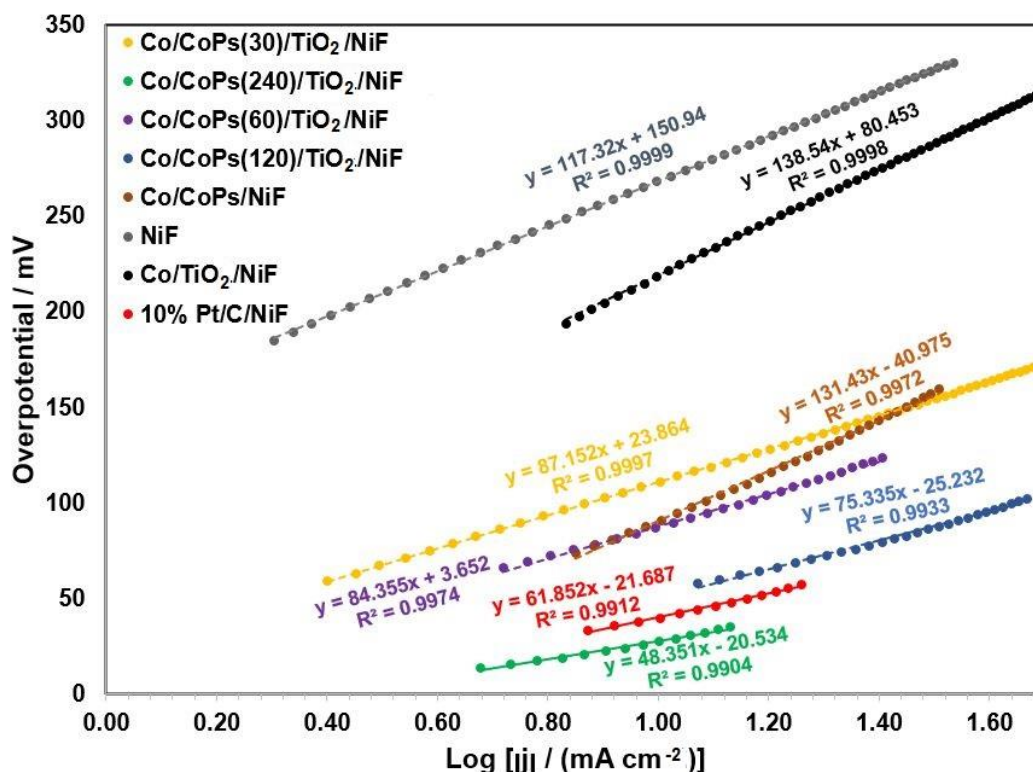


Figure 18 The HER Tafel plot estimated from the polarization curves of the Co/CoPs(30)/TiO₂/NiF, Co/CoPs(60)/TiO₂/NiF, Co/CoPs(120)/TiO₂/NiF, Co/CoPs(240)/TiO₂/NiF, Co/CoPs(240)/NiF, Co/TiO₂/NiF, and 20%P/C/NiF electrocatalysts.

4.2.3 Stability of Co/CoPs(240)/TiO₂/NiF catalyst for HER

For the catalyst to be used practically, stability is a crucial component. Two techniques were used to examine the stability of the Co/CoPs(240)/TiO₂/NiF catalyst: chronopotentiometry and CV, which are discussed in Chapters 2.4.

Cyclic voltammetry stability test

CV stability test was conducted at a scan rate of 100 mV s⁻¹ for 5000 cycles within the potential range of -1.0 V to -1.5 V (vs. 1M Ag/AgCl). Figure 19 shows the CV curves recorded before and after the 5000 cycles. As indicated in the figure, there is no significant difference between the first and the five-thousandth scan, suggesting that the Co/CoPs(240)/TiO₂/NiF catalyst retains its stability during continuous operation. The consistency of the CV curves demonstrates that the catalyst's structure and activity are maintained without any additional oxidation-

reduction reactions occurring within the voltage window and with minimal catalyst detachment. This stability is crucial for the catalyst's long-term use in practical applications.

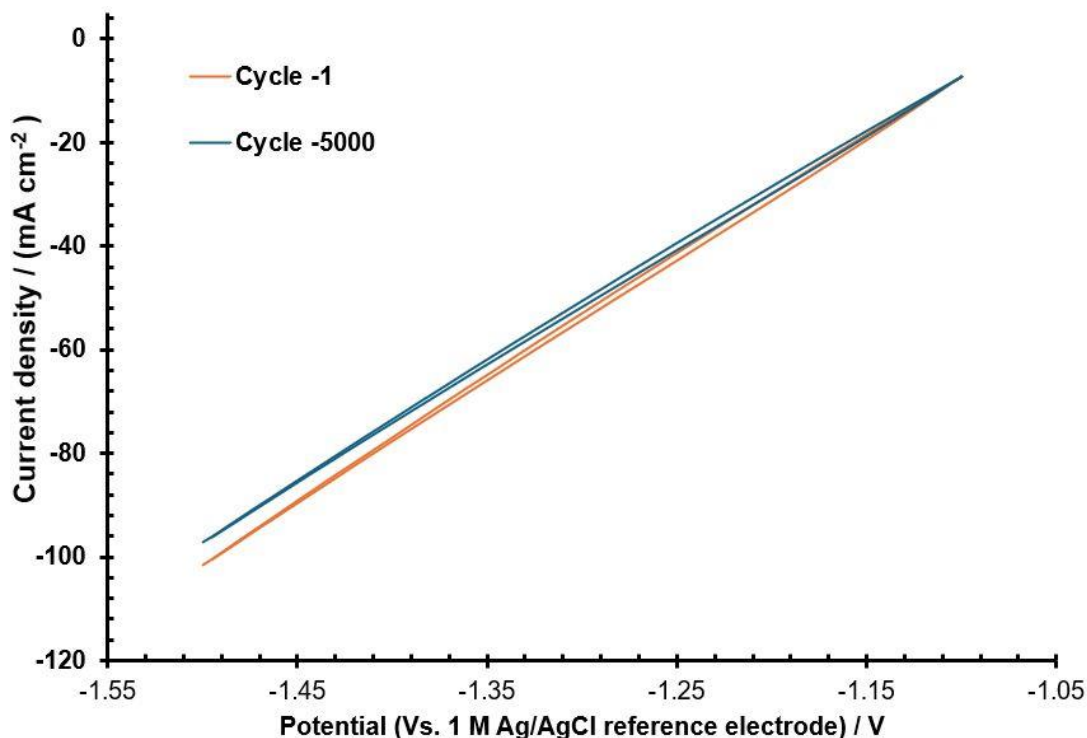


Figure 19: CV curves for the Co/CoPs(240)/TiO₂/NiF electrode in the range of -1.4 to -1.0 V (vs. Ag/AgCl), recorded before and after 5000 cycles.

Chronopotentiometry was utilized to evaluate the long-term stability of the Co/CoPs(240)/TiO₂/NiF by tracking the overpotential needed to attain a current density of 10 mA cm⁻² for a duration of 20 hours. As illustrated in Figure 20, Only 13 mV increase in overpotential was observed after 20 hours of operation, indicating good stability for the catalyst. This minor increase indicates that the Co/CoPs(240)/TiO₂/NiF catalyst can withstand prolonged electrochemical activity with minimal performance degradation. The small fluctuation in the overpotential curve over time is due to the fluctuation of effective surface area brought on by hydrogen bubble accumulation on the electrode surface and their subsequent release. Additionally, the minor increase in overpotential can be attributed to the peeling off the catalyst due to stress created during hydrogen bubbles release.

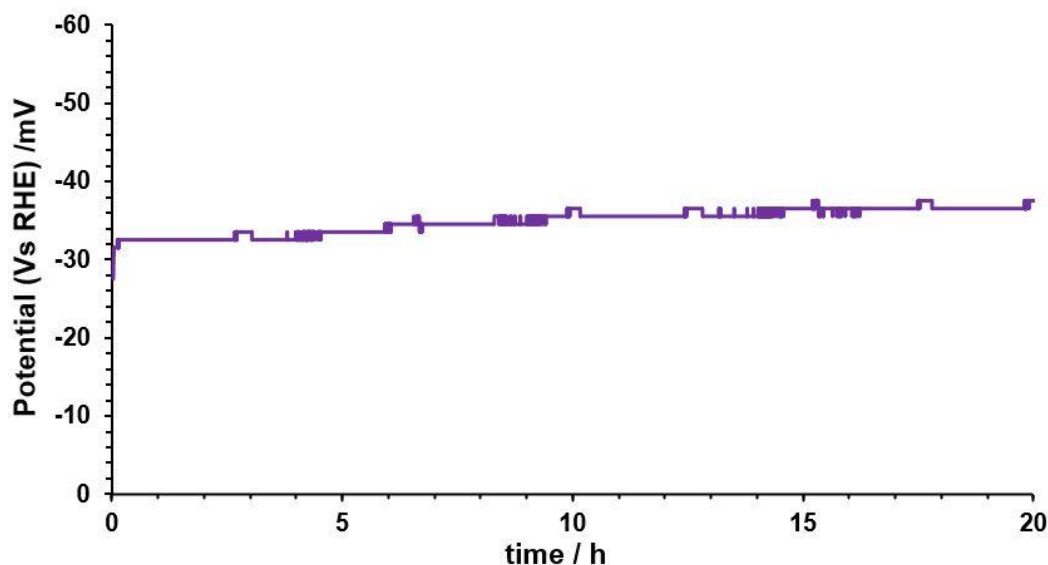


Figure 20 Long-term CP measurement of Co/CoPs(240)/TiO₂/NiF conducted at -10 mA cm⁻² in 1.0 M KOH at 25 °C

According to the above result it could be say that The Co/CoPs(240)/TiO₂/NiF catalyst exhibits excellent HER stability and durability in 1 M KOH electrolyte.

4.2.4 Performance evaluation of Co/CoPs(240)/TiO₂/NiF catalysts and benchmarking for OER

To evaluate the performance and kinetics of the Co/CoPs(240)/TiO₂/NiF electrode for OER, the iR-corrected LSV curves of the Co/CoPs(240)/TiO₂/NiF catalyst, along with those of bare NiF, Co/CoPs/NiF, and commercial RuO₂/C/NiF catalysts, are presented in Figure 21. The η_{10} for OER was determined by interpolating the LSV curve at 10 mA cm⁻² to get potential 'V' (Vs RHE) and subtracting the minimum thermodynamic potential for OER (1.23 V) from V. As shown in the figure, bare NiF required higher overpotentials of 399 mV, to achieve 10 mA cm⁻², indicating its inefficiency as OER catalysts. The Co/CoPs(240)/TiO₂/NiF catalyst required 331.70 mV for η_{10} , while Co/CoPs(240)/NiF needed 350.60 mV to achieve η_{10} . This indicates that the Co/CoPs(240)/TiO₂/NiF catalyst is more efficient than the Co/CoPs(240)/NiF electrodes. The reduction in OER overpotential for Co/CoPs(240)/TiO₂/NiF compared to Co/CoPs(240)/NiF can be attributed to increased catalyst loading due to the presence of the TiO₂ layer, along with the synergistic catalytic effects

of TiO₂, Co, and CoPs. The commercial RuO₂-based RuO₂/C/NiF electrode exhibits the lowest overpotential for η_{10} , at 276.56 mV, which is approximately 55.2 mV lower than that of the Co/CoPs(240)/TiO₂/NiF electrode. This indicates that further research is needed to identify catalysts that can compete with Ru-based electrocatalysts for the OER. However, the η_{10} required for the Co/CoPs(240)/TiO₂/NiF electrode is lower than that of the Co/CoPs(240)/NiF electrode and few other Co and CoP-based catalysts reported in the literature [8], This suggests that the Co/CoPs(240)/TiO₂/NiF catalyst demonstrates better efficiency compared to other reported catalysts.

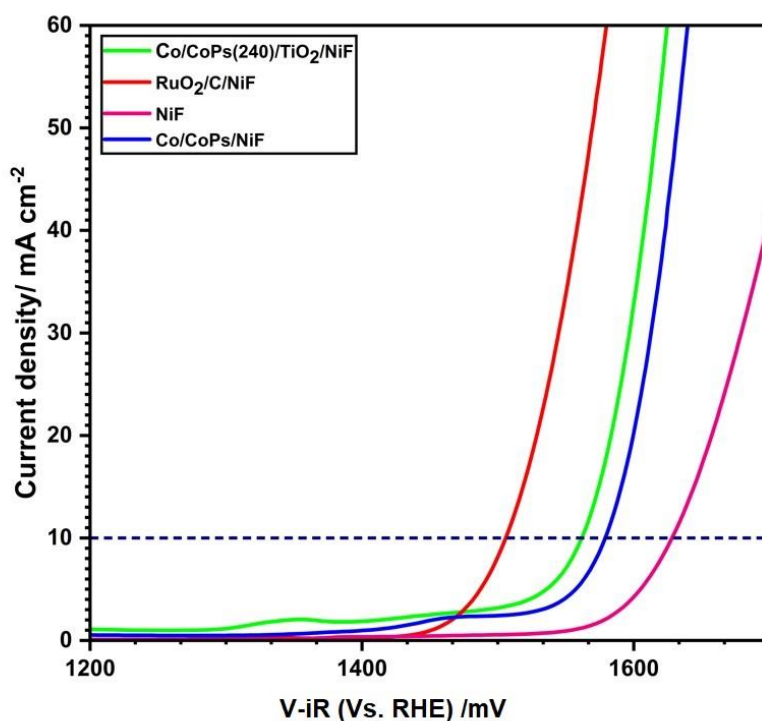


Figure 21: The OER iR-corrected polarization curves for the Co/CoPs/TiO₂(240)/NiF, Co/CoPs/NiF, NiF, and RuO₂/C/NiF conducted at a scan rate of 5 mV s⁻¹ in 1 M KOH.

To assess the OER kinetic performance of the Co/CoPs(240)/TiO₂/NiF catalyst, Tafel analysis was conducted and compared with other electrodes and the commercial RuO₂/C catalyst using the LSV curves. Figure 22 displays the Tafel plot along with the calculated Tafel slopes for each electrode. The results show that the Tafel slopes for the Co/CoPs(240)/TiO₂/NiF, NiF, Co/CoPs/NiF, and

commercial RuO₂/C/NiF electrodes are 73.96 mV dec⁻¹, 73.61 mV dec⁻¹, 70.56 mV dec⁻¹ and 54.54 mV dec⁻¹, respectively.

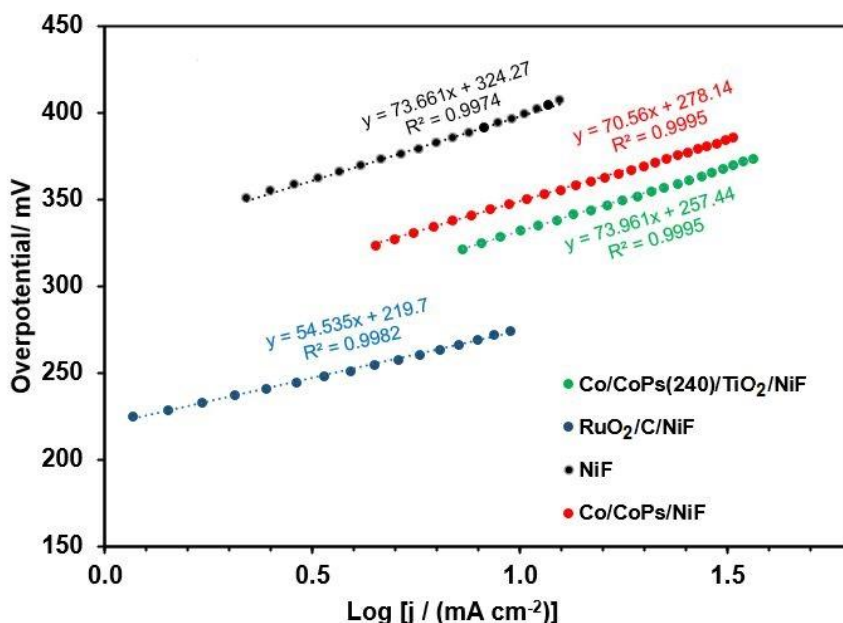


Figure 22 The OER Tafel plot estimated from the polarization curves of the Co/CoPs(240)/TiO₂/NiF, Co/CoPs(240)/NiF, NiF, and RuO₂/C/NiF electrocatalysts.

4.2.5 Stability of Co/CoPs(240)/TiO₂/NiF catalyst for OER

Similar to the hydrogen evolution reaction (HER), the stability of the Co/CoPs(240)/TiO₂/NiF catalyst for the OER was assessed using two analytical techniques: CP and CV.

Cyclic voltammetry stability test

CV stability test was performed at a scan rate of 100 mV s⁻¹ for 1000 cycles within the potential range of 0.3 V to 0.8 V (vs. 1M Ag/AgCl). Figure 23 presents the CV curves before and after the 1000 cycles. According to the figure, there is no noticeable change between the first and the thousandth forward scan of the CV cycle, with only a 20 mV shift observed in the backward scan at 10 mA cm⁻². This minimal shift suggests that the Co/CoPs(240)/TiO₂/NiF catalyst maintains its stability during continuous operation. The consistency in the CV curves indicates that the catalyst's structure and activity are preserved throughout repeated

electrochemical cycling, which is crucial for its long-term use in practical applications.

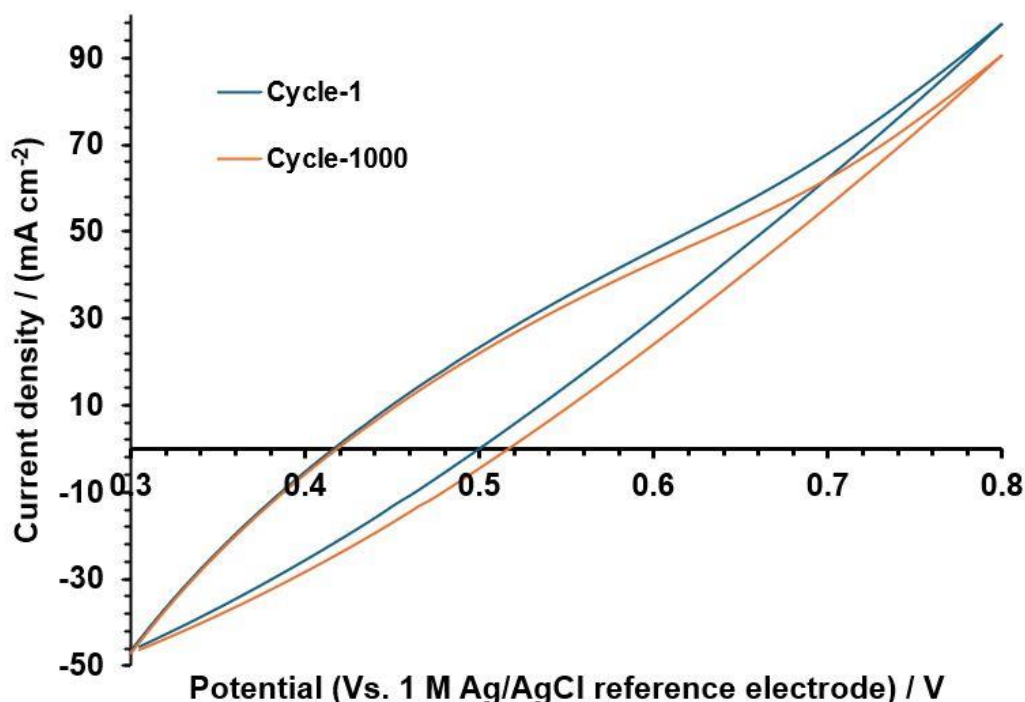


Figure 23 CV curves for the Co/CoPs(240)/TiO₂/NiF electrode in the range of 0.3 to 0.8 V (vs. Ag/AgCl), recorded before and after 1000 cycles.

4.3 Electrochemical surface area measurement

The ECSA of various Co/CoPs/TiO₂/NiF catalysts was determined using electrical double-layer capacitance (C_{dl}) measurements in the non-faradaic region of the CV obtained for the catalysts. The non-faradaic region, characterized by the absence of oxidation-reduction peaks of Co/CoPs/TiO₂/NiF in the CV curve, was identified by potential scanning from -350 to 1650 mV (vs. RHE) [94]. The CV curve of Co/CoPs/TiO₂/NiF scanned in the -1 to -1.5 V (vs. RHE) potential window at a scan rate of 1 mV/s is shown in Figure S3 in the supporting information. According to the voltammogram, the range between 700 mV and 800 mV showed no oxidation-reduction peaks and was thus selected as the non-faradaic region for C_{dl} measurement [94]. This potential region is consistent with the range used for ECSA measurement in other published papers for similar type of Co based catalysts (e.g. [95]).

In the Figure 24, A-E illustrate the CV scans at different scan rates, ranging from 7 mV s^{-1} to 30 mV s^{-1} , within the 700 mV to 800 mV (vs. RHE) potential window for the different prepared catalysts. The average cathodic peak and anodic peak current densities at 750 mV were plotted against the scan rates for each catalyst electrode. The resulting plots are presented in Figure 25. The error bar of each point represents the standard error of the mean.

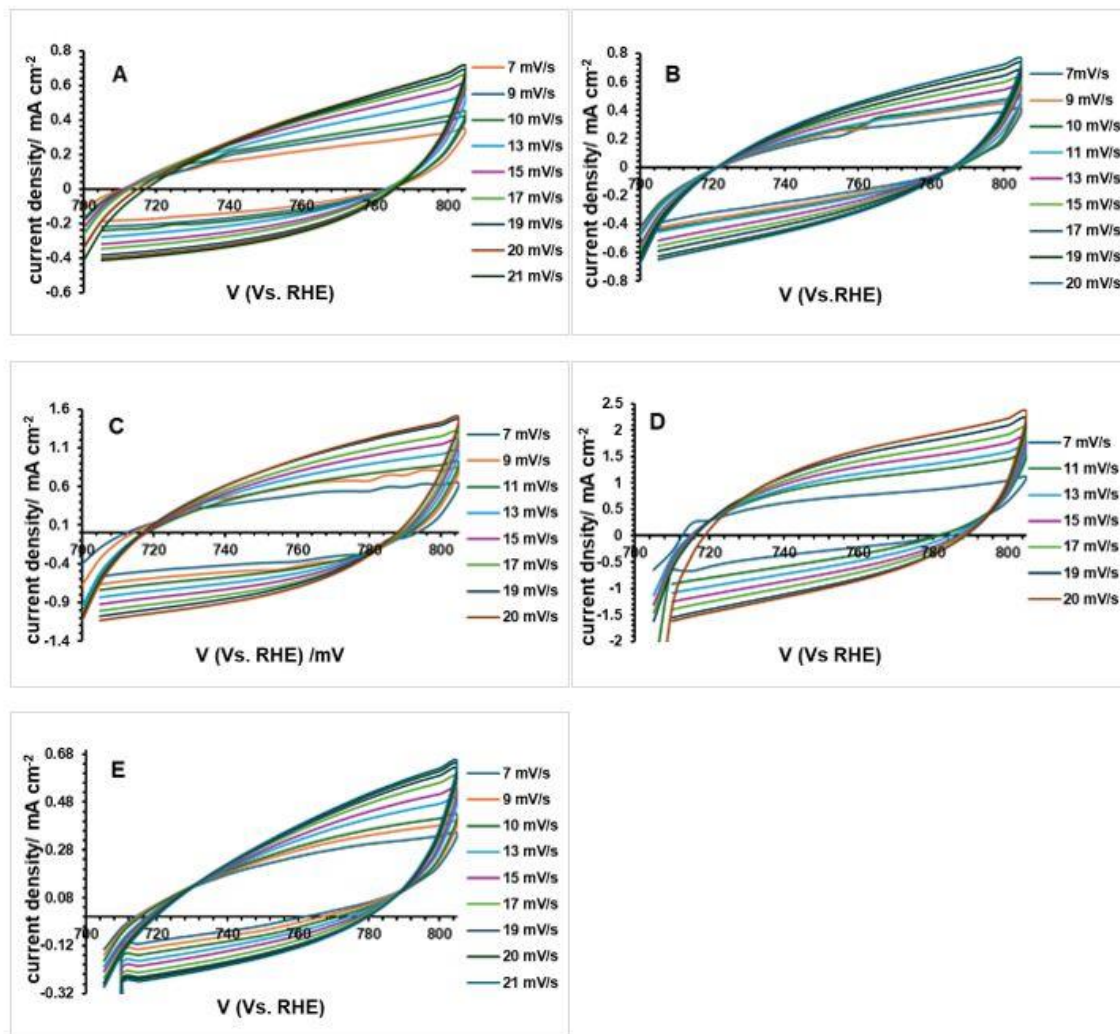


Figure 24 CV curves in the non-Faradaic region at scan rates ranging from 7 to 25 V/s for (A) Co/CoPs(30)/TiO₂/NiF, (B) Co/CoPs(60)/TiO₂/NiF, (C) Co/CoPs(120)/TiO₂/NiF, (D) Co/CoPs(240)/TiO₂/NiF and (E) Co/CoPs(240)/NiF electrodes.

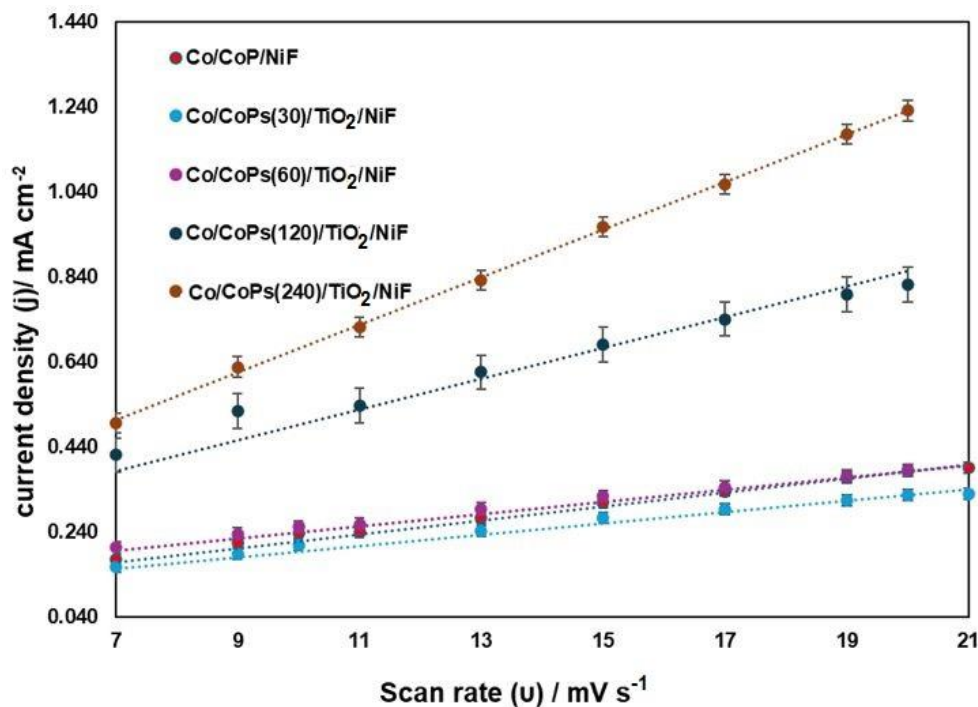


Figure 25 linear curves of average capacitive current density at 760 mV (Vs RHE) Vs. scan rate for different electrodes, the error bars represent the standard mean error of each data points.

The slope of the average current density against the scan rate represents the C_{dl} , which is related to the ECSA. ECSA can be determined by dividing the C_{dl} by the specific capacitance ($0.04 \mu\text{F cm}^{-2}$) of the supporting electrode [96]. The calculated slopes of the linear curves and the ECSA values for each catalytic electrode are given in Table 4-1. According to the ECSA values in the table, it is evident that ECSA increases in the order: $\text{Co/CoPs(30)/TiO}_2/\text{NiF} < \text{Co/CoPs(60)/TiO}_2/\text{NiF} < \text{Co/CoPs(120)/TiO}_2/\text{NiF} < \text{Co/CoPs(240)/TiO}_2/\text{NiF}$. This increase can be attributed to the growing Co/CoPs loading on the TiO_2/NiF with increasing electrodeposition time. As the TiO_2/NiF surface has a high surface area, prolonged deposition time leads to increased Co/CoPs loading. Additionally, SEM analysis has shown that Co/CoPs grow three-dimensionally with more pores and surface area, further contributing to the ECSA enhancement.

Table 4-1 Double layer capacitance of different electrode synthesised and calculated electrochemical surface area

catalyst	C_{dl} / μF	ECSA / cm^2
Co/CoPs(30)/TiO ₂ /NiF	13.4 $\pm$ 0.5	335 $\pm$ 0.5
Co/CoPs(60)/TiO ₂ /NiF	14.4 $\pm$ 0.6	360 $\pm$ 0.6
Co/CoPs(120)/TiO ₂ /NiF	36.2 $\pm$ 2.3	905 $\pm$ 2.3
Co/CoPs(240)/TiO ₂ /NiF	59.6 $\pm$ 1.3	1490 $\pm$ 1.3
Co/CoPs/NiF	16.5 $\pm$ 0.5	412.5 $\pm$ 0.5

For both Co/CoPs(240)/TiO₂/NiF and Co/CoPs(240)/NiF, the same deposition time was used to deposit Co/CoPs. However, the ECSA of Co/CoPs(240)/TiO₂/NiF (1490 $\pm$ 1.3 cm²) is 1037 cm² higher than that of Co/CoPs(240)/NiF (412.5 $\pm$ 0.5 cm²), indicating that the TiO₂ layer on NiF promotes the growth of more Co/CoPs, providing a higher surface area.

The increased ECSA directly correlates with the activity of electrodes for the HER. The trend of increasing ECSA corresponds to the observed decrease in overpotential and Tafel slope, clearly demonstrating that one probable reason for the enhanced HER activity follows the order: Co/CoPs(30)/TiO₂/NiF < Co/CoPs(60)/TiO₂/NiF < Co/CoPs(120)/TiO₂/NiF < Co/CoPs(240)/TiO₂/NiF. This is due to the increasing ECSA.

Moreover, the enhanced HER and OER activity of Co/CoPs(240)/TiO₂/NiF compared to Co/CoPs(240)/NiF is attributed to the presence of the additional TiO₂ layer. This enhancement could be due to two reasons: the increased surface area, which allows for better Co/CoPs loading, and the synergistic catalytic activity between Co/CoPs and TiO₂.

4.4 Electrochemical impedance spectroscopy

Figure 26 displays the Nyquist diagram of the EIS results for various prepared electrocatalysts. The triangular symbols in the figure represent the experimental Nyquist plot data. According to experimental spectra, two distinguishable regions are observed for each experiment. One is a semicircle at the high-frequency range, attributed to the charge transfer resistance of the working electrode [97]. The observed arc at this high-frequency range is mainly due to instrumental

artifacts produced in typical three-electrode system EIS experiments and has no physicochemical significance [97]. Despite this, the primary aim of this EIS investigation is to determine the charge transfer resistance (R_{ct}) and the solution resistance (R_s). Therefore, the semicircle at the high-frequency range is considered in this experiment.

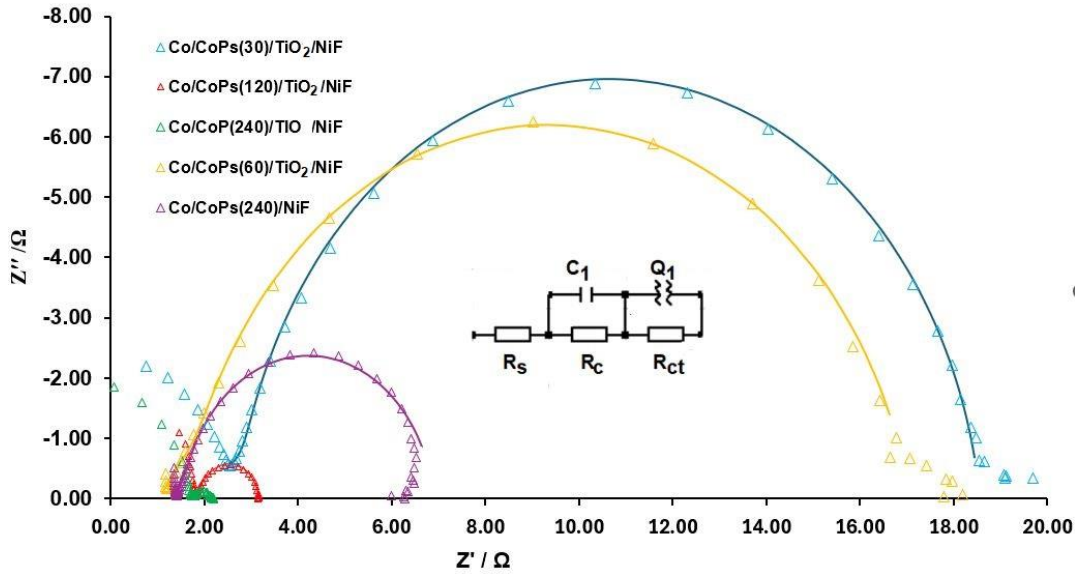


Figure 26 Nyquist plots of various electrodes measured in 1.0 M KOH at -1.2 V (vs. Ag/AgCl). The dotted curves represent the experimental data, while the solid curves represent the fitted data according to the circuit diagram shown in the inset.

The origin of the semicircle associated with charge transfer resistance slightly varies from experiment to experiment due to small differences in the positioning of electrodes [97]. Although the figure provides a clear qualitative comparison of R_{ct} values, it is desirable to evaluate it quantitatively. To achieve this, the semicircle was fitted to a simple equivalent electronic circuit diagram, as shown in inset Figure 26. The fitted curve is depicted by the solid line in the Figure 26. Although the semicircle appears as a single entity, equivalent circuit analysis identified that it should be fitted with two serially connected parallel RC circuits with a serially connected the resistance circuit model reveals that two semicircles overlap each other. Among the two semicircles, the smaller one, which is masked by the larger semicircle, is in the middle-frequency range and has low resistance (R_c). This smaller semicircle is likely associated with the contact between the

catalyst and the supporting electrode. In contrast, the larger semicircle in the low-frequency range is related to charge transfer resistance [98].

The R_s , R_{ct} , and R_c values are shown in Table 4-2 below. According to the results, the R_{ct} values decrease in the following order: Co/CoPs(30)/TiO₂/NiF > Co/CoPs(60)/TiO₂/NiF > Co/CoPs/NiF > Co/CoPs(120)/TiO₂/NiF > Co/CoPs(240)/TiO₂/NiF. This variation in R_{ct} values is inversely correlated with the HER performance of the synthesized electrodes, indicating that decreased charge transfer resistance is one of the reasons for the lower overpotential and Tafel slope observed in the Co/CoPs(240)/TiO₂/NiF catalysts compared to the other synthesized catalysts.

Table 4-2 R_s , R_{ct} and R_c values obtained from the fitted circuit diagram for the Nyquist plots of the various electrodes

	R_s / Ω	R_c / Ω	R_{ct} / Ω
Co/CoPs/NiF	1.42 ± 0.01	0.12 ± 0.13	5.4 ± 0.01
Co/CoPs(30)/TiO ₂ /NiF	2.24 ± 0.04	0.5 ± 0.15	15.8 ± 0.01
Co/CoPs(60)/TiO ₂ /NiF	1.21 ± 0.02	0.43 ± 0.15	15.4 ± 0.02
Co/CoPs(120)/TiO ₂ /NiF	1.8 ± 0.01	0.44 ± 0.22	0.92 ± 0.09
Co/CoPs(240)/TiO ₂ /NiF	1.66 ± 0.01	0.07 ± 0.07	0.43 ± 0.04

Furthermore, the R_{ct} values of Co/CoPs(120)/TiO₂/NiF and Co/CoPs(240)/TiO₂/NiF are lower than those of Co/CoPs/NiF. This consistency with the overpotential and Tafel slope for HER performance suggests that the presence of the TiO₂ layer between the catalyst and NiF in Co/CoPs(120)/TiO₂/NiF and Co/CoPs(240)/TiO₂/NiF plays a significant role.

The effect of TiO₂ on the reduced R_{ct} can be understood in two ways. Firstly, high ECSA due to TiO₂ area allows for increased catalyst loading, which helps decrease R_{ct} by providing more active sites for electrochemical reactions. Secondly, the formation of reduced TiO₂ states may play a significant role. Reduced TiO₂ exhibits higher conductivity compared to its non-reduced form. The -1.2 V (vs. Ag/AgCl), is sufficient to reduce TiO₂ to Ti²⁺, which facilitates electron transfer to cobalt metal. This process enhances the electron density of cobalt and

cobalt phosphides, improving charge transfer efficiency and tuning hydrogen adsorption energy. These adjustments in electronic states contribute to the lower R_{ct} and better HER performance of the electrodes with the TiO_2 layer.

4.5 Overall water splitting reaction

Inspired by the excellent HER performance of $Co/CoP(240)/TiO_2/NiF$, which is characterized by low overpotential, high kinetics, and high exchange current density, along with its moderate OER performance with relatively low overpotential and reasonable kinetics, a full water electrolyser system was set up. This system utilized two $Co/CoP(240)/TiO_2/NiF$ electrodes as both the anode and cathode to investigate the applicability in overall water splitting in 1M KOH. This setup aimed to evaluate the voltage required to achieve a current density of 10 mA cm^{-2} , assess the stability of the electrodes in a real water electrolyser system as bifunctional catalysts, and verify the accuracy of the OER and HER performance and stability evaluations using CP tests. The test result, potential vs. time required to achieve a current density of 10 mA cm^{-2} is shown in Figure 27.

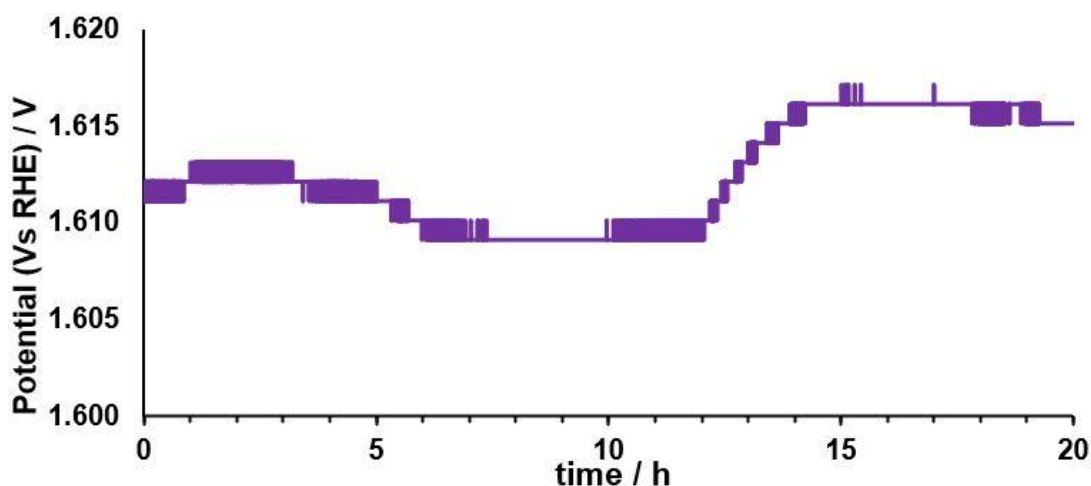


Figure 27: CP test at 10 mA cm^{-2} conducted for a two-electrode water-splitting electrolyser with the $Co/CoP(240)/TiO_2/NiF$ electrode used as both the anode and cathode.

As shown in Figure 27, initially, the electrolyser required only 1.612 V (iR corrected potential) to achieve 10 mA cm^{-2} . This voltage closely matches the sum

of the HER overpotential (27.43 mV), OER overpotential (331.70 mV) to achieve 10 mA cm^{-2} and the thermodynamic water splitting potential (1.23 V), totalling 1.589 V, further validating the previous HER and OER performance evaluations. The small 23 mV deviation between the overall water splitting reaction potential and the separate HER and OER performance evaluation results could be attributed to variations in electrolyte resistance during each experiment, catalyst deactivation or peeling after HER and OER investigations, and differences in the immersed electrode area in the electrolyte. The long-term operation of this electrolyser, as shown in the Figure 27, indicate that the electrodes not only withstand prolonged use in a full water electrolyser system but also confirm the stability observed in earlier HER and OER tests.

This result indicates that the Co/CoPs(240)/TiO₂/NiF electrodes can be effectively utilized in a full water electrolyser system, requiring moderate potential compared to other currently investigated electrodes. Many of those electrodes are synthesized using complex methods, high-end technology, and a substantial amount of chemicals, making them costly, time consuming and potentially hazardous. In contrast, the present electrodes were synthesized using straightforward techniques like electrodeposition, electrophoretic deposition, and annealing, with minimal material consumption.

5 Conclusion and future work

The electrochemical production of green hydrogen offers a promising solution for mitigating climate change and achieving net-zero emissions. However, the widespread use of Pt and Ru-based electrocatalysts is hampered by their high costs and low abundance. This research aimed to develop alternative, cost-effective electrocatalysts with comparable efficiency. The study focused on synthesizing Co/CoPs catalysts using a low-cost deep eutectic solvent mediated electrodeposition on TiO₂-coated nickel foam substrates.

The hypothesis posited that the TiO₂ coating would enhance the electrochemical surface area of Co/CoPs, and that the synergistic effects of CoPs and TiO₂ would tune the electronic environment of the Co/CoPs catalyst, thereby enhancing its catalytic activity for WSR. The research involved several key steps:

TiO₂ Coating and Characterization: TiO₂ nanoparticles were successfully coated on NiF substrates using electrophoretic deposition. Characterization through XRD, SEM, and EDX confirmed the successful coating and revealed a uniform, rough TiO₂ layer on NiF.

Co/CoP Deposition and Characterization: Co/CoPs was deposited on the TiO₂-coated NiF (TiO₂/NiF) using DES-mediated electrodeposition. SEM analysis showed unique cauliflower-like and hexagonal-shaped structures, attributed to either the DES medium or the template effect of the TiO₂ nanoparticles. Further EDX analysis indicated that uniform distribution of Co and P throughout the surface.

Electrochemical Performance Assessment: The HER performance was optimized by varying the Co/CoPs deposition time on TiO₂/NiF. It was observed that the average overpotential for HER in 1 M KOH significantly decreased to 34.42 ± 4.2 mV at 10 mA cm^{-2} for Co/CoPs(240)/TiO₂/NiF from 114.38 ± 2.7 mV for Co/CoPs(30)/TiO₂/NiF based on measurements from three separate batches of samples, with the best low overpotential obtained for Co/CoPs(240)/TiO₂/NiF catalyst being 27.43 mV. This improvement was linked to the increased incorporation of Co/CoPs on the TiO₂/NiF surface, confirmed by increased ECSA

measurements and reduced R_{ct} . Additionally, in considering the best electrodes prepared with different Co/CoPs deposition times, the Tafel slope decreased from 87.15 mV dec⁻¹ for Co/CoPs(30)/TiO₂/NiF to 48.35 mV dec⁻¹ for Co/CoPs(240)/TiO₂/NiF, indicating higher kinetics for the optimized electrode.

Comparative Analysis: The optimized Co/CoPs(240)/TiO₂/NiF electrodes demonstrated superior performance in 1M KOH for HER compared to Co/CoPs deposited on bare NiF (Co/CoPs(240)/NiF) electrode. Specifically, Co/CoPs(240)/TiO₂/NiF showed a significantly lower overpotential (27.43 mV) than Co/CoPs(240)/NiF (91.12 mV) to achieve 10 mA cm⁻² current density. The Tafel slope for Co/CoPs(240)/TiO₂/NiF (48.35 mV dec⁻¹) was much lower than for Co/CoPs(240)/NiF (131.43 mV dec⁻¹), indicating higher kinetics. Additionally, the commercial 10% Pt/C-based electrode required 41.85 mV at η_{10} , consistent with other reported activities of commercial Pt/C on NiF. However, the Tafel slope of Co/CoPs(240)/TiO₂/NiF is slightly higher than that of the Pt/C catalyst (30 mV dec⁻¹), indicating that the kinetics of Co/CoPs(240)/TiO₂/NiF are slightly slower than those of the Pt/C catalyst.

Stability Analysis: The stability of Co/CoPs(240)/TiO₂/NiF was assessed through 5000 CV cycles and long-term durability analysis over 40 hours. There was no significant change in CV cycles before and after 5000 cycles, and the overpotential increased by only 13 mV after 40 hours of operation, indicating excellent stability.

OER Performance: The Co/CoPs(240)/TiO₂/NiF electrode demonstrated efficient OER performance in 1 M KOH, requiring an overpotential of 331.70 mV at 10 mA cm⁻², compared to 350.60 mV for Co/CoPs(240)/NiF and 276.56 mV for the commercial RuO₂/C/NiF electrode. The Tafel slope for Co/CoPs(240)/TiO₂/NiF was 73.96 mV dec⁻¹, indicating good OER kinetics. The enhanced performance was attributed to increased catalyst loading due to the TiO₂ layer and synergistic effects between TiO₂, Co, and CoPs.

Overall Water Splitting (OWS): The full water electrolyser system composed with two Co/CoPs(240)/TiO₂/NiF electrodes as both the anode and cathode showed that the electrolyser required only 1.612 V to achieve 10 mA cm⁻² initially. This

voltage closely matched the sum of the HER overpotential (34.42 mV), OER overpotential (331.70 mV) to achieve 10 mA cm^{-2} , and the thermodynamic water splitting potential (1.23 V), totalling 1.595 V. The long-term operation of this electrolyser indicated that the electrodes not only withstand prolonged use in a full water electrolyser system but also confirm the stability observed in earlier HER and OER tests.

In conclusion, this research successfully developed a cost-effective and efficient Co/CoPs(240)/TiO₂/NiF electrocatalyst for water splitting. The TiO₂ coating significantly enhanced the electrochemical surface area, reduced charge transfer resistance, and improved the overall catalytic performance through synergistic effects with Co/CoPs. The optimized Co/CoPs(240)/TiO₂/NiF electrode demonstrated excellent HER, comparable to commercial Pt catalysts, and showed remarkable stability in both HER and OER conditions. This work provides a viable alternative to expensive and scarce noble metal-based electrocatalysts, contributing significantly to the field of sustainable energy and green hydrogen production.

Despite the promising results achieved in this study, several limitations warrant further investigation and improvement. Firstly, the Co/CoP(240)/TiO₂/NiF catalyst was synthesized with a TiO₂ layer whose thickness was controlled by adjusting the deposition time and the concentration of TiO₂ nanoparticle suspension. While this method provided enhance activity of the catalyst, further optimization of the TiO₂ layer thickness could enhance catalyst efficiency. Future research should explore a broader range of thicknesses to identify the optimal layer configuration for improved performance.

Additionally, the study lacked surface area characterization of the NiF substrate after TiO₂ deposition due to time constraints and constant instrument failure. Measuring the surface area using BET analysis could provide valuable insights into the enhancement achieved through TiO₂ deposition. Future work should focus on assessing the impact of TiO₂ on surface area to better understand its effects on catalytic performance.

The study utilized a single DES for Co/CoP deposition. Comparative analysis with various DESs, ILs, or aqueous media could offer a more comprehensive understanding of how different solvents influence catalyst performance, morphology, and crystal structure. Future investigations should include a range of solvents to optimize the synthesis process and improve catalytic activity.

Although the catalyst demonstrated robustness for water splitting immediately after electrodeposition of Co/CoPs, the stability and crystallinity could be further enhanced with thermal treatment, especially in an inert or reducing environment. This aspect was not explored due to time constraints, and lack of facilities, but future research should consider thermal treatments to potentially improve the catalyst's performance and stability.

The study also did not include X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), measurements of Faradaic efficiency and turnover frequency due to limited access to necessary instruments. XPS could provide insights into hydrogen binding energy optimization resulting from the TiO₂ intermediate layer, while TEM could offer detailed structural information. Faradaic efficiency and turnover frequency measurements are crucial for assessing the true catalytic activity. Incorporating these analyses in future research would offer a more comprehensive understanding of the catalyst's performance and underlying mechanisms.

In this research, the formation of Co and various CoP species could not be conclusively identified, with only a small peak corresponding to CoP (112) at 45.8° being observed. This limitation likely arises from the direct use of the Co/CoPs/TiO₂/NiF electrode in the analysis. Using a powdered sample obtained by scraping the catalyst from the electrode might yield more detailed results. Unfortunately, due to instrument failure during the final phase of the research, this approach could not be implemented. Therefore, future research should focus on fully characterizing the catalyst using XRD.

The study primarily focused on TiO₂ particles. Exploring other TiO₂ nanomaterials (nano tubes, nano rods) and nanomaterials based on different elements could

further enhance catalytic activity. The use of alternative materials might reveal new insights and lead to the development of more efficient catalysts.

Lastly, the excellent performance of Co/CoPs(240)/TiO₂/NiF suggests that future studies should evaluate these electrodes in full water electrolyser systems. This includes testing long-term durability and stability under practical conditions and comparing performance with other state-of-the-art catalysts.

In conclusion, addressing these limitations through targeted research will provide deeper insights into Co/CoPs/TiO₂ catalysts and their potential applications in water splitting and other catalytic processes. Future work should aim to refine the synthesis process, improve characterization techniques, and explore new materials and conditions to optimize catalyst performance.

Contribution to knowledge

This research makes significant contributions to the field of electrocatalysis and green hydrogen production:

Development of Cost-Effective Electrocatalysts: The study successfully developed a low-cost and efficient alternative to Pt and Ru-based electrocatalysts, addressing the issues of high cost and low abundance associated with these materials.

Innovative Synthesis Method: The use of a DES-mediated electrodeposition method for synthesizing Co/CoPs catalysts on TiO₂-coated NiF substrates is a novel approach that can be applied to other catalytic systems.

Enhanced Electrochemical Performance: The research demonstrated that the incorporation of a TiO₂ intermediate layer significantly enhances the electrochemical performance of Co/CoPs catalysts, providing a strategy for improving other electrocatalysts.

Stability and Durability: The study highlighted the excellent stability and durability of the Co/CoPs(240)/TiO₂/NiF catalyst, which is crucial for practical applications in water splitting and other electrochemical processes.

Foundation for Future Research: The findings and methodologies from this study provide a strong foundation for future research aimed at optimizing and applying similar strategies to other electrocatalysts and catalytic applications.

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Appendix A

A.1 Ethical approval letter



8 September 2023

Dear Mr Kulathunga Mudiyansele ,

Reference: CURES/20680/2023

Project ID: 23633

Title: Electrochemical Water Splitting for the Generation of Hydrogen: Co-Ni-TiO₂ Electrode Preparation and Investigation

Thank you for your application to the Cranfield University Research Ethics System (CURES).

We are pleased to inform you your CURES application, reference CURES/20680/2023 has been reviewed. You may now proceed with the research activities you have sought approval for.

If you have any queries, please contact CURES Support.

We wish you every success with your project.

Regards,

CURES Team

A.2 Ethical approval letter



3 August 2024

Dear Mr Kulathunga Mudiyansele ,

Reference: CURES/23269/2024

Project ID: 23633

Title: Improvements of Electrochemical Water Splitting Efficiency by using Economically Viable Co/CoPs/TiO₂/NiF Electrocatalysts

Thank you for your application to the Cranfield University Research Ethics System (CURES).

We are pleased to inform you your project title change request, reference CURES/23269/2024 has been approved.

If you have any queries, please contact CURES Support.

Regards,

CURES Team

A.3 Supporting information

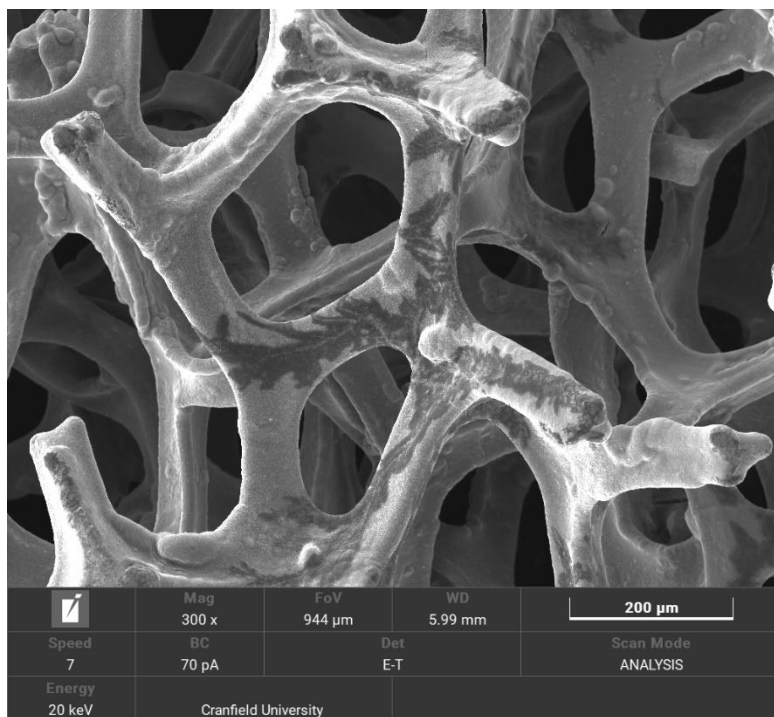


Figure S1: TiO₂ coated NiF,

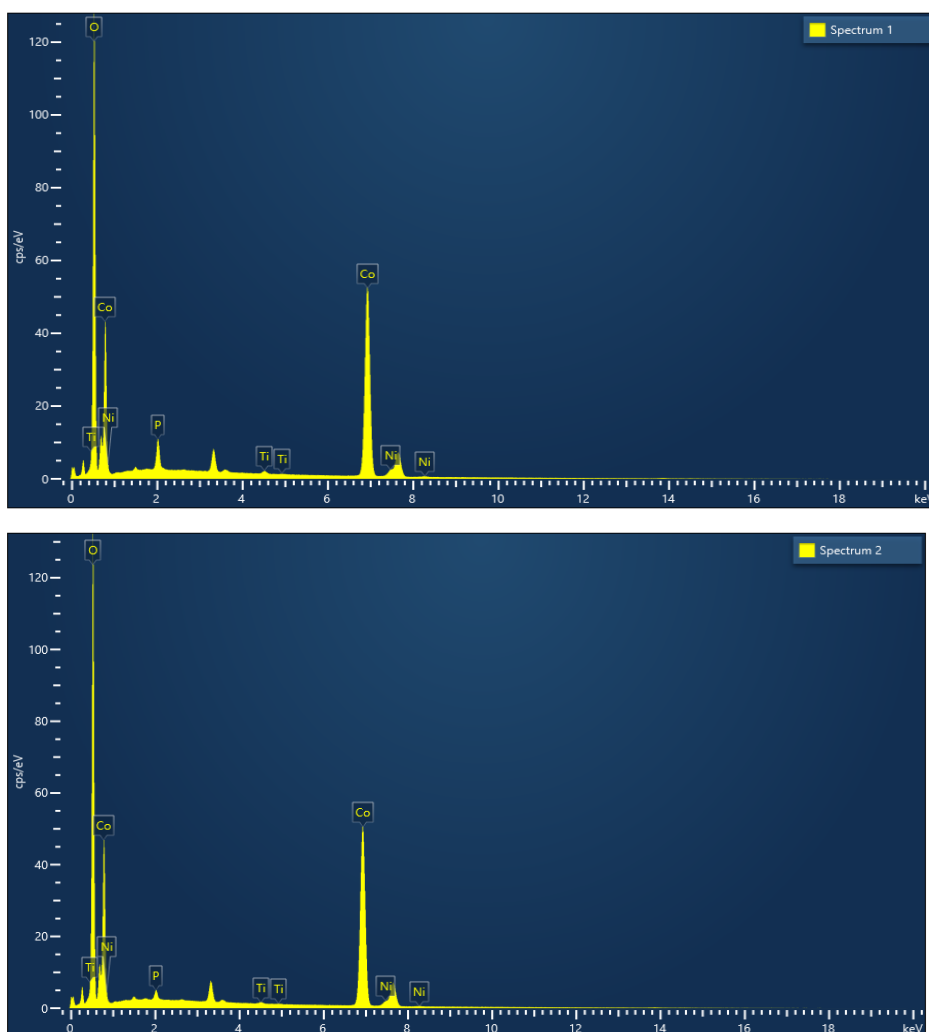


Figure S2: EDX spectrums taken from two different locations of Co/CoPs/TiO₂/NiF

Table S1: Elemental percentage of Co/CoPs/TiO₂/NiF corresponds to two different EDX spectrum shown in Figure S2

Label	O	P	Ti	Co	Total
Spectrum 1	37.07	2.12	0.33	58.54	100.00
Spectrum 2	38.42	0.71	0.19	59.21	100.00
Average	37.75	1.42	0.26	58.87	1.70
Standard Deviation	0.95	1.00	0.10	0.47	0.33

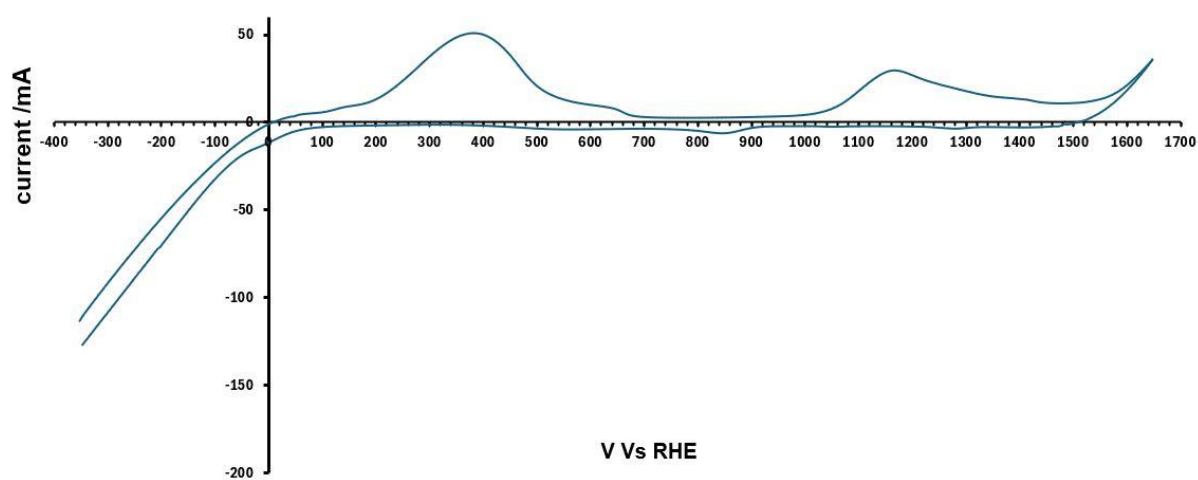


Figure S3: Cyclic voltammogram of Co/CoPs(240) recorded in the scan window of -400 mV to 1640 mV (vs. RHE) at a scan rate of 5 mV s^{-1} .