

Prussian Blue Analogues and Their Derivatives for Water Splitting Reactions

Diao, Fangyuan

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Prussian Blue Analogues and Their Derivatives for Water Splitting Reactions

Fangyuan Diao

Ph.D. Thesis Department of Chemistry, Technical University of Denmark December 2021

Prussian Blue Analogues and Their Derivatives for

Water Splitting Reactions

Ph.D. Thesis

December 14th, 2021

Fangyuan Diao

fandia@kemi.dtu.dk

Main supervisors

Assoc. Prof. René Wugt Larsen and Prof. Jingdong Zhang

Department of Chemistry,

Technical University of Denmark

Co-supervisors

Researcher Xinxin Xiao and Senior Researcher Christian Engelbrekt

Department of Chemistry,

Technical University of Denmark

Preface and Acknowledgements

This thesis is submitted to the Technical University of Denmark (DTU) to fulfill the requirements for the Ph.D. degree. The work presented herein was carried out under the supervision of Assoc. Prof. René Wugt Larsen, Prof. Jingdong Zhang, Researcher Xinxin Xiao, and Senior Researcher Christian Engelbrekt from September 2018 to December 2021 at the NanoChemistry group of the Department of Chemistry, DTU (DTU Chemistry). In addition, a part of the work related to water electrolyzers was carried out at the Department of Energy Conversion and Storage (DTU Energy) with the help of Prof. Qingfeng Li and Dr. Mikkel Rykær Kraglund. The project is financially supported by China Scholarship Council (CSC) for the Ph.D. project (No. 201806220068) and DTU Chemistry.

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December 2021 Kgs. Lyngby, DTU Kemi, Denmark

Fangyuan Diao

Abstract

Electricity produced from renewable energy sources such as solar, wind, hydro, and marine power usually suffers from intermittency, thus requiring additional storage capacity. Conversion of the electricity to chemical fuels for future use is an effective solution. Hydrogen (H₂) is an ideal energy carrier due to its high gravimetric energy density, which can be produced from the electrolysis of water (H₂O \rightarrow H₂ + O₂). However, the efficiency of electrochemical water splitting is impeded by the kinetic energy barriers for cathodic hydrogen evolution reaction (HER) and anodic oxygen evolution reaction (OER). Efficient electrocatalysts are required to lower the overpotentials for HER and OER, thus improving the energy conversion efficiency and reducing the production cost of H₂. Design of optimal electrocatalysts should take the operating condition and the type of electrolyzer (proton exchange membrane electrolysis, alkaline electrolysis, anion exchange membrane electrolysis, and high-temperature solid oxide water electrolysis) into account. In alkaline conditions, non-noble metal-based electrocatalysts are more likely to provide competitive activity over noble metal-based materials (Pt, Ir, Ru, and Pd) on both cathode and anode. Currently, active and robust non-noble metal-based electrocatalysts for HER and OER are urgent. The purpose of this Ph.D. project is to develop efficient and non-noble metal-based electrocatalysts for water splitting in alkaline solutions.

In this Ph.D. thesis, Prussian blue analogues (PBAs), enjoying controllable metal compositions, abundant CN groups, and easy preparation, were explored as the precursors to synthesize active transitional metal-based electrocatalysts for HER and OER. Two efficient electrocatalysts were synthesized by morphology engineering and composition design in this project. Effects of the morphology, composition, and properties upon the optimized electrocatalysts were systematically investigated and explained, as summarized below:

1. Bimetallic NiFeP catalyst coated on NiP rods on Ni foam were successfully synthesized (NiFeP@NiP@NF). The self-supported and interfacial-connected structure favors mass transfer and reduces electrical resistance for electrocatalysis. After optimization of the thickness of NiFe PBA and the phosphidation temperature, the sample exhibited excellent OER performance with a low overpotential of 227 mV at 10 mA cm⁻² and no obvious degradation for 120 h. It can also be applied as an HER electrocatalyst, delivering

10 mA cm⁻² at an overpotential of 105 mV. Therefore, the prepared NiFeP@NiP@NF was tentatively used in an electrolyzer as both cathode and anode, showing a voltage bias of 1.57 V for 10 mA cm⁻² and good stability. Advantages of the structure and composition of NiFeP@NiP@NF for electrocatalytic performance were carefully discussed and explained.

2. CoFe PBAs with different cation species (NH₄⁺, K⁺) in the interstitial spaces can influence the composition, morphology, and crystalline phases of their derivatives after heat-treatment in Ar atmosphere, leading to different performance for OER in 1.0 M KOH. The derivative of CoFe PBA (filled with NH₄⁺) performed best, with overpotentials of 270 and 305 mV at 1 and 10 mA cm⁻², respectively, and remarkable stability. The sample worked well with a Pt/C cathode in a single-cell alkaline electrolyzer, delivering 100 mA cm⁻² at 80 °C at a cell voltage of 1.66 V in 1.0 M KOH solution for 100 h with negligible degradation. The mechanisms of material transformation and the corresponding effects on the OER catalytic performance were thoroughly explored.

Abstract in Danish

Elektricitet produceret fra vedvarende energikilder så som sol-, vind-, vand- og havkraft lider ofte af uregelmæssigheder og kræver yderligere lagringskapacitet. Konvertering af elektriciteten til kemiske brændsler til fremtidig anvendelse er en effektiv løsning. Brint (H2) er en ideel energibærer i kraft af dens høje gravimetriske energitæthed, som kan produceres ved hjælp af vandelektrolyse (H₂O \rightarrow H₂ + O₂). Effektiviteten af elektrokemisk vandelektrolyse er dog hæmmet af de kinetiske energibarrierer, som er associeret med den katodiske brintudviklingsreaktion (HER) og den anodiske iltudviklingsreaktion (OER). Effektive elektrokatalysatorer er påkrævede for at sænke overpotentialerne for HER OER dermed forbedre energikonverteringen reducere og og og produktionsomkostningerne for H₂. Driftsbetingelser og type af elektrolysecelle (protonbyttermembran elektrolyse, alkalisk elektrolyse, anionbyttermembran elektrolyse og højtemperatur keramisk vandelektrolyse) skal tages i betragtning for design af optimale elektrokatalysatorer. Under alkaliske betingelser er det mere sandsynligt at ikke-ædelmetalbaserede elektrokatalysatorer kan levere konkurrencedygtig aktivitet sammenlignet med ædelmetalbaserede materialer (Pt, Ir, Ru and Pd) på både katode og anode. Aktuelt er fremstillingen af aktive og robuste ikke-ædelmetalbaserede elektrokatalysatorer til HER og OER en presserende problemstilling. Formålet med dette ph.d.-projekt er at udvikle effektive og ikke-ædelmetalbaserede elektrokatalysatorer til vandspaltning i alkaliske opløsninger.

I denne ph.d.-afhandling var berlinerblåtanaloger (PBAs), som har kontrollérbare metalsammensætninger, talrige –CN– grupper og let kan fremstilles, udforsket som forstadium til at syntetisere aktive overgangsmetalbaserede elektrokatalysatorer til HER og OER. To effektive elektrokatalysatorer blev syntetiseret ved hjælp af morfologikonstruktion og design af kemisk sammensætning under dette projekt. Effekter af morfologi, sammensætning, og egenskaber på de optimerede elektrokatalysatorer blev systematisk undersøgt og forklaret som sammenfattet nedenfor:

1. Bimetalliske NiFeP-katalysatorer belagt på NiP-stænger på Ni skum (NiFeP@NiP@Ni) blev med succes syntetiseret. De selvstøttende og grænsefladeforbundne strukturer begunstiger masseoverførsel og reducerer elektrisk resistens for elektrokatalysen. Efter optimering af tykkelsen af NiFe PBA og fosfideringstemperaturen udviste prøven fremragende OER-ydeevne med et lavt overpotentiale på 227 mV ved 10 mA cm⁻² og ingen vii tydelig degradering efter 120 timer. Den kan også anvendes som HER-elektrokatalysator, hvor den leverer 10 mA cm⁻² ved et overpotentiale på 105 mV. Derfor blev NiFeP@NiP@Ni forsøgsvist anvendt i en elektrolysecelle som både katode og anode og udviste her en spændingsforskel på 1,57 V ved 10 mA cm⁻² og en god stabilitet. Fordelene ved struktur og sammensætning af NiFeP@NiP@Ni i forhold til elektrokatalytisk ydeevne blev grundigt diskuteret og forklaret.

2. CoFe PBAs med forskellige kationer (NH₄⁺, K⁺) i de interstitielle rum kan påvirke sammensætning, morfologi og krystalfaser af deres afledte materialer efter varmebehandling under argon, som fører til forskellig ydeevne for OER i 1,0 M KOH. Materialet, som er afledt af NH₄⁺-fyldt CoFe PBA ydede bedst med overpotentialer på 270 og 305 mV ved henholdsvis 1 og 10 mA cm⁻² og markant stabilitet. Prøven fungerede godt sammen med en Pt/C katode i en alkalisk elektrolysecelle, hvor den leverede 100 mA cm⁻² ved 80 °C og et cellepotentiale på 1,66 V i 1,0 M KOH-opløsning i 100 timer med ubetydelig degradering. Mekanismerne for materialeomdannelsen og de tilsvarende indvirkninger på OER-katalyseevne blev grundigt udforsket.

Synopsis

Electrolysis of water is regarded as a clean method for H₂ production and renewable energy storage. Efficient and cheap electrocatalysts for HER and OER are required to lower the cost of H₂. This Ph.D. project aims at preparing active, stable, low-cost, and nonnoble metal-based electrocatalysts for HER and OER in alkaline electrolytes. PBAs are mainly explored as precursors to fabricate active electrocatalysts. The Ph.D. thesis is composed of 5 chapters, including an introduction chapter about the renewable energy, electrolysis of water, and electrocatalysts; a summary chapter of the used methodologies for material characterization and performance tests; two research papers on electrocatalysts for OER and HER; and conclusions and perspectives on the project.

Chapter 1 gives an introduction to HER and OER in electrocatalytic water splitting and electrocatalysts. First, a background of energy resources and the urgency of the development of renewable energy resources are presented. Then, the role of hydrogen in society and its importance in the future energy system are explained. Electrolysis of water with electricity from renewable energies is a green method to produce hydrogen. Reaction mechanisms and efficient electrocatalysts incorporated in electrocatalytic water splitting are summarized respectively. Finally, reported PBAs and their derivatives as electrocatalysts for HER and OER are discussed.

Chapter 2 summarizes the techniques for material characterization, including morphology, composition, phase, and surface properties, and the electrochemical methods for performance evaluation. It explains the principles of these techniques and methods.

Chapter 3 introduces a bimetallic NiFeP catalyst coated on NiP rods on Ni foam (NiFeP@NiP@NF), which is a bifunctional electrocatalyst for OER and HER in alkaline condition. After optimization, the sample exhibits excellent OER and HER performance. The effects of material structure and composition on electrocatalytic performance are carefully discussed and explained. The chapter is presented as a research paper entitled "Bifunctional and self-supported NiFeP-layer-coated NiP rods for electrochemical water splitting in alkaline solution", which has been published in ACS Applied Materials & Interfaces. (ACS Appl. Mater. Interfaces **2021**, 13, 23702–23713)

Chapter 4 describes the preparation of CoFe PBA with NH₄⁺ occupying the interstitial spaces and explains the influence of different cation species (NH₄⁺, K⁺) in the interstitial spaces to their derivatives during heat-treatment in Ar atmosphere. Their performance for OER in 1.0 M KOH has been evaluated, and the difference is discussed by the comparison of the structure and composition. This chapter is presented as a manuscript entitled "*Exploration of structure and oxygen evolution reaction performance of CoFe Prussian blue analogue and its three derivatives*". (In preparation)

Chapter 5 summarizes the conclusions of these two research works and gives perspectives of non-noble metal-based catalysts design, synthesis, and characterization for electrocatalytic water splitting.

Scientific Contributions

Publications

Chapter 3 and chapter 4 are the manuscripts of contribution (1) (published on ACS Appl. Mater. Interfaces) and contribution (2) (in preparation), respectively. Contributions (3-6) are cooperative manuscripts where I carried out some tests about materials characterization and electrochemical performance tests, which are not introduced in this Ph.D. thesis.

1. **Fangyuan Diao**, Wei Huang, Georgios Ctistis, Hainer Wackerbarth, Yuan Yang, Pengchao Si, Jingdong Zhang, Xinxin Xiao*, and Christian Engelbrekt*. Bifunctional and self-supported NiFeP-layer-coated NiP rods for electrochemical water splitting in alkaline solution. *ACS Appl. Mater. Interfaces* **2021**, 13, 20, 23702

 Fangyuan Diao, Mikkel Rykær Kraglund, Qingfeng Li, Huili Cao, Kai Gao, Xiaomei Yan, Christian Engelbrekt*, Xinxin Xiao*. Structure and oxygen evolution reaction performance of CoFe Prussian blue analogue and three derivatives. In preparation, 2021

3. Wei Huang, Jing Tang, **Fangyuan Diao**, Christian Engelbrekt, Jens Ulstrup, Xinxin Xiao*, Kristian Mølhave*. Recent progress of two-dimensional metal-organic frameworks and their derivatives for oxygen evolution electrocatalysis. *ChemElectroChem* **2020**, 7, 4695

4. Wei Huang, Chao Peng, Jing Tang, Fangyuan Diao, Murat Nulati Yesibolati,
Hongyu Sun, Christian Engelbrekt, Jingdong Zhang, Xinxin Xiao*, Kristian S.
Mølhave*. Electronic structure modulation with ultrafine Fe₃O₄ nanoparticles on 2D Nibased metalorganic framework layers for enhanced oxygen evolution reaction. *Journal of Energy Chemistry* 2022, 65, 78

5. Wei Huang, Jing Tang, **Fangyuan Diao**, Shuo Li, Hongyu Sun and Xinxin Xiao*. CoP Nanoparticles fabricated through the nanoscale Kirkendall effect immobilized in 3D hollow carbon frameworks for oxygen evolution reaction. *Journal of the Electrochemical Society* **2021**, 168,094501

6. Xiaomei Yan, Charlotte Uldahl Jansen, **Fangyuan Diao**, Katrine Qvortrup, David Tanner, Jens Ulstrup*, Xinxin Xiao*. Surface-confined redox-active monolayers of a

multifunctional anthraquinone derivative on nanoporous and single-crystal gold electrodes. *Electrochemistry Communications* **2021**, 124, 106962

Conferences list

The list includes the conferences I participated in during the Ph.D. project. At these conferences, I gave a presentation to other researchers and I got the opportunity to communicate with them.

 Apr. 22, 2019 - Apr. 22, 2019: Inorganic Graduate Student Seminar, Danish Chemical Society, Denmark (poster)
 Nov. 03, 2019 - 04 Nov. 04, 2019: Ph.D. Symposium in DTU Chemistry, Technical University of Denmark, Denmark (poster)
 Aug. 29, 2020 - Sep. 02, 2020: 71st Annual Meeting of International Society of Electrochemistry, Serbia (poster, online)
 Oct. 27, 2020-Oct. 28, 2020: Annual Meeting of the Danish Electrochemical Society, Denmark (poster and short oral presentation)
 Mar. 28, 2021 - Mar. 30, 2021: Electrocatalysis for Renewable Energy, Leiden University, Netherlands (poster, online)
 Apr. 17, 2021 - Apr. 20 2021: Online 29th Topical Meeting of the International Society of Electrochemistry, Czech Republic (poster and short oral presentation)
 Sep. 21, 2021 - Sep. 25, 2021: INTERFACES: From New Materials to Life Science – Structure, Interactions, Dynamics and Activity, University of Cagliari, Italy (poster)

Abbreviations

| 0D: | Zero-dimensional | | |
|------------------|--|--|--|
| 2D: | Two-dimensional | | |
| 3D: | Three-dimensional | | |
| ΔG : | Change in reaction free energy | | |
| ΔH : | Change in reaction enthalpy | | |
| ΔS : | Change in reaction entropy | | |
| η: | Overpotential | | |
| AEM: | Anion exchange membrane | | |
| CA: | Chronoamperometry | | |
| CC: | Carbon cloth | | |
| Cdl: | Electrochemical double-layer capacitance | | |
| CE: | Counter electrode | | |
| CP: | Chronopotentiometry | | |
| CV: | Cyclic voltammetry | | |
| DFT: | Density functional theory | | |
| DSC: | Differential scanning calorimeter | | |
| ECSA: | Electrochemical surface area | | |
| EDS/EDX: | Energy dispersive X-ray spectroscopy | | |
| EIS: | Electrochemical impedance spectroscopy | | |
| EM: | Electron microscope | | |
| Eq.: | Equation | | |
| F: | Faradaic constant (96485 C mol-1) | | |
| FE: | Faradaic efficiency | | |
| Fig.: | Figure | | |
| FTIR: | Fourier transform infrared spectroscopy | | |
| HER: | Hydrogen evolution reaction | | |
| HRTEM: | High-resolution transmission electron microscopy | | |
| ICSD Coll. Code: | Inorganic Crystal Structure Database Collection Code | | |
| IR: | Infrared spectroscopy | | |
| LSV: | linear sweep voltammetry | | |
| | | | |

| MOF: | Metal-organic framework |
|-------|------------------------------------|
| NF: | Nickel foam |
| OER: | Oxygen evolution reaction |
| PB: | Prussian blue |
| PBA: | Prussian blue analogue |
| PCP: | Porous coordination polymer |
| PDS: | Potential-determining step |
| PEM: | Proton-exchange membrane |
| Rct: | Charge transfer resistance |
| Rs: | Ohmic resistance |
| RDE: | Rotating disk electrode |
| RE: | Reference electrode |
| RHE: | Reversible hydrogen electrode |
| RT: | Room temperature |
| SAED: | Selected area electron diffraction |
| SEM: | Scanning electron microscopy |
| SOEC: | Solid oxide electrolysis cell |
| TEM: | Transmission electron microscopy |
| TGA: | Thermal gravimetric analysis |
| TMP | Transition metal phosphide |
| Urev: | Reversible cell voltage |
| WE: | Working electrode |
| XPS: | X-ray photoelectron spectroscopy |
| XRD: | X-ray diffraction |

Notes:

1. Plural forms are used by adding "-s" at the end of abbreviations.

2. Abbreviations of terms ending with -microscopy, -voltammetry, or -spectroscopy also refer to the same terms ending with -microscopic, -voltammogram, or -spectrum/spectra.

3. Abbreviations listed here do not include the abbreviations of special names of materials in this thesis.

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Chapter 1 Introduction to electrocatalytic water splitting reactions and electrocatalysts

This chapter gives an introduction to hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) in electrocatalytic water splitting and the electrocatalysts used in these reactions. It includes the introduction to the necessary background, concepts, catalytic theories, electrocatalysts, synthesis methods, which are important and inspirational for this Ph.D. project.

1.1 Background

Energy is an essential resource for human beings that plays a crucial role in socioeconomic development. There are several major energy resources in human history, whose evolution greatly affects the economy, society, environment, etc. Traditional energy sources in agricultural economies were mainly biomass, water, and wind power. After the industrial revolution, fossil fuels, including coal, petroleum, and natural gas with greater energy density than biomass and fewer limitations than water or wind power, became the main energy sources (Figure 1.1.1).¹ The demand for fossil fuels increases even faster with the population increase and industry progress in the present era. However, stocks of fossil fuels are limited and dwindling on the earth, and they are not renewable energy sources. Besides this, the serious negative influences on the environment caused by consuming these energy sources are gradually becoming unacceptable for human beings.²⁻⁴ For example, CO₂, the main by-product of using fossil fuels and the main player of global warming, has risen quickly from ~ 280 to ~ 412 ppm in the atmosphere from the 18^{th} century (pre-industrial time) to 2020, and it is estimated to increase to ~550 ppm in 2050, which may lead to catastrophic consequences to the society.⁵ Airborne fine particles generated by the combustion of coal and diesel can cause serious health problems towards lungs and hearts, especially in children, older adults, and people with other lung or heart diseases.3



Figure 1.1.1. (a) Shares of biomass and fossil energy carriers in the global energy use, and (b) per capita energy use of biomass and fossil energy between 1500 and 2010. The x-axis is scaled in 100-year intervals between 1500 and 1900 and in 10-year intervals between 1950 and 2010. Reprinted with permission from ref.¹. Copyright 2015 Materials Research Society.



Figure 1.1.2. Estimated share of renewable energy of the total final energy consumption in 2009 and 2019. Reprinted from ref. ⁶. Open access.

Due to great concerns about fossil fuels and global climate change, the efforts on finding green alternatives in the past decades have been continued. Non-carbon, clean, safe, and renewable energy sources such as solar energy, wind, tidal energy, and geothermal heat are promising substitutes for fossil fuels. Despite considerable efforts and progress, there is still a long way to go before renewable energies can meet our daily demands and support economic development.⁷ As shown in Figure 1.1.2, the share of fossil fuels in the total global energy consumption remained around 80% in the period from 2009 to 2019 due to rising energy demands and large investments in new fossil fuels.⁶ The share of modern renewables such as hydropower, biomass, solar, and ocean power, slightly increased by 2.5% in the decade, while the use of biomass declined. Although modern renewable energy increased faster than total final energy consumption (TFEC), it accounted for only 25% of the TFEC increase during 2009-2019 (Figure 1.1.3).⁶ In conclusion, we are still in an early and challenging stage to shift our energy system to sustainable and renewable energy.



Figure 1.1.3. Estimated growth of the share of modern renewables for total final energy consumption in 2009 and 2019. Reprinted from ref.⁶. Open access.

1.2 The role of hydrogen in society

In 1776, Henry Cavendish firstly isolated hydrogen gas (H₂) and later Lavoisier recognized that hydrogen was a constituent of water in 1783. Nicholson and Carlisle discovered the process of electrolysis of water to produce hydrogen in 1800. After these discoveries, hydrogen gradually attracted researchers' attention and has become an important member in the energy field due to its high energy content (120 MJ/kg at 298

K).⁸ Jules Verne described water as a clean fuel in the fiction novel *The Mysterious Island* in $1874.^9$

"Yes, my friends, I believe that water will someday be employed as fuel, that hydrogen and oxygen, which constitute it, used singly or together, will furnish an inexhaustible source of heat and light I believe, then, that when the deposits of coal are exhausted, we shall heat and warm ourselves with water. Water will be the coal of the future."

In this paragraph, water was thought to be a desirable fuel of the future because it was composed of hydrogen and oxygen, which could produce heat and light. It is not difficult to realize that Verne's thought has a logical problem based on the law of conservation of energy. Hydrogen, instead of water, is a clean fuel, but its production from water requires energy input. Hydrogen works as an energy carrier, with water as the only product. Hydrogen can be an important part of the future energy system, though it is necessary to find sustainable, clean, and abundant energy sources for green hydrogen production (Figure 1.2.1).



Figure 1.2.1. A hydrogen fuel cycle starting from water splitting using renewable energies. Modified with permission from ref. ¹⁰. Copyright 2008 Springer Science+Business Media, LLC.

Table 1 lists some important properties of hydrogen. Hydrogen is a colorless, odorless, and nontoxic gas at ambient temperature and pressure. The leakage of hydrogen is dangerous. The density of hydrogen is 0.083 kg m^{-3} , much lighter than air (1.225 kg m⁻³)

at 25 °C and 1 atm. So, hydrogen will dissipate quickly if leakage occurs. Incidental sparks from valves, electrostatic discharges, personnel smoking, and other ignition methods could cause fires and explosions when the ratio of hydrogen in air reaches the flammability range (4 - 75 vol% at 20 °C in air).¹⁰ Thus, a hydrogen sensor is necessary to detect hydrogen leakage in the storage place. For a long time, H₂ was mainly produced by the gasification of coal and wood. Hydrogen is a constituent of syngas, mainly used for heating and cooking. Nowadays, the majority of hydrogen is produced by steam reforming of methane. Electrolysis of water is an old but more efficient and greener method, especially using electricity from renewable energy sources like wind and solar energy, over the aforementioned two methods that involve the emission of carbon dioxide. Besides being used as an energy carrier, hydrogen plays an important role in methanol and ammonia synthesis and fossil fuel refining. The global demand for water-derived hydrogen has been continuously increasing since 1980, and the trend will be maintained upon the call for clean energy.¹¹ With the development of technologies related to renewable energies and policy support, the cost of hydrogen produced by the electrolysis of water will be lowered gradually.¹²⁻¹⁴

| Property | Value |
|------------------------------------|------------------------------------|
| Molcular weight | $2.016\mathrm{g\ mol^{-1}}$ |
| Density | 0.083 kg m ⁻³ |
| Boiling point | -252.8 °C |
| Melting point | -259.2 °C |
| Vapor pressure at -252.8 °C | 101.283 kPa |
| Density of the gas at -252.8 °C | 1.331 kg m ⁻³ |
| Density of the liquid at -252.8 °C | 67.76 kg m ⁻³ |
| Lower calorific value | 120 MJ kg ⁻¹ |
| Higher calorific value | 142 MJ kg-1 |
| Ignition limit in air | 4-75 vol% |
| Diffusion coefficient in air | $0.61 \text{ cm}^2 \text{ s}^{-1}$ |
| Adiabatic flame temperature in air | 2045 ℃ |
| Autoignition temperature | 400 °C |
| Cp | 14.34 kJ (kg.°C)·1 |

Table 1. Hydrogen properties.

| Cv | 10.12 kJ (kg.°C)-1 |
|----------|--------------------|
| Toxicity | Nontoxic |

*The physical properties are defined at 20 °C and 1 atm if not specifically mentioned. **The properties are adapted from ref.^{8,10,15}.

1.3 Reactions in the electrolysis of water

The electrolysis of water involves two half-cell reactions: cathodic hydrogen evolution reaction (HER) and anodic oxygen evolution reaction (OER). Figure 1.3.1 illustrates an archetypal electrolysis cell for water splitting, consisting of a cathode, an anode, electrolyte, membrane, and a power supply. At different pH levels, the total reaction is the same (Eq. 1), but the half-reactions occurring on the cathode and the anode differ. In acidic electrolytes, abundant H⁺ is beneficial for cathodic HER (Eq. 2). Water is oxidized to produce O₂ and protons at the anode (Eq. 3). Protons working as charge carriers move from the anode to the cathode to take part in the cathode (Eq. 4). OH⁺ take the role of charge carriers and are oxidized at the anode to produce O₂ (Eq. 5).^{16,17}

Total reaction: $2 H_2 O \rightarrow 2 H_2 + O_2$ (1)

In the acidic electrolyte:

| Cathode: $4 H^+ + 4 e^- \rightarrow 2 H_2$ | (2) |
|--|-----|
|--|-----|

Anode: $2 H_2 O \rightarrow O_2 + 4 H^+ + 4 e^-$ (3)

In the alkaline electrolyte:

Cathode:
$$4 H_2O + 4 e \rightarrow 2 H_2 + 4 OH^2$$
 (4)

Anode: $4 OH \rightarrow O_2 + 2 H_2O + 4 e^{-1}$ (5)



Figure 1.3.1. An illustration of an electrolysis cell for water splitting.

The cell voltage required by an electrochemical reaction is determined by thermodynamics. The change in reaction free energy (ΔG) can be calculated with the change in reaction enthalpy (ΔH), temperature (T), and the change in reaction entropy (ΔS) as shown in Eq. 6. The reversible cell voltage (U_{rev}) can be determined by the ratio of ΔG to the number of exchanged electrons (z) for the product and the Faradaic constant (F, 96485 C mol⁻¹) (Eq.7). For the electrolysis water splitting process to produce 1 mol H₂, the ΔG is 237 kJ, leading to the U_{rev} to be 1.23 V at standard conditions (25 °C and 1 atm). In other words, the theoretical thermodynamic potential of water splitting is 1.23 V at 25 °C and 1 atm regardless of the electrolyte pH.¹⁸ However, a higher potential than 1.23 V is always required to practically split water into H₂ and O₂. The overall excess potential for the electrolysis cell is defined as overpotential (η) , including the overpotentials to overcome the activation energy of HER (η HER) and OER (η OER), the IR drop (η Other) caused by the resistance from the electrolyte, contact, membrane, and some side reactions like electrode corrosion and dioxygen reduction. Thus, the applied potential (E_{aq}) for an electrolysis cell is calculated following Eq. 8 (Figure 1.3.2). To reduce η , various measures are taken. Using concentrated electrolytes and using electrodes with excellent conductivity and corrosion resistance are practical to reduce η_{other} . Efficient electrocatalysts can significantly reduce the activation energy for HER and OER and thus η HER and η OER.^{19–22}

$$\Delta G = \Delta H - T \cdot \Delta S \tag{6}$$

$$U_{\rm rev} = \frac{-\Delta G}{z \cdot F} \tag{7}$$

 $E_{aq} = U_{rev} + \eta_{HER} + \eta_{OER} + \eta_{other}$



(8)

Figure 1.3.2. Schematic drawing of the polarization curve for water electrolysis at 25 °C and 1 atm. Adapted with permission from ref.²³. Open access

1.3.1 HER mechanisms

The generally accepted HER mechanisms in both acidic and alkaline media involve three possible reactions (Figure 1.3.3). In the first step (Volmer reaction, Eq. 9 and 10), a proton from the hydronium cation (H_3O^+) in acidic media or the water molecule (H_2O) in alkaline media reacts with an electron to generate an absorbed hydrogen atom (H^*) on the surface of the electrode (M). In the second step, dihydrogen could be produced via the Heyrovsky reaction (Eq.11 and 12), or Tafel reaction (Eq.13), or both. In the Heyrovsky reaction, another proton diffuses to the $M - H^*$ and then reacts with another electron to produce a H_2 . In the Tafel reaction, two vicinal $M - H^*$ on the surface of the electrode combine to form a H_2 .²⁴⁻²⁶

Volmer reaction (electrochemical hydrogen adsorption):

| Acidic media: | $H_{3}O^{+}$ | $H_3O^+ + M + e^- \rightleftharpoons M - H^* + H_2O$ | | |
|-----------------------|--|--|------|--|
| Alkaline media: | H ₂ 0 | $H_2O + M + e^- \rightleftharpoons M - H^* + OH^-$ | | |
| Heyrovsky reaction (e | electrochemical | desorption): | | |
| Acidic media: | Н | $^{+}+e^{-}+M-H^{*} \rightleftharpoons H_{2}+M$ | (11) | |
| Alkaline media: | $H_2O + e^- + M - H^* \rightleftharpoons H_2 + M + OH^-$ | | (12) | |
| Tafel reaction (cher | mical desorpt | ion): | | |
| Acidic and alkalir | ne media: | $2 M - H^* \rightleftharpoons H_2 + 2 M$ | (13) | |



Figure 1.3.3. Illustration of the HER mechanism on the surface of an electrode in the acidic (a) and alkaline (b) solution. Reprinted from ref.²⁷. Open access

The Tafel slope (*b*) signifies the dependence of the current density (*j*) and the variation of the overpotential (η) ($\eta = a + b \times \log j$), which is related to the electrocatalytic mechanism of the HER process and the activity of electrocatalysts. The Tafel slope could reveal the rate-determining step of HER. When the *b* of 30 mV dec⁻¹ is observed at room temperature, it indicates that the Volmer reaction is fast and the chemical desorption (Tafel reaction)

is the rate-determining step. If the b is close to 40 mV dec⁻¹ at room temperature, it means that the Volmer reaction is fast and electrochemical desorption (Heyrovsky reaction) is the rate-determining step. If the Volmer reaction is slow, the b should be larger than 120 mV dec⁻¹ at room temperature.^{28,29} The Sabatier principle, firstly proposed by French chemist Paul Sabatier in 1913, states that the interaction between the reactant and the catalyst should be neither too weak nor too strong. If the interaction is too weak, the reactant and the catalyst will hardly interact with each other, whereas if the bond is too strong, the reactant will be difficult to desorb from the catalyst surface, thus blocking the active sites and inhibiting further reactions.³⁰ In the HER process, both the H^* adsorption and H_2 desorption can be evaluated by the Gibbs free energy for atomic hydrogen adsorption (ΔGH^*). According to the Sabatier principle, ΔGH^* should be zero with the highest exchange current density (jo, the current density under equilibrium conditions, when all forward and backward reactions are equal) under ideal conditions for HER. If ΔGH^* is negatively large, it indicates the interaction is too strong, while too weak for positively large $\Delta GH^{*,31,32}$ Nørskov et al. successfully calculated the ΔGH^{*} for various metals by density functional theory (DFT), obtaining a volcano curve of ΔGH^* versus the logarithm of the corresponding jo to compare the activity of different metals for HER (Figure 1.3.4).³³ The volcano plot shows that Pt is at the summit of the volcano, close to zero hydrogen absorption, indicating it is a better electrocatalyst than other metals for HER. The volcano plot is a useful reference for designing electrocatalysts.



Figure 1.3.4. A volcano plot of experimentally measured j_0 as a function of DFT-calculated Δ GH* for different metals in acidic solutions. Adapted with permission from ref. ³³. Copyright 2005 ECS - The Electrochemical Society.

1.3.2 OER mechanisms

Growing attention is paid to OER, as it is one of the major bottlenecks to improve the overall Faradaic efficiency of the water splitting electrolyzer. The electrocatalytic OER is a more complex reaction than HER because OER involves four electrons transferred per oxygen molecule produced, and the sluggish kinetics require a high overpotential to overcome the activation barrier.^{34,35} It is noted that the mechanisms of OER in acidic conditions differ from those in alkaline conditions (Figure 1.3.5). In acidic media, a water molecule first dissociates and the $M - OH_{ads}$ (Eq. 14) forms on the surface of the electrode. The proton in $M - OH_{ads}$ is then removed to form $M - O_{ads}$ in the second step (Eq. 15). Subsequently, the second water molecule performs a nucleophilic attack on the $M - Oa_{ads}$ and forms the $M - OOH_{ads}$ (Eq. 16). Finally, a O_2 desorbs from the $M - OOH_{ads}$ and is released from the active site (Eq. 17). In alkaline electrolyte, OH^- adsorbs on the metal surface, forming intermediate $M - OH_{ads}$ and $M - O_{ads}$ at the first two steps (Eq. 18 and 19). Then $M - O_{ads}$ combines with a OH^- , forming $M - OOH_{ads}$ (Eq. 20). Finally, $M - OOH_{ads}$ reacts with another OH^- to produce a O_2 (Eq. 21).^{34,36}

In acidic media:

$$M + H_2 O \to M - OH_{ads} + H^+ + e^-$$
 (14)

$$M - OH_{ads} \rightarrow M - O_{ads} + H^+ + e^- \tag{15}$$

$$M - O_{ads} + H_2 O \to M - OOH_{ads} + H^+ + e^-$$
 (16)

$$M - 00H_{ads} \rightarrow M + 0_2 + H^+ + e^-$$
 (17)

In alkaline media:

$$M + OH^- \to M - OH_{ads} + e^- \tag{18}$$

$$M - OH_{ads} + OH^- \rightarrow M - O_{ads} + H_2O + e^-$$
(19)

$$M - O_{ads} + OH^- \rightarrow M - OOH_{ads} + e^-$$
(20)

$$M - 00H_{ads} + 0H^- \to M + 0_2 + H_2 0 + e^-$$
 (21)



Figure 1.3.5. Illustration of OER mechanisms in acidic (A) and alkaline (B) electrolytes. Reprinted with permission from ref.³⁷. Open access.

The theoretical potential of oxygen evolution is 1.23 V under standard conditions, with the change in Gibbs free energy of the overall reaction (ΔGo_2) calculated to be 4.92 eV under equilibrium conditions. ΔGo_2 equals to the sum of the change in Gibbs free energy for every individual proton-electron transfer step (ΔG_x , x=1,2,3, and 4, representing each step). The step with the maximum Gibbs free energy (ΔG_{max}) is generally defined as the potential-determining step (PDS), further determining the theoretical overpotential for the OER (ηOER) (Eq. 23).

$$\eta_{\text{OER}} = \frac{\Delta \text{Gmax}}{e} - 1.23 \text{ V}$$
(23)

As reported by Isabela et al., the ideal catalyst should require the same reaction free energy of 1.23 eV at zero potential (4.92 eV/4 = 1.23 eV) as Figure 1.3.6a shows. However real catalysts do not behave like this. The calculated free energy diagrams for each step of OER on the surface of LaMnO₃, SrCoO₃, and LaCuO₃ at standard conditions at different potentials are displayed in Figure 1.3.6, which indicates the difference of the three samples in PDS. For SrCoO₃, the O* level is placed more perfectly between those of HO* and HOO* than LaMnO₃ and LaCuO₃, leading to a smaller overpotential (η OER of SrCoO₃ = 0.25 V) for the OER process.³⁸ Therefore it is significant to modify the catalyst's surface to provide optimum bindings of intermediates.



Figure 1.3.6. Calculated standard free energy diagram for OER at equilibrium potential (U=1.23
V) and zero potential (U=0 V) at pH 0 and 298 K. At U=1.23 V on a) the ideal catalyst, b) LaMnO₃,
c) SrCoO₃, and d) LaCuO₃. At U=0 V for e) the ideal catalyst, f) LaMnO₃, g) SrCoO₃, and h) LaCuO_a
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1.3.3 Electrocatalysts for HER and OER



Figure 1.3.7. Electrocatalysts for HER and OER in acidic and alkaline media.

Noble metal-based materials. Great efforts have been made to develop efficient and reliable catalysts for HER and OER in water electrolysis (Figure 1.3.7). Noble metalbased materials especially the platinum group (including Pt, Ir, Ru, Rh, Ir, and Pd) based materials are the best known HER and OER catalysts.³⁹⁻⁴¹ However the application of noble metals is greatly prohibited by their low abundance and high cost. One strategy to reduce the usage of noble metals is to fabricate dispersed micro/nanostructured materials to maximize the utilization of noble metal atoms. Pt is the most popular and reliable HER catalyst in both acid and alkaline electrolytes. D.V. Esposito et al. deposited a monolayer of Pt atoms on tungsten monocarbide (WC) films through a thermal evaporation method to allow nearly all Pt atoms to be in contact with the electrolyte. The monolayer Pt on WC showed comparable HER activity with the bulk Pt foil in 0.5 M H₂SO₄ at room temperature.⁴² C. Cui et al. fabricated a composite of Pt nanoparticles in the porous MXene monolith with a Pt loading of 8.9 μ g cm⁻², requiring a low overpotential of 43 mV to deliver 10 mA cm⁻² in acid conditions. Pt nanoclusters with an average diameter of 2.58 nm on hollow graphene spheres (Pt/HGSs) (Figure 1.3.8a) reported by C. Fan et al. exhibited similar HER performance of a commercial 20 wt% Pt/C catalyst with five-time Pt loading of that in the Pt/HGSs in 1 M KOH.43





Ir/Ru-based materials have also been widely reported for electrocatalysis of HER and OER. C. V. Pham et al. prepared novel IrO₂ coated TiO₂ microparticles with a low Ir loading of 0.4 mg cm⁻² as the anode for OER, outperforming commercial catalysts from Alfa Aesar (IrO₂) and Umicore ($50 \mu g_{Ir} \text{ cm}^{-2}$ in the IrO₂/TiO₂) in a proton exchange membrane (PEM) water electrolyzer.⁴⁶ D. Böhm et al. developed IrO₂ (2-3 nm) nanoparticles decorated Sb-doped SnO₂ (ATO) (Figure 1.3.8b and c) by a multistep synthesis procedure in which properties of the support and the loading of Ir were independently optimized. The optimal composite with an Ir loading of 25 wt% exhibited good OER performance, delivering 63.5 A g⁻¹ at the overpotential of 300 mV in 0.5 M H₂SO₄ at room temperature.⁴⁴ Chen et al. synthesized Ru (1.08 wt%) modified transitional 15

metal phosphide (MnFeP) nanosheets on Ni foam, performing well as both HER (η =35 mV for 10 mA cm⁻²) and OER electrocatalyst (η =191 mV for 20 mA cm⁻²) in 1 M KOH.⁴⁷ Y. Qin et al. successfully incorporated high-valence metal atoms (including Ir, Rh, and Ru) into PdCu nanoparticles using Fe³⁺ as the oxidation agent, finding that high-valence metal atoms favor both HER and OER due to the optimized binding energy of the intermediates on the electrodes' surface.⁴⁵



Figure 1.3.9. (a) Schematic illustration for the fabrication of Co-Fe-Ga-Ni-Zn HEA, and (b-e) X-ray diffraction (XRD) analysis, TEM image, and HRTEM images of Co-Fe-Ga-Ni-Zn HEA. (a-e) are reprinted with permission from ref.⁵¹. Copyright 2021 Tsinghua University Press and Springer-

Verlag GmbH Germany, part of Springer Nature. (f) Schematic illustration for the preparation of amorphous CoMo phosphides nanosheets on carbon fiber paper (CFP), and (g-i) Scanning electron microscopic (SEM) images of CoMo phosphides nanosheets on CFP. (f-i) are reprinted with permission from ref.²⁰. Copyright 2020 Wiley-VCH GmbH.

Non-noble metal-based electrocatalysts. Due to the limitations of noble metals regarding abundance and cost, it is important to develop non-noble metal-based electrocatalysts with competitive activity and stability.48 A great number of electrocatalysts like alloys, metal phosphides, metal sulfides, metal carbides, and metal nitrides based on transitional metals (Ni, Fe, Co, Mo, Cu, W, and et al.) have been reported for HER and OER.^{49,50} In order to improve their performance, various strategies such as doping, morphology engineering, defect engineering, and phase engineering are employed for materials design and synthesis. L. Sharma et al. fabricated a nanocrystalline high entropy alloy (HEA) consisting of equiatomic Co, Fe, Ga, Ni, and Zn. The HEA shows outstanding OER activity and durability with a tailored metallic composition providing optimal surface absorption energies for catalysis, a layer of metallic oxides formed on the surface as the active components, and alloy inside contributing to the stability (Figure 1.3.9 a-e).⁵¹ A system involving transitional metal-based materials and carbon materials is preferred by researchers because carbon materials not only provide large surface areas and excellent electronic conductivity but can prevent electrocatalysts from aggregation. J. Ding et al. prepared FeNi3 alloy embedded in carbon materials for OER through the calcination of a metal-organic framework (MOF) precursor.⁵³ G. Tian et al. designed and fabricated a novel porous structure with MoNi4-MoO₂ on carbon cloth (CC) by annealing the NiMo(OH)_x/CC at 600 °C under a flow of Ar/H₂. An electrolyzer using the sample both as the anode and the cathode required only 1.49 V to achieve 10 mA cm^{\cdot 2} and could be operated for 150 h without activity degradation.⁵⁴ H. Huang et al. utilized a defective and porous CoMoO₄ as the precursor to fabricate amorphous CoMo phosphide nanosheets supported on CFP, exhibiting good HER activity in the alkaline electrolyte (η_{10} = 59 mV) (Figure 1.3.9f-i).⁵² K. Lemoine et al. obtained an amorphous MnFe oxyfluoride (MnFeF4.6Oo.2) by thermal decomposition of a new type of hydrated fluoride (MnFeF5(H2O)2) in air (Figure 1.3.10a-c). The MnFe oxyfluoride showed good stability (15 h) as the OER catalyst in acidic condition because the dissolution of Mn and Fe was effectively retarded by the unique composition and amorphous nanostructure (Figure 1.3.10d).55



Figure 1.3.10. (a) The Rietveld refinement of the XRD pattern of MnFeF₅(H₂O)₂. (b) SEM and (c) TEM images of MnFeF_{4.6}O_{0.2}. The inset of (c) is the corresponding selected area electron diffraction (SAED) image. (d) Chronopotentiometric measurements of the prepared samples at 10 mA cm⁻² in 0.5 M H₂SO₄. Reprinted with permission from ref.⁵⁵. Copyright 2021 American Chemical Society.

Metal-free electrocatalysts. Apart from metal-based catalysts, metal-free electrocatalysts especially carbon-based materials are attracting increasing attention, benefiting from their good conductivity and durability in a broad range of pH and their earth-abundance. Nanoengineering to produce more active sites is also a useful strategy for high-performance non-metal-based catalysts.^{56,57} H. Begum et al. synthesized hollow carbon nanoballs (average size: ~20 nm in diameter, sidewall thickness: ~5 nm) on graphene using polyacrylonitrile and graphene oxide through a two-step thermal treatment at 280 and 700 °C. The graphene oxide was reduced and polyacrylonitrile was calcined into a microporous carbon matrix with a high density of active sites, graphitic-N, and pyridinic-N. The product showed enhanced electrocatalytic performance with overpotentials of 217 and 108 mV at 10 mA cm⁻² for OER and HER in 1.0 M KOH, respectively.⁵⁸ Boron carbon nitride (BCN) nanosheets with the properties of twodimensional (2D) hexagonal boron nitride (h-BN) and graphene and the N and B synergistic molecular structure, creates desirable nanoplatforms for electrocatalysis.^{7,59} However the tunability of the electronic, physical, and chemical properties of BCN is limited in the 2D structure. M. A. Ahsan synthesized a 0D-2D nanohybrid using fullerenes (C₆₀) and BCN nanosheets to introduce new tunable interfacial active sites (Figure 1.3.11). C₆₀ molecules integrated on the BCN surface could distort BCN, making the electronic coupling between C₆₀ and BCN possible and allowing the formation of interfacial active sites for electrocatalysis. The loading of C₆₀ on BCN has a great influence on catalytic activity. The optimized sample C₆₀/BCN exhibited excellent performance for both HER (0.5 M H₂SO₄) and OER (0.5 M NaOH).⁶⁰ However carbon materials suffer from slow corrosion due to the high anodic potential in OER.⁵⁷ To date, precious metal-based materials (Pt-, Ir-, and Ru-) are still the best performing electrocatalysts for practical applications, especially in acidic media and for cathodic HER. The development of more efficient and stable non-noble metal-based and metal-free catalysts for HER and OER is of great importance for the widespread application of water electrolysis technology.



Figure 1.3.11. Schematic illustration of the synthesis procedure of C60/BCN (top) and TEM image of BCN and 10 wt% C60/BCN (bottom left). Reprinted with permission from ref.⁶⁰. Copyright 2021 American Chemical Society.
1.4 Prussian blue analogues and their derivatives for electrocatalytic HER and OER

1.4.1 Prussian blue and Prussian blue analogues

Porous coordination polymers (PCPs) constructed by metal cations and organic ligands are showing considerable potentials in various applications, such as catalysis, drug delivery, energy storage, gas storage and adsorption, and so on. PCPs have a wide range of compositions and morphologies with tunable physical and chemical properties. Prussian blue (PB) and Prussian blue analogues (PBAs) are well-explored PCPs with a general chemical formula of AxM[M'(CN)6]1-yyy · nH2O (where A represents alkali metal ions like Na⁺ and K⁺, M and M' correspond to different transition metals (e.g. Fe, Co, Ni, and Cu), and γ represents the [M'(CN)6] vacancy). M and M' are connected by cyanide group with M and M' atoms coordinated to six nitrogen and carbon atoms, respectively, forming a 3D framework with large voids. When M and M' both are Fe, the formula represents PB, which was the first synthetic pigment found by the paint maker Diesbach in the early 18th century. In 1936, Keggin and Miles first described the structure of PB as a cubic network constructed by $Fe^{II}-C \equiv N-Fe^{3+}$. Figure 1.4.1 illustrates the crystal structure of PB according to XRD pattern analysis.⁶¹ In general, each crystallographic unit cell with a lattice parameter of 10.2 Å consists of eight cubes, whose space can host species with an ionic radius less than 1.6 Å.⁶² The dark blue color of PB is due to the electron transfer from Fe^{II} to Fe³⁺ causing absorption of orange-red light (around 680 nm). A classical preparation method of PB is co-precipitation: an aqueous solution with hexacyanoferrate $([Fe^{II}(CN)_6]^4)$ is mixed with another aqueous solution of Fe³⁺, forming a deep blue precipitate. Insoluble PB refers to PB containing little alkali metal ions at the zeolitic sites but accommodating lots of water molecules (Figure 1.4.1a). Insoluble PB is formed when there is abundant Fe³⁺ in the solution, with a chemical formula of Fe₄³⁺ [Fe^{II}(CN)₆]₃ • nH₂O. About a quarter of the [Fe^{II}(CN)₆]⁴⁻ sites are vacant in insoluble PB. Water molecules coordinate with Fe³⁺ ions and occupy vacant sites. Therefore, there are two kinds of water molecules in the crystalline structure of insoluble PB: coordinated and non-coordinated water molecules at the zeolitic sites. As Figure 1.4.1b illustrates, PB's zeolitic sites can be occupied by alkali metal ions like K⁺ and Na⁺, which happens when there are excess $[Fe^{II}(CN)_6]^4$. It is called soluble PB as it easily forms a colloidal

solution, which can be described as AFe^{3+} [Fe^{II}(CN)6] • nH₂O. P.R. Bueno et al. pointed out that the soluble PB crystalline structure is also not perfect (Figure 1.4.1b), with almost 25% of the [Fe^{II}(CN)6]⁴⁻ absent from the framework.⁶³ The major difference between soluble PB and insoluble PB is the existence or not of alkali metal ions.



Figure 1.4.1. Illustration of the crystalline structure of (a) insoluble PB (with vacancies) and (b) perfect soluble PB. Reprinted with permission from ref.⁶¹. Copyright 2018 the Author(s).

If Fe³⁺ or/and [Fe^{II}(CN)6]⁴⁻ in solutions are replaced by other transitional metal ions or hexacyanometallates, PBA is formed with a similar crystalline structure as PB. Fe can be substituted by Ni, Co, Cu, Mn, Zn, and Cr, leading to a big family of PBAs. Advantages, including crystalline structure, simple synthesis, and numerous choices of metals, make PB and PBAs attractive PCPs. PB and PBAs have been applied as electrodes materials for batteries such as lithium, potassium, sodium, and ammonia ion batteries. PB/PBAbased sensors for Cs⁺, Tl⁺, K⁺, and Rb⁺ have been developed.^{64,65} It is also indicated that they can absorb or store water, ethanol, H₂, CO₂, NH₃, and C₂H₄.^{61,66-68} Some PB and PBAs are also applied in electrocatalytic reactions like oxygen reduction reaction and OER.⁶⁹⁻⁷² However PB and PBAs fabricated by the one-step co-precipitation method are generally less active than their derivatives. Growing efforts have been made to develop their derivatives by thermal treatment, structure design, doping, composites, etc. The following section is going to focus on the fabrication of PB and PBAs' derivatives and their applications in electrocatalytic water splitting reactions.

1.4.2 PB and PBAs derivatives as electrocatalysts for HER and OER in water electrolysis



Figure 1.4.2. PB/PBA derived nanomaterials applied in electrochemical water splitting, including the characteristics of PB and PBAs and methods towards their derivatives. Reprinted with permission from ref.⁷³. Copyright 2020 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

PB and PBAs are widely utilized as precursors to prepare non-noble metal-based electrocatalysts for HER and OER, benefiting from their porous structure, open framework, easy preparation, abundant cyanide linkers, and diverse transition metal options (like Ni, Fe, Co, Cu, and Zn). Some researchers have tried to improve the electrocatalytic activity of PBAs without changing the cubic phase. A commonly used method is by introducing defects to the PBA structure.^{74–76} For example, Y. Kang et al. developed a facile post-oxidation method using H_2O_2 solution at room temperature to prepare defective CoFe PBA (Co₃[Fe(CN)₆]₂) with more [Fe(CN)₆] vacancies and more exposed Co (III) sites. Rietveld refinement of XRD patterns shows that the lattice 22 parameter (a=10.1982 Å) of defective CoFe PBA is smaller than that of the pristine CoFe PBA (a=10.2436 Å). FESEM and TEM results indicate that post-oxidation treatment doesn't influence the morphology of CoFe PBA. DFT calculations indicate that the [Fe(CN)6] vacancy regulates the CoFe PBA's electronic structure and reduces the reaction barrier of the rate-determining step (from *OOH to *O) in the OER process. The defective CoFe PBA requires an overpotential of 400 mV at 10 mA cm⁻², 50 mV lower than pristine CoFe PBA in 1 M KOH.⁷⁶ Z. Yu et al. found that N₂ plasma could break Fe-C and Ni-N bonds in Fe-CN-Ni units, leading to the formation of CN vacancies and exposed Fe and Ni sites in the NiFe PBA structure (VCN-NiFe PBA) (Figure 1.4.3 a). The VCN-NiFe PBA treated by N₂ plasma showed the best OER performance, requiring a low overpotential of 283 mV to reach 10 mA cm⁻² in 1 M KOH, which was comparable with NiFe layered double hydroxide (NiFe-LDH). Electrochemical tests show that VCN-NiFe PBA has a smaller Tafel slope (54 mV dec⁻¹), a smaller charge transfer resistance (11 Ohms), and a higher electrochemical surface area (214 μ F cm⁻²) than untreated NiFe PBA and NiFe-LDH, indicating an excellent OER activity of the VCN-NiFe PBA. The enhanced OER performance of VCN-NiFe PBA is due to the following reasons: 1) CN vacancies modulate oxidation states of Ni and Fe, where Ni²⁺ is partially boosted to Ni³⁺, and Fe³⁺ is reduced to Fe²⁺ by accepting the electron from adjacent Ni sites. These sites are transformed into an active NiFeOOH layer during OER (Figure 1.4.3b).2) The unsaturated Fe sites around the CN vacancies tend to bond with oxygen, suppressing the leaching of Fe atoms during OER. The pristine NiFe PBA suffers from anion exchange between [Fe(CN)6]⁴ and OH. leading to heavy loss of Fe.75



Figure 1.4.3. (a) Schematic illustration of the formation of CN vacancies in NiFe PBA (V_{CN}-NiFe PBA) framework by N₂ plasma. (b) Illustrations of the surface reconstruction on the NiFe PBA and V_{CN}-NiFe PBA during the OER process. Reprinted with permission from ref.⁷⁵. Open access.

Besides keeping the crystalline phase of PBAs, a large number of derivatives of PB and PBAs with different morphologies, phases, and compositions and thus enhanced electrocatalytic performance have been fabricated. PBAs can be easily grown, carved, and transformed by various engineering strategies such as etching, annealing, introducing supports, and template methods. For example, L. Han et al. etched NiCo PBA nanocubes with ammonia solution to obtain NiCo PBA nanocages (Figure 1.4.4).⁷⁷ TEM images in Figure 1.4.4e indicate that etching on NiCo PBA cubes is inhomogeneous, which starts on

the corners and extends along the body diagonal direction, finally leading to hollowed cubes with pyramid-like walls (6 h). This is due to the higher surface energy of corners and more defects in cubes' interior than walls. NiCo hollow nanocages showed the same XRD pattern and SAED pattern as their precursor. A subsequent annealing treatment at 350 °C in air was used to further convert it into NiCo oxides (NiO and NiCo₂O₄). NiCo oxides nanocages exhibited better OER performance (η_{10} , OER = 0.38 V) than NiCo oxides nanocubes derived from NiCo PBA nanocubes (η_{10} OER = 0.43 V) in 1.0 M NaOH at room temperature.⁷⁷ Another similar etching method with hot urea solution (100 °C) was used by Y.B. Lian et al. to fabricate CoFe PBA nanoframes.⁷⁸ Planes were preferentially etched, due to urea coordination at the edges and corners locally slowing down the etching by ammonia ions. CoFe PBA nanoframes were further transformed into CoFe phosphide (CoFeP) nanoframes by phosphidation at 300 °C (Figure 1.4.5a-d). CoFeP exhibited good performance towards both HER and OER in alkaline condition (η_{10} , HER = 0.133 V, η_{10} , OER = 0.298 V). The electrolysis cell using CoFeP as both the anode and cathode required a lower cell voltage of 1.57 V for 10 mA cm⁻², comparable with the cell using Pt/C based cathode and RuO₂ based anode (1.52 V) (Figure 1.4.5e).⁷⁸



Figure 1.4.4. TEM images exhibiting the evolution of NiCo PBA morphology after etching with ammonia for 0 (a), 0.5 (b), 2 (c), and 6 h (d) at room temperature. (e) Schematic illustration of the

evolution of NiCo PBA's etching, corresponding to TEM results. Reprinted with permission from ref.⁷⁷. Copyright 2016 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.



Figure 1.4.5. (a) Schematic illustration of the fabrication procedure of the carved CoFeP nanoframes. SEM images of CoFe PBA (b), etched CoFe PBA nanoframes (c), and CoFeP nanoframes (d). Performance for the overall water splitting in 1.0 M KOH. (e) Polarization curves and (f) amperometric *i*-t curve of the electrolysis cell. Inset of (e): photo of the two-electrode electrolysis cell. Inset of (f): Polarization curves of CoFeP for HER and OER including the curves of 1st, 1000th, and 5000th. Reprinted with permission from ref.⁷⁸. Open access.

In addition to carving the nanocube to create a higher specific surface area and more accessible active sites for electrocatalysis, the etching of PBA cube also happens when it 26

is utilized to create a template for growing functional nanomaterials. X.Y. Yu et al. used ammonium thiomolybdate dissolved in N, N-dimethylformamide to react with NiCo PBA at 210 °C for 20 h, resulting in the Ni and Co incorporated MoS₂(NiCo-MoS₂) nanoboxes. The structural formation process of nanoboxes was investigated by observing the sample's morphology after different reaction durations (Figure 1.4.6). Etching of the nanocube started from the corners, extended along the diagonal direction (6 h), and finished after the nanocube became hollow (20 h). During the process, thin nanosheets grew larger, forming the shell of the nanobox, while Ni and Co atoms could intercalate into MoS2 interlayers, leading to the formation of NiCo-MoS₂ nanoboxes. The obtained NiCo-MoS₂ nanoboxes were employed as the electrocatalyst of HER in 0.5 M H₂SO₄, requiring an overpotential of 155 mV at 10 mA cm⁻² which was 30 mV smaller than bare MoS₂ and better than most MoS₂-based electrocatalysts. The excellent performance is attributed to a high surface area of MoS₂ nanosheets on the hollow nanobox structure inherited from NiCo PBA nanocube, as well as the modulation of the MoS2 electronic structure by Ni and Co.79 Y. Guo et al. fabricated a core-shell and hollow Co3S4@MoS2 heterostructure based on CoFe PBA nanocubes, combining the good OER activity of Co₃S₄ and HER activity of MoS_{2.80} F. Wang et al. synthesized an excellent OER electrocatalyst based on Fe-Ni sulfide porous nanosheets obtained by chemical etching of NiFe PBA on Ni(OH)2 sheets with hot Na₂S solution at 100 °C for 10 h. It only required an overpotential of 238 mV to deliver 10 mA cm⁻², with negligible degradation in a stability test of 24 h.⁸¹



Figure 1.4.6. SEM and TEM images of NiCo PBA collected after reacting with ammonium thiomolybdate for 1 h (a,e), 6 h (b, f), 12 h(c, g), and 20 h (d,h). (i-l) illustration of the formation process of NiCo-MoS₂nanoboxes from NiCo PBA cube. Reprinted with permission from ref.⁷⁹. Copyright 2016 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

Growing active electrocatalysts on conductive and porous substrates minimizes the electronic resistance of the electrode. Meanwhile, a rational design of the nanostructure can expose more active sites and improve the utilization of active materials. For example, L.M. Cao et al. and S. Lei et al. successfully grew CoFe PBA on the surface of Ni foam with different morphologies by slightly modifying the precipitation method. The precursors on Ni foam were then transformed into Fe-CoP and CoFe₂O₄ by annealing in Ar together with NaH₂PO₂ and in air, respectively.^{82,83} However, SEM images show that CoFe PBAs directly growing on Ni foam either aggregate and stack (Figure 1.4.7 a), or form a thin layer (Figure 1.4.7 b). Not all the surface of the active materials can be in contact with electrolyte in the former example, while the surface area of the sample is not high in the latter example. In order to overcome these disadvantages, a new two-step strategy (Figure 1.4.7c and e) to grow PBA on the template/conductive substrates is proposed to obtain a hierarchical structure.⁸⁴⁻⁸⁹ The template could be metal hydroxide,

metal oxide, metal phosphate, and metal-organic framework. PBA cubes can grow tightly on templates by using metal ions released from these templates, forming hierarchical morphology as shown in Figures 1.4.7d and f.



Figure 1.4.7. (a) SEM image of stacked CoFe PBA growing on Ni foam. Reprinted with permission from ref.⁸². Open access. (b) SEM image of oriented CoFe PBA thin film on Ni foam. Reprinted with permission from ref.⁸³. Copyright 2018 Elsevier B.V. (c) Schematic illustration of the fabrication procedure of oxygen-doped NiFe phosphide nanocubes array on Ni₂P sheets on Ni foam derived from NiFe PBA nanocubes on Ni(OH)₂ sheets on Ni foam (NiFe PBA@Ni(OH)₂@NF). (d) SEM image of NiFe PBA@Ni(OH)₂@NF. (c,d) are reprinted with permission from ref.⁸⁴. Copyright 2018

WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. (e) Schematic illustration of the fabrication procedure of Ni₂P/Fe₂P on Ni foam derived from NiFe PBA growing on metal-organic framework-Ni (MOF-Ni) on Ni foam (NiFe PBA@MOF-Ni@NF). (f) SEM image of NiFe PBA@MOF-Ni@NF. (e, f) are reprinted with permission from ref.⁸⁹. Copyright 2020 American Chemical Society.

In this Ph.D. project, NiFe PBA and CoFe PBA were utilized to fabricate NiFeP and CoFe PBA derivatives, respectively, for better electrocatalytic OER and HER in alkaline conditions.

1.5 Water electrolyzers for hydrogen production

Based on the electrolyte, membrane, and operation temperature, four main kinds of water-splitting electrolyzers exist: alkaline electrolyzer, anion exchange membrane (AEM) electrolyzer, proton exchange membrane (PEM) electrolyzer, and solid oxide electrolysis cell (SOEC) (Figure 1.5.1).⁹⁰ The characteristics of these four types of electrolyzers are summarized in Table 2.

Alkaline electrolyzer has a design composed of the anode and cathode electrodes (mainly Ni-based materials), a highly concentrated alkaline aqueous electrolyte (usually 20-30 wt% KOH solution), and a robust ZrO₂ based diaphragm as illustrated in Figure 1.5.1. The ionic charge carrier is OH, and OH and water molecules participate in electrochemical functions. The porous diaphragm allows ions and water to pass through it. It can separate the produced gas products, but cannot prevent the intermixing of the dissolved gases (H₂ and O₂) in the electrolyte, causing a degraded overall performance, limited operation at higher pressure levels, and serious safety issues.⁹⁰ The current density of the commercial alkaline electrolyzer is around 100 to 400 mA cm⁻². The working temperature is around 60-80 °C. The electrodes of alkaline electrolyzers with an area of about 3 m² are low-cost nickel or nickel-coated stainless-steel plates, making them easy for commercial manufacture. Despite its disadvantages like low efficiency and low operating pressure, alkaline electrolyzers are the most commonly used commercial electrolyzers, with a long service lifetime of 60000-10000 hours and a low capital cost (€ 800 -1000/kW).⁹¹ Nowadays, advanced designs, including the "zero-gap" alkaline electrolyzer reducing the ohmic resistance to improve the efficiency^{92,93} and the decoupled alkaline electrolyzer separating the HER and OER spatially and temporally by coupling



an intermediate redox mediator to avoid gas crossover⁹⁴, make alkaline electrolyzers still competitive.

Figure 1.5.1. Schematic illustration of the alkaline, AEM, PEM, and solid oxide electrolyzer. Reprinted with permission from ref.⁹⁰. Copyright 2020 IRENA - International Renewable Energy Agency.

Proton-exchange membrane (PEM) electrolyzer is also commercially available (Figure 1.5.2). A PEM electrolyzer consists of numerous parts such as the acidic media, the PEM, catalysts layers, current collectors, and bipolar plates. The cathodic

catalyst layer consisting of Pt/C and Nafion ionomer and the anodic catalyst layer made up of IrO2 and Nafion ionomer are respectively coated onto each side of the PEM (Nafion 117 membrane).95 During the electrocatalytic water splitting, water is pumped to the anode where it loses electrons and produces O_2 and protons (H⁺). Then these protons are transported through the PEM to the cathode to combine with electrons, which pass through the external power circuit to move from the anode to the cathode side, to form H₂ (Figure 1.5.1). The PEM electrolyzer operates at a low temperature (50-80 °C) similar to the alkaline electrolyzer, where water is liquid. A thin and robust polytetrafluoroethylene sulfonated (PFSA) membrane can improve the efficiency and allow the PEM electrolyzer to operate at a higher pressure (≤ 70 bar for the H₂ side). Gas crossover can also occur in PEM electrolyzers, but to a lesser extent than the alkaline electrolyzer. The acidic environment, high voltages, and oxygen dissolved in the liquid together create a harsh and oxidative environment, which can corrode current collectors, degrade the performance of electrocatalysts, and reduce cell efficiency. Electrode areas of the PEM electrolyzer can approach 2000 cm², which is still far from the requirement of large MW stack units.⁹⁰ Because of the use of noble metal catalysts, the expensive polymeric membrane, and expensive current collectors (e.g. porous titanium), the capital investment cost for PEM electrolyzers is around €1400-2100 kW^{-1,91} Despite the disadvantages mentioned above, PEM electrolyzers have several advantages over alkaline electrolyzers such as the compact system design, higher purity of hydrogen, easier hydrogen compression, and a wide range of operating power inputs. At present, undergoing research is focusing on i) developing efficient non-noble metal electrocatalysts to reduce the cost and ii) fabricating more robust PEMs to increase the operating temperature and service lifetime.⁹⁶



Figure 1.5.2. Main components of a typical PEM electrolyzer. Reprinted with permission from ref. ⁹⁵. Copyright 2013 Hydrogen Energy Publications, LLC. Published by Elsevier Ltd.

Anion exchange membrane (AEM) electrolyzer is developed to combine the advantages of the alkaline electrolyzer and PEM electrolyzer and to overcome their drawbacks. An AEM electrolyzer with a similar configuration to the PEM electrolyzer utilizes an AEM to replace PEM. It needs alkaline electrolytes with low concentration to serve as the charge carrier (OH⁻). AEMs and ionomers are fundamental components of AEM electrolyzers. However, anion exchange polymers suffer from limited stability at high temperature (> 60 °C) in concentrated alkaline solution (> 1 M KOH) and a low OH⁻ conductivity.⁹⁷ Well-designed and cheap non-precious electrocatalyts (HER catalysts like Ni, NiFeCo, Ni-Mo alloy, OER catalysts like NiFe oxide, CuCo oxide, NiFe, and NiAl)⁹⁸ perform better in AEM electrolyzers than in PEM electrolyzers, where the working environment is too harsh for these electrocatalysts. However, electrocatalysts for commercial application are still under exploration. In summary, lots of difficulties need to be solved before bringing AEM electrolyzer into commercialization.⁹⁹

Table 2. Summary of characteristics of the alkaline, AEM, PEM, and solid oxide electrolyzers.Reprinted with permission from ref.⁹⁰. Copyright 2020 IRENA - International Renewable EnergyAgency.

| | Alkaline | PEM | AEM | Solid Oxide |
|---|--|--|---|-------------------------------------|
| Operating temperature | 70-90 °C | 50-80 °C | 40-60 °C | 700-850 °C |
| Operating pressure | 1-30 bar | < 70 bar | < 35 bar | 1 bar |
| Electrolyte | Potassium hydroxide (KOH) 5-7 molL ⁻¹ | PFSA membranes | DVB polymer support with | Yttria-stabilized Zirconia (YSZ) |
| | | | KOH or NaHCO3 1molL ⁻¹ | |
| Separator | ZrO ₂ stabilized with PPS mesh | Solid electrolyte (above) | Solid electrolyte (above) | Solid electrolyte (above) |
| Electrode / catalyst (oxygen side) | Nickel coated perforated stainless steel | Iridium oxide | High surface area Nickel or NiFeCo alloys | Perovskite-type (e.g. LSCF, LSM) |
| Electrode / catalyst (hydrogen side) | Nickel coated perforated stainless steel | Platinum nanoparticles on carbon black | High surface area nickel | Ni/YSZ |
| Porous transport layer anode | Nickel mesh (not always present) | Platinum coated sintered porous titanium | Nickel foam | Coarse Nickel-mesh or foam |
| Porous transport layer cathode | Nickel mesh | Sintered porous titanium or carbon cloth | Nickel foam or carbon Cloth | None |
| Bipolar plate anode | Nickel-coated stainless steel | Platinum-coated titanium | Nickel-coated stainless steel | None |
| Bipolar plate cathode | Nickel-coated stainless steel | Gold-coated titanium | Nickel-coated Stainless steel | Cobalt-coated stainless steel |
| Frames and sealing | PSU, PTFE, EPDM | PTFE, PSU, ETFE | PTFE, Silicon | Ceramic glass |

Note: Coloured cells represent conditions or components with significant variation among different companies. PFSA = Perfluoroacidsulfonic; PTFE = Polytetrafluoroethylene; ETFE = Ethylene Tetrafluorethylene; PSF = poly (bisphenol-A sulfone); PSU = Polysulfone; YSZ = yttriastabilized zirconia; DVB = divinylbenzene; PPS = Polyphenylene sulphide; LSCF = La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O₃- δ ; LSM = (La_{1.4}Sr₂)_{1.9}MnO₃; \$ = Crofer22APU with co-containing protective coating. Based on IRENA analysis.

Solid oxide electrolysis cell (SOEC) has been intensively developed over the past decades. Typically, an SOEC is made up of two electrodes and the solid electrolyte illustrated in Figure 1.5.1. Figure 1.5.3b displays an SEM image of the detailed cross-section of an SOEC. The electrolyte is a dense ceramic membrane usually made of yttria-stabilized zirconia (YSZ) containing and conducting ions (O²⁻) for the water electrolysis process.¹⁰⁰ A thinner electrolyte generally has higher ionic conductivity, lowering the SOEC's ohmic resistance. The commonly used cathode material (hydrogen electrode) is a porous Ni-YSZ (Ni: YSZ= 40 vol.%: 60 vol.%, YSZ: Zr0.84Y0.16O1.92), with similar composition



as the cell support (Ni: YSZ= 40 vol.%: 60 vol.%, YSZ: Zr0.94Y0.06O1.92) but finer structure and lower porosity.

Figure 1.5.3. (a) Configuration of SOEC stack with heat exchangers and base manifold unit. Reprinted with permission from ref.¹⁰¹. (b) Color-overlaid SEM image of the cross-section of an SOEC with reactions occurring on electrodes during water electrolysis (Ni-YSZ: nickel-yttria stabilized zirconia, CGO: gadolinia-doped ceria, (Gd, Ce)O₂, LSC: strontium-doped lanthanum cobaltite). Adapted with permission from ref.¹⁰⁰. Open access.

Strontium-doped lanthanum cobaltite (LSC) is a common oxygen electrode material. It is a conductor for both O²⁻ and electrons at the SOEC working temperature (\geq 750 °C). A reaction barrier (gadolinia-doped ceria, CGO) is placed between the oxygen electrode and the electrolyte to prevent the cross-reaction of LSC and YSZ at sintering temperature.¹⁰⁰ The oxygen electrode is the composite of LSC and CGO. Single flat-plate cells (quantity: 30 to 100) are assembled in series into a stack (Figure 1.5.3a). Stacks will be built into modules and work in systems, providing a desired hydrogen production rate. The SOEC operates at a much higher temperature (700-850 °C) than the alkaline, PEM, and AEM electrolyzers, because ceramic materials require high temperature significantly favors the water splitting from thermodynamics and kinetics, meaning the SOEC can attain a higher current density at a low operating potential (SOEC: 1.29 V, 1.5 A cm⁻² ¹⁰⁰, PEM: 1.47 V, 0.5 A cm⁻², reported by ref.¹⁰²), which drastically increases the efficiency of energy conversion (up to 95%).^{103,104} Although the SOEC has advantages in abundant raw materials, its practical application faces challenges regarding to durability, scale-up, and capital cost.^{103,105}

In this Ph.D. project, the synthesized samples were assembled into a single-cell alkaline electrolyzer and AEM electrolyzer for further evaluation of their performance in DTU energy.

1.6 Conclusions

Water electrolysis is an important technology to produce green hydrogen using electricity from renewable energy. Two basic electrochemical reactions (HER and OER) are involved in different types of electrolyzers. Efficient electrocatalysts are required to minimize the working overpotentials, thus reducing the cost of green hydrogen. In this chapter, various electrocatalysts and synthesis methodologies are summarized. Especially, PBAs with diverse transition metal atoms and porous structures are easy to synthesize and can be transformed into active electrocatalysts like alloys, oxides, phosphides, nitrides, and sulfides, holding the promise for efficient HER and OER. This Ph.D. project aims to fabricate PBA derivative—based electrocatalysts with excellent activity and stability by morphology engineering and composition tuning.

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Chapter 2 Methodology

A brief description of techniques used for material morphology, structure, and performance characterization is given in this chapter. It covers microscopic and spectroscopic techniques for understanding morphology and structure, nitrogen absorption-desorption isotherm analysis for specific surface area, and electrochemical methods for performance evaluation.

2.1 Microscopic techniques

Two typical electron microscopes including the scanning electron microscope and transmission electron microscope are used in this thesis. The electron microscope uses a beam of accelerated electrons as the source of illumination and uses magnetic lenses to focus electrons, leading to a much higher resolution than the optical microscope. This is because the limit of resolution is directly related to the wavelength of the light source. Electron microscopes (EMs) are very useful tools in the study of material morphology, structure, and chemical composition.

2.1.1 Scanning electron microscope

Scanning electron microscope (SEM) is a widely used type of EMs. An SEM produces the image of a sample by scanning the surface with a focused beam of electrons, which interact with atoms of the sample to produce various signals containing information about the sample's surface topography and composition. An SEM generally consists of the electron column, specimen chamber, pumping system, and computerized control system as illustrated in Figure 2.1.1. An electron gun at the topmost of the electron column generates an electron beam. The beam is focused into a small diameter probe (a few nanometers) by electromagnetic lenses. The scanning coils located within the bore of the objective lens are two sets of deflection electromagnetic coils and connect to a scan generator that creates the raster on the specimen, enabling the beam to sweep across the area of interest on a specimen. The focused electron beam could penetrate a depth of a

few microns into a specimen, generating various signals like secondary and backscattered electrons and characteristic X-rays (Figure 2.1.2).



Figure 2.1.1. Schematic diagram of an SEM. Reprinted with permission from ref. ¹. Copyright Springer Nature Switzerland AG 2018.

The penetration depth and the shape of the interaction volume largely depend on the applied accelerating voltage and the average atomic number of the specimen. Detectors in the specimen chamber collect these signals and interpret them into information related to the topography and composition of the specimen. An SEM usually requires a high vacuum in the electron column and specimen chamber to ensure the lifetime of the filament and other units and the good resolution of the acquired images.¹ In this Ph.D. project, an AFEG 250 analytical ESEM was used for the morphology characterization of synthesized samples. Sample preparation for SEM is also important for obtaining clear images. Prior to the sample's preparation, it is necessary to consider properties of the sample such as size, shape, conductivity, and state under the electron beam. The sample must be totally dry before putting into the specimen chamber. Non-conductive samples 48

can be coated with a thin layer of gold (~5 nm).² In this project, powdery samples or small pieces of samples are involved, which can be fixed on aluminum stubs with conductive adhesive tape (like carbon, Al, or Cu tape).



Figure 2.1.2. Various signals resulting from the interaction of the electron beam with the specimen. Reprinted with permission from ref. ³. Open access.

2.1.2 Transmission electron microscope

The transmission electron microscope (TEM) uses a beam of electrons to generate a highly magnified image of the specimen. The basic principle for TEM is similar to that of an optical microscope. The resolution of the optical microscope is limited by the wavelength of the light according to the Abbe theory ($d = 0.61\lambda$ /N, where λ is a wavelength and N is a numerical aperture). Electrons behave as both particles and waves and have a wave property with very short wavelengths that depend on their kinetic energy. This laid the foundation for the development of TEM with high resolution. In 1931, Ruska and Knoll successfully developed the first TEM, whose resolution was only 50 nm. Now it has been improved to 50 pm by using a spherical aberration corrector.⁴ A modern TEM typically comprises four main components: an electron optical column, a vacuum system, the necessary electronics, and control software. Electrons are easily deflected or stopped by 49

matters, requiring to be manipulated in vacuum. Therefore, the whole column from the electron gun to the camera needs to be evacuated. Also, to avoid evacuating the whole column every time a specimen or a filament is changed, several airlocks and separation valves are built in between them. Figure 2.1.3 illustrates the typical construction of the electron optical column in a TEM including the electron source, magnetic lenses, and the detector.⁵ The electron gun produces the electron beam, and the condenser system focuses the beam before it passes through the objective. The image-producing system, consisting of the objective lens, the specimen stage, intermediate lens, and projector lenses, focuses the electrons passing through the specimen to form a highly magnified image. Finally, the image-recording system makes the electron image visible on a fluorescent screen or records the image by a charge-coupled device (CCD) camera. The bright-field mode for imaging is mainly used in this project, where the scattered electrons are blocked, the unscattered electrons are selected by the objective aperture, and the areas with the sample will appear darker (Figure 2.1.4a). Under the dark-field mode, the unscattered electrons are blocked and the areas with the sample are brighter (Figure 2.1.4b).⁶ TEM can not only provide an image of the specimen, but also diffraction patterns by removing the objective aperture and inserting a selected area electron diffraction (SAED) aperture to analyze the crystal structure of the specimen as Figure 2.1.4c shows. The specimen for TEM should be thin enough (< 200 nm) to permit the transmission of sufficient electrons to form an image with minimum energy loss. For materials growing on Ni foam and nanoparticles synthesized in this project, they are dispersed in ethanol by sonication, then dropped onto TEM grids (Lacey carbon, 300 mesh, copper grid, purchased from TED PELLA, INC.), and dried in air before TEM tests. In this Ph.D. project, a Tecnai T20 G2 (200 kV) was used for the structure and composition characterization of the synthesized samples.



Figure 2.1.3. Schematic diagram of a TEM. Reprinted with permission from ref. ⁵. Copyright 1994 Elsevier Masson SAS.



(a) bright-field image (b) dark-field image (c) electron diffraction
 Figure 2.1.4. Electron beam paths for different modes of TEM. Reprinted with permission from ref.⁷. Copyright 2019 Springer Nature Singapore Pte Ltd.

2.2 Spectroscopic techniques

Spectroscopic techniques employ different forms of electromagnetic radiation (including infrared, near-infrared, ultraviolet-visible, and X-ray) to interact with matters and thus probe certain features of them by analysis of the interaction between matter and radiation. These techniques are widely applied in chemistry, materials science, biology, and physics to understand the composition, crystal structure, and electronic structure of materials.

2.2.1 Powder X-ray diffraction

Crystal structure characterization is significant to the development of new materials because materials' crystal structure determines their properties. Powder X-ray diffraction (XRD) is the most commonly used tool for determining crystal structure. German physicist Max von Laue first proposed the XRD technique in 1912. In 1913, William Henry Bragg and William Lawrence analyzed the crystal structures of NaCl and other simple

compounds by XRD. A few years later, this method was applied to determine the crystal structures of more complex inorganic compounds.⁸ Nowadays, XRD has become a rapid and non-destructive technique for structural analysis of crystalline materials, which can identify crystalline phases, determine atomic arrangement, and determine structural properties such as lattice parameters, strain, grain size, and epitaxy.^{8–11} XRD is based on constructive interference of monochromatic X-rays and a crystalline sample. Assuming that the crystal with periodically spaced atoms arranged regularly in three dimensions, behaving as a diffraction grating for X-rays, constructive interference can occur when the optical path difference of the different diffracted beams is equal to an integer multiple of wavelength λ (n λ), leading to the deduction of Bragg's law (Figure 2.2.1). It implies that the scattering intensity for a crystal is only along with a few defined directions which comply with Bragg's law: n $\lambda = 2d_{hklsin}\Theta_{hkl}$, where λ is the X-ray wavelength, dhkl is the distance between successive and parallel crystallographic planes defined by the Miller indices h k l, and θ is the angle between the direction of the incident beam and the crystallographic plane.^{12,13}



Figure 2.2.1. Scheme for the condition of Bragg's law.¹²

A typical X-ray diffractometer comprises three important components: X-ray source, the sample holder, and the X-ray detector. X-rays are generated by using accelerated electrons to bombard a target material (Cu, Fe, Mo, or Cr) in the X-ray tube to produce a series of characteristic X-rays as well as Bremsstrahlung X-rays. Then, these X-rays are

filtered, collimated, and directed to the sample. As the sample is rotated, the intensity of the diffracted X-rays is recorded. When Bragg's law is satisfied, an intensity peak occurs. The X-ray detector records and processes the signal.¹⁴ Powder XRD patterns reported in this thesis were collected with a Huber G670 powder diffractometer (Figure 2.2.2) in the 2θ range of 3 to 100° in steps of 0.005° using Cu Ka1 radiation ($\lambda = 1.54056$ Å) with 40 kV and 40 mA. Data were collected in transmission mode from a rotating flat plate sample inclined 45° relative to the primary beam.



Figure 2.2.2. Digital photo of the Huber G670 powder diffractometer used in this thesis.

2.2.2 X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS), also known as electron spectroscopy for chemical analysis (ESCA), is a heavily used surface analysis technique for compositional and chemical state analysis. The photoelectric effect of XPS was discovered by Hertz in 1887 and was theoretically explained by Einstein until 1905. In the mid-1960s, it was applied to surface analysis by K. Siegbahn and his group. XPS is a kind of photoemission spectroscope, where photoelectrons are emitted by irradiating a sample's surface with an X-ray beam (Figure 2.2.3a, c). The relationship between kinetic energy (EK) of the emitted electron, electron binding energy (EB), and the X-ray energy (*hv*) follows the equation: EB = $hv - E\kappa - \Phi$, where Φ is the work function of the instrument (Figure 2.2.3b).¹⁵ Therefore, by counting ejected electrons over a range of electron kinetic energies, the XPS spectrum

is recorded. The energies and intensities of the photoelectron peaks enable the identification and quantification of all surface elements (except hydrogen and helium).¹⁶ Depending on the outer valence configuration of the element, the photoelectrons could be emitted from the core level. XPS can analyze a sample to a depth of 1 to 10 nm because only the emitted electrons successfully escaping from the solid sample can be detected. XPS requires ultrahigh vacuum conditions (P < 10^{-7} Pa) to make sure that most photoelectrons can reach the detector. XPS can be used to analyze various materials including metals, semiconductors, polymers, bio-materials, and many others. In this Ph.D. thesis, XPS data were collected on the Thermo Scientific K-Alpha XPS spectrometer and Thermofisher Scientific Nexsa XPS spectrometer and were analyzed by the Thermo Avantage software.



Figure 2.2.3. (a) Schematic of the photoelectron's emission with X-rays. (b) Energy-level diagram of the sample and the spectrometer for core-level photoemission. (c) Schematic illustration of the
XPS spectrometer. Top left of (c): A typical photon flux curve. Reprinted with permission from ref.¹⁶. Copyright 2015 Springer-Verlag Berlin Heidelberg.

2.2.3 Fourier transform infrared spectroscopy

Infrared (IR) spectroscopy is a technique used for the identification and structural analysis of chemical compounds by measuring how much light the sample absorbs at each wavelength. Peaks on the IR spectrum represent the excitation of vibrational modes of chemical bonds or functional groups. Thus, IR spectra show a "fingerprint" feature and are powerful in the characterization of samples in chemistry, materials, biology, and food research fields.¹⁷ During measurement, a monochromator generates infrared radiation with a narrow frequency range, passing through the sample. The change of the radiation intensity relative to the background at each frequency is subsequently measured, leading to a slow process to scan the entire IR region. Fourier-transform infrared (FT-IR) spectroscopy solves this problem by introducing a Michelson interferometer and using the Fourier transform. IR radiations from all wavelengths are allowed to be measured simultaneously. An interference wave is produced in the Michelson interferometer (Figure 2.2.4). A computer will control the interferometer, collect and store detected data, and perform the Fourier transformation and further spectroscopic operations.^{18,19} FT-IR spectroscopy shows a high signal-to-noise ratio, multiplex advantage, and high throughput, making it also suitable for quantitative analysis.¹⁹ In this Ph.D. project, FT-IR spectra were all collected on a Bruker Alpha-P FT-IR spectrophotometer.



Figure 2.2.4. Scheme of the FT-IR spectrophotometer. Reprinted with permission from ref.²⁰. Open access.

2.2.4 Raman spectroscopy

Raman scattering, which is a phenomenon discovered by C.V. Raman in 1928, originates from the inelastic collisions between molecules and photons. The monochromatic light beam, usually from a laser, is illuminated on a sample, and only a minor fraction $(10^{-5} - 10^{-6})$ of the light beam undergoes Raman scattering with some chemical bonds or structures within the sample such as C-C, C=C, radial breathing mode of single-walled carbon nanotubes, and pyrrole ring. In the Raman scattering process, the molecule can be excited to a higher virtual energy state and immediately returns to a different vibrational state from its beginning state by re-emitting a photon, leading to scattered light. The vibrational quantum energy is either added to the photon energy (Anti-Stokes process) or gained by the molecule (Stokes process) for Raman scattering (Figure 2.2.5).^{21,22} The difference between the energy of the incident photon and the scattered photon is called the Raman shift. It is typically reported in wavenumbers (cm⁻¹) by the following equation:

$$\Delta \tilde{v} = \frac{1}{\lambda 0} - \frac{1}{\lambda 1},$$

where λo represents the excitation wavelength, and λi is the wavelength of the Raman spectrum. The intensity of the Raman effect is related to the change of the molecular polarizability with respect to vibrational coordination. However, the strength of the IR effect is determined by the derivative of the dipole moment. Therefore, a given vibration may be observable by Raman spectroscopy and not by IR, and vice visa.²¹ These two methods are regarded as complementary methods to understand molecular structure. In this Ph.D. thesis, all reported Raman spectra were obtained by the collaborators Hainer Wackerbarth and Georgios Ctistis in Institut für Nanophotonik Göttingen e.V., Department of Photonic Sensor Technology on a Horiba XploRa Plus confocal Raman microscope 606 (excitation wavelength: 532 nm).



Figure 2.2.5. Jablonski diagram displaying Rayleigh scattering (a), Stokes (b), and Anti-Stokes (c) Raman scattering. Reprinted with permission from ref.²². Open access.

2.2.5 Energy dispersive X-ray spectroscopy

Energy dispersive X-ray spectroscopy (EDS or EDX) is a useful technique for elemental composition qualitative and quantitative analysis. The fundamental principle of EDS is that the electron beam can eject electrons from the core shell of an atom on the sample's surface. Then, the left hole on the core shell will be filled in by an outer and higher energy electron, and this process will release energy as it relaxes (X-ray). The energy released during this relaxation process is unique to each element. Therefore, it can be used to identify the elements in samples, as well as the proportion of these elements.^{23,24} An EDS detector is typically equipped on an electron microscope, such as SEM and TEM. In this Ph.D. thesis, all presented EDS spectra were collected by the EDS system associated with the SEM and TEM. However, there exist some drawbacks of EDS. It is not a particularly sensitive technique. If an element's concentration in a sample is too low, the proportion measured by EDS is not accurate. EDS cannot detect elements with a low atomic number such as H, He, Li, and Be. Besides this, the X-rays are emitted from a region about 1- 2 microns deep, and EDS should be considered as a surface analysis technique when applied to analyze bulk samples.

2.3 Thermal gravimetric analysis

Thermal gravimetric analysis (TGA) is a thermal analysis method in which the mass of a sample is monitored during a defined temperature ramping process. Therefore, mass, temperature, and time are the basic parameters in TGA. The main part of a thermal gravimetric analyzer is a sample pan supported by a precision balance, which is located in a furnace and will be heated and cooled with programmable temperature control.²⁵ The temperature is generally increased at a constant rate. The thermal reaction can occur under a variety of atmospheres such as air, O₂, N₂, and Ar, and different pressure conditions such as constant pressure or high vacuum. TGA is widely used in different areas of materials study, for example, the thermal stability of polymers, combustion of carbon materials, and oxidation of metals and alloys. In this Ph.D., TGA was measured with a Mettler Toledo Thermogravimetric Analyzer/Differential Scanning Calorimeter (TGA/DSC) 1 to explore the stability of CoFe PBA and its derivatives.

2.4 Electrochemical methods

To explore the electrochemical and catalytic performance of the synthesized materials, different electrochemical analysis methods were utilized. These tests reported in this thesis were performed with either an Autolab PGSTAT12 (Metrohm Autolab, the Netherlands), a CHI 760C electrochemical workstation (CH Instruments, Inc. USA), or a PalmSens3 compact 616 electrochemical interface (PalmSens BV, the Netherlands).

2.4.1 Cyclic voltammetry

Cyclic voltammetry (CV) is a powerful and popular electrochemical method, which is commonly employed to study the electron transfer process of electrode materials or molecules in the electrolyte. It is also invaluable to investigate the reduction and oxidation process, reversibility of reactions, electron transfer kinetics, electrode capacitance, electrochemical active surface area, and stability of materials, and to determine the concentration of molecules. In the cyclic voltammogram, the x-axis represents the applied potential (E, V), while the y-axis is the resulting current or current density (j, mA cm⁻²). There are two conventions to display CV data: the IUPAC convention, used in this thesis, and the US convention. The IUPAC convention exhibits the negative potential to the left and the positive potential to the right of the x-axis. However, the US convention displays the potential of the CV curve inversely. An arrow can be used to indicate the sweep direction of the voltammogram.²⁶ Another crucial parameter is the scan rate $(v, \text{ mV s}^{-1})$, indicating the speed at which the potential is linearly varying. During the CV test, the potential is swept with a defined scan rate from the starting potential (E1) negatively or positively to the switching potential (E2). Then the scan direction is reversed and the potential is swept back to E1 (E1 is another switching potential in this example, and it is possible to start from any potential between the defined potential range) (Figure 2.4.1a and Figure 2.4.2a). This cycle will be repeated for a planned number of segments before ending.²⁶ The current passing the working electrode and the counter electrode is recorded while the potential between them varies. It is displayed on the y-axis. Experiment parameters should be adjusted according to electrodes and electrolytes, the studied reactions, and the limitation of an instrument in order to get reasonable and useful CV curves.

| Cyclic Voltammetry Parameters | ×b | Linear Sweep Voltammetry Parameters | |
|--|--------------|--|--------------|
| Init E (V) | OK Cancel | Init E (V) | OK |
| Low E (V) | Help | Einaite (V) | Cancel |
| Final E (V) 0 Initial Scan <u>P</u> olarity Positive v | | Scan <u>H</u> ate (V/s) | Help |
| Scan <u>R</u> ate (V/s) | | | |
| Sweep Segments | | | |
| Sample Interval (V) | | Sensitivity (A/V) 1.e-002 | |
| Quiet Time (sec)2 | | Electrode 2 | |
| Sensitivity (A/V) 1.e-002 - | | | |
| Electrode 2 | | Potential (V) 0 | • Uff |
| | • Off | Differential E (V) | C Constant E |
| Potential (V) | Constant E | | C Scan |
| Differential E (V) 0 | C Scan | Sensitivity (A/V) 1.e-006 | C Diff Scan |
| Sensitivity (A/V) 1.e-006 | C Diff Scan | | |
| | | <u>Open Circuit Potential as the Center Pote</u> | ential |
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| Auxiliary Signal Recording if Scan Rate <= I | 0.25 V/s | I Auxiliary Signal Recording if Scan Rate | <= 0.25 V/s |

Figure 2.4.1. (a) CV and (b) LSV parameters on the CHI 760C electrochemical workstation.



Figure 2.4.2. Linear potential sweeping with time and resulting current-potential plot for (a) CV and (b) LSV methods, respectively. E_p^a and E_p^c represent the anodic peak potential and cathodic peak potential. I_p^a and I_p^c represent the anodic peak current at E_p^a and E_p^c .

2.4.2 Linear sweep voltammetry

For a linear sweep voltammetry (LSV) test, the potential is swept from an initial potential (E1) to the final potential (E2) with the required scan rate (v), while the current passing the working electrode is recorded (Figure 2.4.1b and Figure 2.4.2b).²⁷ For some irreversible reactions, LSV is usually performed instead of CV because LSV can provide enough data and save time. To evaluate the performance for OER and HER of samples reported in this Ph.D. thesis, LSV is commonly used and tests are always carried at a low scan rate like 2 and 5 mV s⁻¹ to obtain the nearly steady-state polarization curves of electrocatalysis reactions. From the obtained LSV curves, the overpotential (η) at certain currents and the Tafel slope, two important parameters to evaluate electrocatalysts' performance, can be calculated.

2.4.3 Chronopotentiometry, chronoamperometry, and amperometric i-t curve

Chronopotentiometry (CP) is a galvanostatic method for which the current at the working electrode is held at a constant level for a given period of time. The potential on the working electrode is recorded as a function of time. This method is employed to study chemical reaction mechanisms and kinetics. It is also frequently used to study batteries and electrodeposition. Chronoamperometry (CA) is a potential step method, also known as constant potential bulk electrolysis, potential pulse electrolysis, and controlled potential amperometry, where the current is recorded as a function of time. CA can be applied in a lot of situations, including the study of reaction kinetics, diffusion process, and reversibility of a reaction. Amperometric i-t curve (i-t) is a controlled potential technique, where only one potential is applied to the cell for a period of time, and the current is recorded. Figure 2.4.3 shows the parameters required by the three methods on the CHI 760C electrochemical workstation. They are generally used for stability tests in this Ph.D. thesis.



Figure 2.4.3. (a) CP, (b) CA, and (c) i-t parameters on the CHI 760C electrochemical workstation.

2.4.4 Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) is a technique in which a perturbation signal (usually a small sinusoidal voltage, $v(t) = V_m \sin(wt)$) at a series of frequencies is applied to a cell and the response (current, $i(t) = I_m \sin(wt + \theta)$, where θ is the phase difference between v(t) and i(t)) is measured. Thus, the impedance is calculated according to the Ohm's law-like relationship (Z = $V_m \sin(wt)/(I_m \sin(wt + \theta))$). Through Euler's 62

formula and using complex representation, the impedance is divided into the real and imaginary parts: Z = Z' + jZ'', where Z' is the resistive part and Z'' represents the reactive part of the impedance.²⁸ Nyquist plot is plotted by drawing the points of (Z', -Z'') collected at different frequencies on a diagram, which is mostly used. To interpret the EIS data and understand the process on the electrode, an analogy of the experimental data and an equivalent circuit containing common electrical elements like resistors, capacitors, and inductors is made. Every electrical element should have its physical meaning in order to use a proper model with the right electrical elements. For example, Figure 2.4.4 shows the scheme of cell components and corresponding equivalent circuit elements.²⁹ In this thesis, the EIS was collected on the Autolab PGSTAT12, and analyzed by Nova 2.1 developed by Metrohm Autolab. EIS makes high-precision measurements in a stable system and rejects random noise very efficiently. The measurement can be over a wide frequency from 10⁻³ to 10⁶ Hz. It is a useful tool in the interpretation of electrochemical and electronic processes.



Figure 2.4.4. Scheme of cell components and equivalent circuit elements in a Li-ion battery. Reprinted with permission from ref. ²⁹. Open access.

2.4.5 Electrochemical cells

A three-electrode electrochemical cell consisting of a working electrode (WE), a counter electrode (CE, also called an auxiliary electrode), and a reference electrode (RE) is commonly utilized when studying electrochemical reactions. A typical three-electrode configuration is displayed in Figure 2.4.5. The WE is where the studied electrochemical reaction happens. The CE's responsibility is to carry the current and to complete the circuit. The reaction occurring on the CE may be or not be important to specific research topics. The potential or current steps on the WE are controlled against the RE in the three-electrode setup. An electrochemical cell must contain the WE and the CE. If possible, a RE is preferred to be included in an electrochemical cell. The function of the RE is to provide a known and stable potential against which other potentials can be measured. The electrochemical potential of the RE should theoretically stay at its equilibrium potential and no current passes through it. In practice, a tiny current will pass through the RE in order to measure the potential. But the current cannot move the RE from its equilibrium potential.³⁰ Several factors should be taken into consideration when choosing these three electrodes. If we are interested in the redox reactions of a species in the electrolyte, and the WE only provides a surface for the electron transfer process, a polished glassy carbon or gold electrode that is stable over a wide range of potential may fit the purpose. However, for some electrochemical investigations like battery electrode material testing, electrocatalyst performance, and metal/alloy corrosion, the WEs participate in these electrochemical reactions. Selecting a proper RE for the specific electrode is also important. The ideal RE for an electrochemical system should involve an ion in the electrolyte so that liquid junctions can be avoided and it is not necessary to make additional corrections to the potential. The reliable performance of the RE is important for electrochemical measurements.^{31,32} However, REs all have unstable liquid junction potentials which are influenced by temperature and chemical composition around the frit. For example, the liquid junction potential for the Ag/AgCl (filled with saturated KCl aqueous solution) electrode used in the non-aqueous solution can be hundreds of millivolts. It would be only several millivolts if using the RE in an aqueous solution for one year. Therefore, it is necessary to check the RE's potential with a standard RE before measurements and to use a proper RE for a specific electrochemical measurement. The CE is generally made of a stable and conductive material such as Pt, Au, or carbon. Reactions on the CE may not be important, but sometimes they influence 64

the results. For example, the minute dissolution of metal from the CE can be deposited on the WE and interfere with the electrochemical reactions, significantly changing catalytic activity. The surface area of the CE should be much larger than the WE to avoid the cell current being limited by reactions on the CE. In addition, there are a lot of other factors that should be considered before electrochemical tests, including the choice of electrolyte, temperature, and degassing. In this thesis, most of the electrochemical tests were performed with a three-electrode setup with the synthesized samples as WEs, a carbon electrode as the CE, and an Ag/AgCl (filled saturated KCl aqueous solution) or a Hg/HgO (filled with 1 M KOH) electrode as the RE. Some tests were done using twoelectrode cells, especially for long-term water electrolysis tests of the optimized samples.



Figure 2.4.5. Illustration diagram of a typical three-electrode setup.¹⁴

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Chapter 3

Bifunctional and self-supported NiFePlayer-coated NiP rods for electrochemical water splitting in alkaline solution

Transition metal phosphides (TMPs, where TM includes Ni, Fe, Co, Cu, Zn, etc.) have been explored as a type of excellent bifunctional electrocatalysts for HER and OER due to their high electrocatalytic activity, good chemical stability, and tunable structure and composition. Generally, precursors with designed structure and composition are fabricated first before the phosphidation step that produces the final TMP. PBAs have advantages of controllable metal compositions, abundant CN groups, and easy preparation, which could be ideal precursors for synthesizing TMPs. Powdered electrocatalysts need binders to attach to the conductive electrodes, suffering from poor stability and insufficient utilization in strong acid or alkaline solution and at large current densities. In situ growth of electrocatalysts on porous and conductive substrates (like metal foams, metal foils, carbon cloth, and carbon paper) can avoid the usage of binders, simplify procedures, and lower the electrode resistance. Furthermore, a hierarchical structure can be designed on the substrate for better performance. Although a lot of related TMPs on conductive substrates have been reported, stable and efficient bifunctional electrocatalysts for overall water splitting are still under exploration.

In this work, we gave a design of the rationally tailored hierarchical structure of different types of TMPs, including the optimized bimetallic NiFeP catalyst coated on nickel phosphide rods grown on nickel foam (NiFeP@NiP@NF). The precursor is a NiFe Prussian blue analogue (NiFe PBA) conveniently forming on the surface of nickel phosphate hydrate (NiPO) rods on Ni foam (NiFePBA@NiPO@NF). Directly growing NiPO rods on NF by a microwave-assisted hydrothermal method in the first step and growing NiFe PBA layer on the surface of NiPO rods can effectively reduce the electrical resistance of the

final product. For NiFeP@NiP@NF, the NiFeP layer derived from NiFe PBA provides abundant active sites for OER and HER, and NiP rods derived from NiPO rods provide a large surface area for NiFe PBA and is robust during water splitting at large current densities for the long-term application. It displays excellent electrocatalytic activity for both OER and HER (η_{10} , OER = 227 mV, η_{10} , HER = 105 mV) and good stability.

This work has been published in the journal ACS Applied Materials & Interfaces, coauthored by Fangyuan Diao, Wei Huang, Georgios Ctistis, Hainer Wackerbarth, Yuan Yang, Pengchao Si, Jingdong Zhang, Xinxin Xiao, and Christian Engelbrekt. Besides this, the experimental data about electrochemical tests with the alkaline electrolyzer performed in DTU Energy is included in the Appendix.

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Research Article

Bifunctional and Self-Supported NiFeP-Layer-Coated NiP Rods for Electrochemical Water Splitting in Alkaline Solution

Fangyuan Diao, Wei Huang, Georgios Ctistis, Hainer Wackerbarth, Yuan Yang, Pengchao Si, Jingdong Zhang, Xinxin Xiao,* and Christian Engelbrekt*

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ABSTRACT: Designing efficient and robust nonprecious metal-based electrocatalysts for overall water electrolysis, which is mainly limited by the oxygen evolution reaction (OER), for hydrogen production remains a major challenge for the hydrogen economy. In this work, a bimetallic NiFeP catalyst is coated on nickel phosphide rods grown on nickel foam (NiFeP@NiP@NF). This self-supported and interfacially connected electrocatalysis. The preparation of NiFeP@NiP@NF is optimized in terms of (i) the coprecipitation time of the NiFe Prussian blue analogue layer that serves as phosphides precursor and (ii) the phosphidation temperature. The optimized sample exhibits excellent OER performance delivering current densities of 10 and 100 mA cm⁻² at low overpotentials of 227 and 252 mV in 1.0 M KOH, respectively, and maintaining 10 mA cm⁻² for more than 120 h without obvious degradation. Moreover, it can also be operated as a hydrogen evolution electrocatalyst, requiring an overpotential of 105 mV at 10 mA cm⁻² in the same medium.



Thus, the as-prepared material was tentatively utilized as a bifunctional electrocatalyst in a symmetric electrolyzer, requiring a voltage bias of 1.57 V to afford 10 mA cm⁻² in 1.0 M KOH, while exhibiting outstanding stability.

KEYWORDS: Nickel iron phosphides, Prussian blue analogue derivative, core-shell structure, overall water splitting, excellent stability

1. INTRODUCTION

Hydrogen (H₂) is an ideal energy carrier due to its high specific energy density (more than 120 MJ kg⁻¹) and its oxidation with air only produces nontoxic water.¹⁻⁴Electrochemical water splitting for hydrogen production involves the cathodic hydrogen evolution reaction (HER) and anodic oxygen evolution reaction (OER) and represents a green energy storage platform when using sustainable but intermittent electricity sources like solar and wind.⁵ Pt- and Ir (or Ru)-related materials are the benchmark electrocatalysts for HER and OER, respectively.⁶⁻¹⁰ However, their high cost and scarcity in nature pose significant difficulties in large-scale applications.¹¹⁻¹³ Thus, research on well-engineered and efficient electrocatalysts employing high-abundance elements as alternatives is attracting increasing attention.¹⁴⁻¹⁶

Among various nonprecious electrocatalysts, transition metal phosphides (TMPs) have emerged as a desirable electrocatalyst toward electrocatalytic water splitting.¹⁷ In the HER process, the metal and phosphorous sites of TMPs can form hydrides and trap protons, respectively, similar to the catalytic mechanisms of hydrogenases.^{18,19} Meanwhile, the real catalytic sites for OER are surface metal oxides/hydroxides derived in situ.^{20,21} Until now, TMPs including Mo-,^{22–24} Co-,^{18,25} Fe-,²⁶ and Ni-^{19,27,28} phosphides have been reported with reasonable activities toward HER in an acidic or alkaline solution, with a fair number of them such as Ni- and Co-related metal phosphides, ^{29–34} also showing efficient OER performance. Bimetallic phosphides show better performance than monometallic phosphides due to synergistic effects and modified electronic structures.^{28,29} For instance, Yang et al. found that Fe-doped Co₂P required a much lower overpotential to reach the same current density compared with Co₂P, Ni₁₂P₅, and Fe₂P.²⁹ Ren et al. optimized the performance of FeNiP nanoparticles on carbon sheets toward OER and HER by tuning the ratio of Fe₃P and Ni₂P.³⁵ However, challenges still remain for obtaining TMP-based bifunctional electrocatalysts with high efficiency and long-term stability for HER and OER in the same electrolyte.^{32,36,37} Facile and reproducible methods for scalable production of catalysts are also desired.

In situ preparation of electrocatalysts on conductive substrates, such as nickel foam (NF),^{32,38} carbon cloth,³⁹ and titanium foil,⁴⁰ is a practical synthesis route. It not only simplifies the electrode production but can also lead to reduced contact resistance between catalysts and substrates.⁴¹ NF is desirable for in situ construction of TMP micro-

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Figure 1. Overview of synthesis procedure. (a) Photographs (width: ~1 cm; length: ~3 cm), (b) synthesis scheme with representative conditions, and (c) false-colored SEM images of (left to right) NF, NiPO@NF, NiFe PBA@NiPO@NF, and NiFeP@NiP@NF.

structures as it is cheap, hydrophilic, and conducting. Furthermore, its macroporous structure provides open paths for H₂ and oxygen (O₂) liberation during electrolysis. There is a growing number of reports on bifunctional catalysts on NF for HER and OER, which would greatly simplify the catalyst preparation process. For example, Xu et al. synthesized threedimensional porous FeP/Ni₃P hybrids by treating NF with iron nitrate and subsequent phosphidation.³² Ahn and associates reported porous and carbon-incorporated Ni–Fe– P nanorods on NF derived from Ni–Fe metal–organic frameworks.³⁸ Both cases achieved a benchmark current density of 10 mA cm⁻² with a whole-cell voltage less than 1.60 V toward water splitting in 1.0 M KOH and good stability. Rationally tailored hierarchical structures of different types of TMPs for better performance remain rarely studied.

In this work, we design a hierarchical structure of nickel and iron phosphide hybrids coated on nickel phosphide rods that have been grown on NF (NiFeP@NiP@NF). The NiFeP is derived from a NiFe Prussian blue analogue (NiFe PBA), which is conveniently formed on nickel phosphate hydrate (NiPO) rods, which are themselves grown on NF (NiFePBA@ NiPO@NF), and subsequently converted to NiP. NiFeP@ NiP@NF is successfully synthesized by a reproducible and facile method and shows excellent activity and outstanding stability toward both OER and HER in 1.0 M KOH. The optimized sample registers low overpotentials of 227 and 105 mV for OER and HER at a current density of 10 mA cm⁻², respectively. Moreover, a symmetrical two-electrode alkaline electrolyzer with NiFeP@NiP@NF as both cathode and anode only required 1.57 and 1.64 V to reach 10 and 20 mA cm⁻² respectively, outperforming major bifunctional catalysts in the literature.

2. RESULTS AND DISCUSSION

2.1. Preparation and Structural Characterization. The synthesis procedure of NiFeP@NiP@NF involves three steps, as shown in Figure 1. NF with its macroporous structure (pore size: $277 \pm 133 \ \mu$ m, frame width: $64 \pm 6 \ \mu$ m), large surface area, and good conductivity served as the scaffold for the active catalyst (Figures 1 and S1). In the first step, NiPO rods were constructed on the surface of NF (NiPO@NF) via a

hydrothermal method in a microwave synthesizer. Then, a NiFe PBA layer was grown on the NiPO rods through a facile coprecipitation method during which the sample color changed from light green to yellow (Step 2, Figure 1). Finally, NiFe PBA@NiPO@NF was transformed into the black NiFeP@NiP@NF via phosphidation under an Ar atmosphere, where NaH_2PO_2 at the upstream releases PH_3 as the phosphorus source (Step 3, Figure 1).⁴²

The peaks in the powder X-ray diffraction (XRD) pattern of NiPO@NF in Figure S2 match well with monoclinic Ni₃(PO₄)₂·8H₂O (Inorganic Crystal Structure Database Collection Code, ICSD Coll. Code, 240946) and also includes expected peaks from the NF support, indicating that a pure phase of NiPO is obtained in the first step. Energy-dispersive spectroscopy (EDS) analysis (Figure S3c) confirms a Ni/P atomic ratio of 3.1:2, consistent with the XRD results and the formula above. The Fourier-transform infrared (FT-IR) spectrum of NiPO@NF is shown in Figure S4a. The peaks at 3426, 3139, and 3000 cm⁻¹ are assigned to O-H stretching vibrations in water, and at 1587 and 740 cm⁻¹ to bending and vibrational modes of water molecules.43 The bands in the regions of 1100-800 and 580-540 cm⁻¹ are assigned to the vibration of PO4^{3-.44,45} Scanning electron microscopy (SEM) micrographs in Figures 1c and S3a,b show the morphology of NiPO@NF. Small amounts of Ni2+ and Fe3+ in the solution aid in achieving uniformly distributed and regularly shaped NiPO rods on the NF, as seen from the morphology of reference samples made without these additives (Figure S5). The optimized NiPO rods show a prismatic shape with a length of tens of micrometers, a width of $1.51 \pm 0.44 \,\mu\text{m}$, and smooth surfaces (Figure 1c). This morphology can provide a large surface area and abundant nucleation sites for the growth of NiFe PBA in the following step.

To grow a thin layer of NiFe PBA on the surface of the NiPO rods, coprecipitation of PBA in a solution containing Ni²⁺ and $[Fe(CN)_6]^{3-}$ was carried out. Nickel ions from local dissolution act as nucleation sites to react with $[Fe(CN)_6]^{3-}$, leading to the formation of a NiFe PBA layer along the NiPO rod surface. During growth, nickel ions can be supplemented from bulk solution, resulting in the complete coverage of the rods with NiFe PBA.^{46,47} Extending the growth time leads to



Figure 2. (a) XRD patterns and (b) XPS survey spectrum of NiFeP@NiP@NF. (c-f) High-resolution XPS spectra and (g-j) elemental mapping of elemental Ni, Fe, P, and O of NiFeP@NiP@NF, respectively.

thicker NiFe PBA layers and the formation of cubic NiFe PBA features. Figures 1c and S6 show the SEM images of NiFe PBA@NiPO@NF obtained with different NiFe PBA growth durations ranging from 1 to 24 h. Characterization with XRD, FT-IR, and X-ray photoelectron spectroscopy (XPS) was conducted to verify the crystal phase and composition of NiFe PBA@NiPO@NF. Compared to the XRD patterns of NiPO@ NF in Figure S7a, several additional peaks appear at 17.57, 24.95, 35.61, and 39.97° in the pattern of NiFe PBA@NiPO@ NF, ascribed to cubic KNiFe(CN), (ICSD Coll. Code: 89338), confirming the formation of PBA.48,49 This is further supported by the appearance of a peak at 2089 cm⁻¹ in the FT-IR spectrum (Figure S4b) and 2100-2200 cm⁻¹ in the Raman spectrum (Figure S4) representing the CN group coordinated by Ni and Fe.^{50,51} Figure S4g shows the Raman spectrum of NiFe PBA@NiPO@NF between 1900 and 2400 cm-1 in which two peaks at 2103 and 2140 cm⁻¹ are attributed to the CN vibration of Fe^{II}-CN-Ni^{II} and Fe^{II}-CN-Ni^{III}, respectively, and another peak at 2174 cm⁻¹ is from the CN vibration in Fe^{III}–CN–NiII.^{52,53} The surface elemental composition of NiFe PBA@NiPO@NF is determined through quantification of the high-resolution XPS spectra of K 2p, Ni 2p, Fe 2p, and N 1s, showing an atomic K:Ni:Fe:N ratio of approximately 1.03:1.03:1:5.00, in agreement with the expected NiFe PBA composition (Figure S8). SEM images (Figure S7b) indicate that the thickness of the NiFe PBA layer is 120-160 nm. All these results verify that the core-shell structure of NiFe PBA@ NiPO@NF was successfully constructed. In the final step,

NiFe PBA@NiPO@NF was calcined together with NaH2PO2. H2O under Ar atmosphere at 450 °C to obtain NiFeP@NiP@ NF. During this process, NiFe PBA and NiPO were completely reduced by PH3 released by the decomposition of NaH2PO2. H₂O. The peaks in the XRD pattern of NiFeP@NiP@NF in Figure 2a are indexed to a mixture of Ni₂P (ICSD Coll. Code: 105306), Ni12P5 (ICSD Coll. Code: 646121), and Fe2P (ICSD Coll. Code: 70113). The SEM images of NiFeP@NiP@NF (Figures 1c and S9) suggest that the rod-like structure is maintained after phosphidation, guite different from NiP@NF consisting of deformed and granular rods (Figure S10). Elemental mapping demonstrates a uniform distribution of Ni, Fe, P, and O on the surface of NiFeP@NiP@NF, proving further that the precursor was transformed into a phosphide composite (Figure 2g-j). The TEM images in Figure S11 also indicate a core-shell structure where the NiP rod is fully covered by a layer of NiFeP with a thickness of approximately 140 nm (Figure S11c). EDS analyses were carried out at both the edge and center of the rod, which further supports Fe localization in the shell (Figure S11d). In the FT-IR spectrum of NiFeP@NiP@NF, there are no remaining peaks from water and CN vibration, which confirms the conversion of the material during phosphidation (Figure S4c). Besides, Raman spectra of NiFeP@NiP@NF and NiFeP@NF (prepared by phosphidation of NiFe PBA directly grown on NF) exhibit peaks around 1375 and 1570 cm⁻¹ corresponding to the Dand G-band of the disordered structure and graphitic sp² hybridized carbon materials, respectively (Figure S4h).54 This



Figure 3. OER performance tests in 1.0 M KOH. (a) *iR*-corrected polarization curves. Scan rate: 2 mV s^{-1} . (b) OER overpotentials at current densities of 100 mA cm⁻² (left, dark color) and 400 mA cm⁻² (right, light color). (c) Tafel curves. (d) Nyquist plots. Inset in (d) is the equivalent circuit used to fit the Nyquist plot. (e) CP tests recorded at different current densities from 10 to 100 mA cm⁻². The inset shows the corresponding overpotentials at different current densities. (f) Long-term stability test of NiFeP@NiP@NF. Inset: *iR*-corrected polarization curves before and after stability test for 120 h. Scan rate: 2 mV s^{-1} .

indicates the formation of graphene-like carbon structures in the PBA-derived NiFeP during phosphidation. Such features were not found for NiP@NF.

The chemical state and composition of the surface of NiFeP@NiP@NF were further disclosed by XPS demonstrating the presence of Ni, Fe, K, C, N, O, and P (Figure 2b). The atomic ratio of K:Ni:Fe:P on the surface of NiFeP@NiP@NF was found to be 0.37:1.4:1:6.5. In comparison to the surface composition of NiFe PBA@NiPO@NF (K:Ni:Fe = 1.03:1.03:1), the relative content of Fe and K decreases for NiFeP@NiP@NF (K:Ni:Fe = 0.37:1.44:1), which is caused by the rearrangement of atoms during phosphidation. The sharp doublet at 853.1/870.3 eV in the high-resolution XPS spectrum of Ni 2p (Figure 2c) is assigned to Ni^{δ^+} (0 < δ < 2) in the nickel phosphide species, with a shake-up satellite doublet (marked Sat.) at 859.5/877.3 eV.55 The binding energy (BE) of $Ni^{\delta+}$ is close to the metallic Ni $2p_{3/2}$ BE of 852.6 eV.56 The doublet at around 856.6/874.4 eV with a satellite at 863.1/881.0 eV corresponds to Ni²⁺, probably in connection with phosphate arising from surface passivation of the phosphide.^{55,37} In the high-resolution XPS spectrum of Fe 2p (Figure 2d), two broad core doublets located at 711.0/ 724.8 and 714.3/730.7 eV are ascribed to the Fe^{3+} in Fe-O-Pof iron phosphate formed due to superficial oxidation.⁵ ⁸ The high-resolution spectrum of P 2p in Figure 2e shows a doublet at 129.8/130.7 eV, representing P in metal phosphide species with a slightly negatively charged P. The doublet at 134.7/ 135.6 eV corresponds to P-O in the surface metal phosphates formed due to exposure to air. Moreover, two O 1s peaks at 531.9 and 533.7 eV, respectively, correspond to nonbridging oxygen (P-O) and bridging oxygen (P-O-P) species.^{58,59} In addition, no characteristic peak of metal oxides is observed at around 530 eV in Figure 2f, which demonstrates that metal ions are bound in phosphides and phosphates.⁵⁸⁻⁶⁰ During phosphidation at 450 °C for 2 h, NiFe PBA decomposed, and the CN ligands were removed from the sample. Some of the CN ligands may have been reduced by PH3, resulting in small amounts of carbon and nitrogen in the NiFeP matrix.⁶¹ As discussed above, carbon elements should be present in graphene-like carbon structures, which is consistent with the C 1s spectrum analysis in Figure S12a. In Figure S12b, the relatively weak peak around the binding energy of 402 eV represents N 1s, which could be assigned to some oxygenated nitrogen species.⁶² This is not from the remaining CN as evidenced by the lack of characteristic peaks in the Raman, IR, and XPS spectra, although it is difficult to determine the precise chemical nature of the N-dopant.

2.2. Electrochemical Catalytic Activity. The electrocatalytic OER activity of NiFeP@NiP@NF was investigated using a three-electrode setup in 1.0 M KOH at room temperature (RT). Figure 3a displays iR-corrected polarization curves of NiFeP@NiP@NF, NiP@NF (prepared by phosphidation of NiPO@NF), NiPO@NF, NiFe PBA@NiPO@NF, RuO₂ paste on NF (RuO₂@NF), and bare NF. NiPO@NF shows much better OER performance than the bare NF and RuO₂@NF. With the coating of NiPO@NF by a NiFe PBA layer, the OER performance improves slightly. The phosphidation products, including NiP@NF and NiFeP@NiP@NF, register the best OER performances. Figure 3b summarizes the observed overpotentials at current densities of 100 and 400



Figure 4. HER performance in 1.0 M KOH. (a) *iR*-corrected polarization curves. Scan rate: 2 mV s^{-1} . (b) Overpotentials at current densities of 10 and 100 mA cm⁻². (c) Tafel plots obtained from the polarization curves in a. (d) Nyquist plots. Inset in (d) is the equivalent circuit used to fit the Nyquist plot. (e) CP tests at different current densities from 10 to 100 mA cm⁻². Inset shows overpotentials for delivering different current densities. (f) Long-term stability test of NiFeP@NiP@NF at 10 mA cm⁻². Inset: *iR*-corrected polarization curves before and after stability test over 120 h. Scan rate: 2 mV s^{-1} .

mA cm-2 for all samples. NiFeP@NiP@NF requires the lowest η_{100} of 252 mV, which outperforms the RuO₂ on NF (η_{100} = 352 mV) and other related materials in this work, including NiFe PBA@NiPO@NF ($\eta_{100} = 310 \text{ mV}$), NiP@NF ($\eta_{100} =$ 299 mV), NiPO@NF (η_{100} = 326 mV), and NF (η_{100} = 445 mV). The same trend is found for η_{400} . We also explore the OER performance of NiFe PBA grown directly on the nickel foam (NiFe PBA@NF, $\eta_{10} = 352$ mV), and the corresponding phosphidation material (NiFeP@NF, $\eta_{10} = 262$ mV; Figure S14). Furthermore, NiFeP@NiP@NF exhibits an electrocatalytic OER performance comparable to various nonprecious metal phosphides, oxides, and other related electrocatalysts in the literature (Table S1). Figure 3c displays the Tafel behavior of the tested materials, with smaller Tafel slopes indicating more favorable OER kinetics. NiFeP@NiP@NF possesses the smallest Tafel slope of 60.7 mV dec⁻¹ and maintains linearity in the higher current density region of the polarization curves, which illustrates fast electron and mass transport between the electrolyte and the catalyst.²¹ The Nyquist plots show that the charge transfer resistance (R_{ct}) of NiFeP@NiP@NF at a potential of 1.5 V is approximately 2.4 Ω , far smaller than those of other samples at the same potential (Figure 3d and Table S4). All the performance metrics, including the η_{100} of 252 mV, Tafel slope of 60.7 mV dec⁻¹, and R_{ct} of 2.4 Ω @1.5 V, highlight NiFeP@NiP@NF as the best candidate for OER in terms of reaction kinetics. To further evaluate the application potential of the material, the operational stability of NiFeP@ NiP@NF (Figure 3e) studied via multistep chronopotentiometry (CP) tests in the current density range from 10 to 100 mA cm⁻² and back to 10 mA cm⁻² (1 h duration for each current density). The overpotential increases with current density (inset of Figure 3e), while no discernable increase of the operational potential when returning to 10 mA cm⁻² after the 6 h test was observed (Figure 3e). This reveals that NiFeP@ NiP@NF is capable of functioning over a wide range of current densities with good stability. The long-term operation of NiFeP@NiP@NF over a course of 120 h at 10 mA cm⁻² barely sees an increase in potential (3 mV), and almost overlapping polarization curves are recorded before and after the stability test (Figure 3f). Further, stability is evaluated at a higher current load of 500 mA cm⁻² for 30 h leading to a minimal potential increase of just 1 mV, validating that the sample is also very stable at a much larger current density and thus shows robust OER performance (Figure S17).

The HER performance of NiFeP@NiP@NF has also been evaluated in the same alkaline environment as the previous OER experiments (Figure 4). The commercial 20 wt % platinum on graphitized carbon black pasted on NF (Pt/C@ NF) displays excellent HER activity with an onset potential near 0 V, requiring small overpotentials of 21 and 95 mV to drive 10 and 100 mA cm⁻², respectively (Figure 4a). NiFeP@ NiP@NF also exhibits outstanding electrocatalytic activity toward HER with an overpotential of 105 mV to yield 10 mA cm⁻², lower than those of NiP@NF ($\eta_{10} = 129$ mV), NiPO@ NF ($\eta_{10} = 148$ mV), NiFe PBA@NiPO@NF ($\eta_{10} = 158$ mV), and NF ($\eta_{10} = 171$ mV) (Figure 4b). To achieve a high current density of 300 mA cm⁻², NiFeP@NiP@NF requires an overpotential of 246 mV, which is just 48 mV higher than that of Pt/C@NF. The HER activity of NiFeP@NiP@NF is comparable to high-performance Ni-based catalysts, as shown



Figure 5. Overall water splitting test with two-electrode systems in 1.0 M KOH. (a) Polarization curves without *iR* compensation for NiFeP@ NiP@NF (+,-), NiFeP@NiF@NF (+) and Pt/C (-), RuO₂ (+) and Pt/C (-), and NF (+,-). Scan rate: 2 mV s⁻¹. (b) Long-term stability tests of NiFeP@NiP@NF (+,-) at 10 mA cm⁻² and 2.0 V, respectively. (c) Photographs of the electrolyzer powered by a commercial solar panel with an open-circuit potential of ~2.0 V under sunlight. (d) Plot of the displaced volume of water by produced H₂ (blue) and O₂ (red) with time. (e) Photograph of the setup for the measurement of Faradaic efficiency in overall water splitting.

in Table S2, only surpassed by trimetallic catalysts. The Tafel slope of NiFeP@NiP@NF is 97.9 mV dec-1, which is smaller than all other synthesized samples. The Tafel slope of Pt/C@ NF is much lower (46.2 mV dec⁻¹) indicating a different reaction mechanism on Pt than the Ni-based catalysts. The Tafel slope value suggests that NiFeP@NiP@NF catalyzes hydrogen production via a Volmer-Heyrovsky mechanism with the electrochemical desorption of dihydrogen as the ratedetermining step.⁶³ NiFeP@NiP@NF possesses an R_{ct} of 8.2 Ω at -0.20 V, while R_{ct} values of NiP@NF and NiFe PBA@ NiPO@NF are calculated to be 12.5 and 24.5 Ω , respectively (Figure 4d and Table S5). The small R_{ct} value of NiFeP@ NiP@NF demonstrates an overall fast electron transfer during HER. Besides activity, stability is a vital criterion for evaluating HER catalysts. Figure 4e represents the HER CP tests of NiFeP@NiP@NF at different current densities, with no obvious decay during the continuous operation over 7 h. Furthermore, a 120 h HER stability test at 10 mA cm⁻² was conducted on NiFeP@NiP@NF (Figure 4f). At the initial 60 h test, the recorded potential shows negligible changes. However, the overpotential required to reach 10 mA cm⁻² increases to 207 mV after 120 h (an increase of 86 mV). Polarization curves of NiFeP@NiP@NF tested before and after the 120 h test (inset in Figure 4f) indicate a slight decay of HER activity. For stability test at 500 mA cm⁻² for 30 h in Figure S17, the potential decreased from -0.501 to -0.521 V after 30 h of continuous testing. Despite insufficient stability, NiFeP@

NiP@NF shows the potential to work as the cathode in an alkaline electrolyzer.

The number of electrocatalytic active sites on NiFeP@NiP@ NF and its precursors is roughly probed by the electrochemical surface area (ECSA), proportional to the electrochemical double-layer capacitance (C_{di} , Figure S19). NiFeP@NiP@NF exhibits a much larger ECSA with a C_{di} value of 4.86 mF cm⁻², which is 2.1 times higher than that of NiP@NF. By normalizing to ECSA, NiFeP@NiP@NF still outperforms NiP@NF for both OER and HER (Figure S20). This further highlights the advantage of the bimetallic surface of NiFeP@ NiP@NF for water splitting and that the performance is not simply boosted by the surface area. Through the controllable pyrolysis step, the obtained derivatives of PBAs, such as oxides, sulfides, selenides, and phosphides, could work as excellent candidates for electrocatalytic OER and HER.^{46,64–67}

To further demonstrate the promising bifunctional properties of NiFeP@NiP@NF, two identical samples are further employed as both the anode and cathode in a two-electrode water splitting setup with 1.0 M KOH electrolyte at RT. A cell voltage of 1.64 V is required to achieve a current density of 20 mA cm⁻², very close to that of RuO₂||Pt/C (1.61 V) and much smaller than that of NF||NF (1.92 V), as shown in Figure 5a. NiFeP@NiP@NF as the bifunctional catalyst for water splitting is comparable with the previously reported nonprecious Ni-based bifunctional electrocatalysts (Table S3). Besides, NiFeP@NiP@NF as anode cooperates well with the Pt/C@NF cathode. The cell, NiFeP@NiP@NF (+) and Pt/

C@NF (-), yields 20 mA cm⁻² at a cell voltage of 1.49 V, which is much smaller than the cell voltage required for other electrode couples, as shown in Figure 5a. To reach a higher current density of 100 mA cm⁻², the symmetric NiFeP@NiP@ NF (+,-) requires a cell voltage of 1.86 V, only 0.09 and 0.24 V higher than RuO2llPt/C and NiFeP@NiP@NFllPt/C@NF, respectively. In addition, the cell NiFeP@NiP@NF(+,-) shows good stability in long-term stability tests. When working at a fixed current density of 10 mA cm⁻² for 120 h, the required voltage increased by 0.04 V after the stability test. When applying a fixed bias of 2.0 V for 98 h (Figure 5b), the current in the circuit decreased slightly from 196 to 180 mA cm⁻². During the stability test at 2.0 V, there are large amounts of gas bubbles generated on the surface of both electrodes, which influence the contact between electrodes and electrolyte leading to fluctuations in the current density. Removing the bubbles on the electrode by purging the electrolyte with Ar sees the performance of the electrolysis cell recover, as indicated by the purple arrows in Figure 5b. To demonstrate solar to hydrogen generation, a commercial 2 V solar cell (15.75 cm²) under natural sunlight (September in Lyngby, Denmark) was used to drive the symmetric NiFeP@NiP@ NF(+,-) cell (Figure 5c), enabling continuous bubble generation. H₂ and O₂ produced by water splitting were collected by the drainage method, as shown in Figure 5d. At a current density of 50 mA cm⁻², the volume of water displacement by H2 and O2 production increased linearly with time (Figure 5d). The production rates of H2 and O2 were 0.259 and 0.127 μ mol^{s⁻¹}, respectively. The Faradaic efficiency for overall water splitting was found to be excellent at around 97%. These results highlight that NiFeP@NiP@NF is an excellent bifunctional candidate for overall water splitting.

Microstructure and composition changes of Ni-based phosphides are quite common phenomena during OER and HER processes, which influence the operational stability and practical application of the catalysts.^{21,68} Herein, the morphology and composition evolution of NiFeP@NiP@NF working as both the cathode and anode in a two-electrode water splitting setup after the 120 h stability test at 10 mA cm⁻² are characterized by SEM, XRD, and XPS. Similar XRD patterns of the fresh and spent samples after HER and OER stability tests (Figure S21) suggest that the major crystalline phases have not changed greatly, confirming the compositional durability of the core-shell structure. This is further supported by the SEM images (Figure S22) displaying large amounts of rod-like materials still present on the NF framework. However, slight changes after the operation are found by comparing the XRD patterns of the fresh samples and the samples after OER and HER tests carefully. In Figure S21a, the differences between the XRD patterns of the fresh sample and NiFeP@ NiP@NF after OER appear around 34.0, 38.2, and 60.3°, which might be broad peaks arising from small Ni(OH)2 (ICSD Coll. Code: 24015) nanoparticles forming during the OER operation. After HER testing, a peak at 43.4° appears in the XRD pattern in addition to the three peaks mentioned above, which may be from NiO (ICSD Coll. Code: 92127). XPS is more sensitive than XRD to surface state changes. NiFeP@NiP@NF after OER and HER are therefore also evaluated by XPS analysis (Figures S23 and S24). The low energy peak at 852.6 eV attributed to Ni-P in the Ni 2p spectrum of the fresh NiFeP@NiP@NF (Figure 2c) disappears after a long-term water splitting test on the surface of both electrodes (Figures S23a and S24a). This coincides with the

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disappearance of the M-P in the P 2p spectrum, in which only a weak broad hump from phosphate species can be observed (Figures S23c and S24c). The XPS-derived atomic ratio of Ni, Fe, and P changes from 1.4:1:6.5 in the fresh NiFeP@NiP@ NF to 1.9:1:0.21 and 2.0:1:0.33 in NiFeP@NiP@NF after OER and HER, respectively. The M/P ratio (M = Ni + Fe) increases dramatically from ~0.36 to ~14 and ~9.0 for NiFeP@NiP@NF after OER and HER, respectively. The decrease in the relative P content on the surface could be due to two reasons: (a) dissolution from the metal phosphides into the alkaline electrolyte and (b) surface oxidation during electrocatalysis.⁴⁶⁶⁹

For the anode where the OER occurs, the general mechanisms in an alkaline solution have been proposed as follows 70,71

$$M_{cat} + OH^{-}(aq) \rightarrow M_{cat}OH_{ads} + e^{-}$$
 (1)

 $M_{cat}OH_{ads} + OH^{-}(aq) \rightarrow M_{cat}O_{ads} + H_2O(l) + e^{-}$ (2)

$$M_{cat}O_{ads} + OH^{-}(aq) \rightarrow M_{cat}OOH_{ads} + e^{-}$$
 (3)

$$M_{cat}OOH_{ads} + OH^{-}(aq) \rightarrow M_{cat}OO_{ads}^{-} + H_2O(l)$$
 (4)

$$M_{cat}OO_{ads}^{-} \rightarrow M_{cat} + O_2(g) + e^{-}$$
(5)

According to its Tafel slope, steps shown in eqs 1 and 2 are both rate-determining steps for NiFeP@NiP@NF.^{72,73} During the OER process in an alkaline electrolyte, NiFeP@NiP@NF works at a potential higher than the oxidation potentials of Ni and Fe, and metals atoms (including Ni and Fe) are continuously oxidized to species such as $M_{cat}OH_{ads} M_{cat}OOH_{ads}$ before O₂ is liberated from the surface. As confirmed by XPS analysis (Figure S23a), a thin layer of metal hydroxides/oxyhydroxide is formed after OER testing. The outer layer works in synergy with the phosphide core, where the former provides active sites and the latter assists with faster electron diffusion, promoting the OER process.²¹

On the cathode where dihydrogen is generated, the mechanism in an alkaline solution is defined as follows according to the Tafel $slope^{74}$

Volmer step :
$$M_{cat}+H_2O(l) + e^- \rightarrow M_{cat}H_{ads} + OH^-(aq)$$
(6)

Heyrovsky step: $M_{cat}H_{ads} + H_2O(l) + e^{-1}$

$$\rightarrow$$
 H₂(g) + OH⁻(aq) + M_{cat} (7)

In the Volmer step, the formation and desorption of OH- and the adsorption of H atom from the adsorbed H2O could be regarded as the rate-determining steps. OH- preferentially attaches to oxide sites, while H atoms prefer sites with a negative charge. In the composite of NiFeP@NiP@NF, the negative P species on the surface of the catalyst could collect protons while the metal oxides from surface oxidation could provide sites for OH⁻, facilitating the process of HER.^{21,73} Moreover, bimetallic Ni and Fe phosphides derived from NiFe PBA could modify the electronic structure and optimize the hydrogen adsorption energy, leading to a better catalytic activity. Although there is more P in NiFeP@NiP@NF after HER in comparison with NiFeP@NiP@NF after OER, the leaching of the P element is thought to be the main reason for the degradation of HER performance of NiFeP@NiP@NF in Figure 4f.21,

3. CONCLUSIONS

In summary, NiFeP@NiP@NF with a hierarchical structure has been successfully synthesized by phosphidation of the precursor NiFe PBA@NiPO@NF. To reduce the electrical resistance, NiPO rods were directly grown on NF by a microwave-assisted hydrothermal method, which is more efficient than the conventional hydrothermal synthesis. The robust rod-like structure of NiPO@NF synthesized by this method has been rarely reported. The NiFe PBA layers were also grown directly on the surface of the NiPO rods by a facile method to ensure intimate contact between the catalyst layer and the conductive support. The NiFe PBA layer helped to maintain the rod-like microstructure in the final phosphidation step to fabricate NiFeP@NiP@NF. For this catalyst, NiFeP derived from NiFe PBA at the surface works as the active material providing abundant active sites for OER and HER, while NiP, mainly derived from NiPO, supports the structure and provides a large active surface area. NiFeP@NiP@NF displays excellent electrocatalytic performance toward both OER and HER in an alkaline electrolyte, requiring low overpotentials of 227 and 105 mV, respectively, to achieve a current density of 10 mA cm⁻². A symmetrical electrolyzer using two NiFeP@NiP@NF electrodes only requires a cell voltage of 1.64 V to deliver 20 mA cm⁻², and exhibits robust stability over 120 h at 10 mA cm⁻². Furthermore, the electrolyzer cell was operated at a relatively high current density (~180 mA cm⁻²) by applying a fixed bias of 2.0 V providing good stability over 100 h. The excellent catalytic activity and stability of NiFeP@NiP@NF are attributed to the following aspects: (1) The NiFeP layer derived from NiFe PBA provides a large surface area and a composite nickel and iron phosphide, providing more active sites and a modified electronic structure with enhanced activity. (2) The hierarchical structure enables the utilization of the good conductivity of the nickel phosphide rods and NF to reduce resistance losses and thus facilitate high reaction rates. (3) The rod structure on NF can be maintained preventing structural degradation and delamination caused by H₂ and O₂ bubbles generated during water splitting in the course of long-term application. The synthesis method and design can further be extended to the fabrication of other inexpensive multicomponent catalyst materials.

4. EXPERIMENTAL SECTION

4.1. Chemicals and Materials. Nickel(II) nitrate hexahydrate (Ni(NO3)2.6H2O, 97.0%), hydrochloric acid (HCl, 37 wt %, 1.2 g mL⁻¹ at 25 °C), platinum on graphitized carbon black (Pt/C, 20 wt % Pt loading on Vulcan XC72), iron(III) chloride hexahydrate (FeCl₃. 6H₂O, ≥97%), sodium hypophosphite monohydrate (NaH₂PO₂· H₂O, \geq 99%), ruthenium(IV) oxide (RuO₂, \geq 99.9%), Nafion perfluorinated ion-exchange resin (10 wt % dispersion in water), ammonium dihydrogen phosphate (NH4H2PO4, ≥99%) and trisodium citrate dihydrate (C6H5Na3O7.2H2O, ≥99%) were obtained from Sigma-Aldrich. Nickel(II) chloride hexahydrate (NiCl₂·6H₂O, \geq 98%) was purchased from BDH Chemicals. Potassium hexacyanoferrate(III) ($K_3Fe(CN)_6$, $\geq 99\%$) was purchased from Riedel-de Haën. Potassium hydroxide (KOH, 1.0 M, pH 14) solution was purchased from Fisher Chemical. All chemicals were used directly as received. All aqueous solutions were prepared with 18.2 M Ω ·cm ultrapure water (arium pro VF Ultrapure Water System, Sartorius AG, Germany). NF sheets with a thickness of 300 μ m were purchased from Suzhou Jiashide Metal Foam Co., Ltd. (China). Prior to use, NF was cleaned with ethanol, 1.0 M HCl solution, and water successively

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under ultrasonication to remove contaminants and nickel oxides from the surface.

4.2. Synthesis of NiPO@NF. Nickel phosphate hydrate (NiPO, Ni₃(PO₄)₂:8H₂O) rods were grown on NF (NiPO@NF) by a microwave-assisted method. In a typical synthesis, 0.10 mmol NiCl₂· 6H₂O, 0.05 mmol FeCl₃:6H₂O, and 0.21 mmol NH₄H₂PO₄ were dispersed in 15 mL water under vigorous stirring for 30 min at RT. The obtained solution was then transferred into a 10–20 mL microwave reaction vial containing a piece of NF (1 × 3 cm²). The sealed vials were heated in a microwave synthesizer (Biotage Initiator, Biotage, Sweden) at 180 °C for 60 min. After the vial had cooled to RT, the sample was washed with water five times before it was dried in a vacuum oven at 80 °C for 8 h. As a reference, two samples were prepared without adding either FeCl₃:6H₂O or both NiCl₂:6H₂O and FeCl₃:6H₂O to the growth solution.

4.3. Synthesis of NiFe PBA@NiPO@NF. NiFe PBA (potassium nickel hexacyanoferrate(III), KNiFe(CN)₆) rods were grown on the surface of the NiPO rods by a facile precipitation method.⁶⁶ About 10 mL aqueous solution of 20 mM K3 [Fe(CN)6] was slowly poured into a stirred 10 mL mixture containing 45 mM trisodium citrate and 30 mM $Ni(NO_3)_2$, and stirring was maintained for 10 min. Then, a piece of NiPO@NF was immersed in the mixture, which was transferred to an oven and kept at 40 °C for different durations (1, 3, 6, 12, and 24 h). Finally, the obtained samples were rinsed with water five times followed by drying treatment at 80 °C for 8 h in a vacuum oven. The samples with different reaction durations are denoted as NiFe PBA@ NiPO@NF-t, where t represents the NiFe PBA growth time. If not specified, NiFe PBA@NiPO@NF refers to the sample NiFe PBA@ NiPO@NF-6 h. NiFe PBA directly grown on NF for 6 h (NiFe PBA@NF) was prepared following the same procedure by replacing NiPO@NF with NF.

4.4. Synthesis of NiFeP@NiP@NF. In a typical synthesis, a dry piece of the as-prepared NiFe PBA@NiPO@NF and 0.50 g of NaH₂PO₂·H₂O were put in two porcelain boats, respectively, in a tube furnace with NaH₂PO₂·H₂O at the upstream. The tube furnace was heated to different temperatures (250, 350, 450, and 550 °C) with a heating rate of 2 °C min⁻¹ under an Ar atmosphere and kept at the chosen temperature for 2 h. The samples obtained at this phosphidation step are denoted as NiFeP@NiP@NF-T, where T represents the calcination temperature. If not specified, NiFeP@NiP@NiFers to the NiFeP@NiP@NF-450 °C sample. NiFeP@NiP@NiF refers to the NiFeP@NiP@NF-450 °C. Caution: ensuring a leak-free environment in the tube furnace and safe management of the furnace exhaust during the reaction are crucial to avoid exposure to toxic gaseous byproducts (PH₃).

4.5. Characterization of Materials. Powder XRD patterns were acquired with a Huber G670 Guinier camera using Cu K α radiation $(\lambda = 1.5406 \text{ Å})$. XPS data were collected on a Thermo Scientific K- α XPS spectrometer. The material morphology was characterized using an SEM (FEI Quanta FEG 250 Analytical ESEM) with EDS. FT-IR spectra were obtained on a Bruker α -P FT-IR spectrophotometer. Raman spectra in a Stokes-shift range of 50-4000 cm-1 were recorded on a Horiba XploRa Plus confocal Raman microscope (excitation wavelength: 532 nm, excitation power: 4 mW, acquisition time: 30 s, accumulations: 10, grating: 1200 g mm⁻¹, confocal aperture: 300 µm, slit: 100 µm). Transmission electron microscopy (TEM), high-resolution TEM (HRTEM), and the corresponding EDS characterization were performed on a Tecnai T20 G2 at 200 kV equipped with a TVIPS XF416 4k \times 4k camera. The electrochemical performance was measured with either an Autolab PGSTAT12 (Metrohm Autolab, the Netherlands), a CHI 760C electrochemical workstation (CH Instruments, Inc. USA), or a PalmSens3 compact electrochemical interface (PalmSens BV, the Netherlands). A typical three-electrode system was used with the active material on NF as the working electrode, a carbon rod counter electrode, an Ag/AgCl (saturated KCl) reference electrode, and 1.0 M KOH electrolyte. All potentials were converted to the reversible hydrogen electrode (RHE) scale through the following equation: E (vs RHE) = E (vs Ag/AgCl) + 0.197 + 0.059 × pH. OER and HER overpotentials (η) were calculated based on the following equations: $\eta_{OER} = E$ (vs RHE) -

1.23 V; for HER, $\eta_{\rm HER}$ = 0 V - E (vs RHE). Linear sweep voltammetry (LSV) and cyclic voltammetry (CV) were conducted at a scan rate of 2 mV s⁻¹. The overpotential at 10 mA cm⁻² for OER of NiFeP@NiP@NF without iR correction was taken after 0.5 h of the CP testing at 10 mA cm⁻²; otherwise, overpotentials reported in this work were taken from iR-corrected LSV curves. The solution was quiescent during electrochemical tests. LSV and CV curves for OER and HER were collected without iR correction unless otherwise specified. Electrochemical impedance spectroscopy (EIS) measurements were carried out at 1.50 V for OER and -0.20 V for HER in a frequency range of $10^4 - 10^{-2}$ Hz and an amplitude voltage of 5 mV. For comparison, benchmark Pt/C and RuO2 were painted on NF with a mass loading of 3.0 mg cm $^{-2}$. The ECSA of a catalyst was assessed by the C_{dl} values. CV curves in the potential range of 0.65-0.75 V (vs RHE) at different scan rates of 10, 30, 50, 70, and 90 mV s^{-1} were recorded. C_{d1} was calculated by plotting the half of the current variation ($\Delta J = J_a - J_c$) at 0.72 V (vs RHE) against the scan rate. The linear slope of the curve is equal to the value of $C_{\rm db}$. The overall water splitting test was performed in a two-electrode electrolysis cell in 1.0 M KOH at RT. Long-term stability was evaluated by CP and amperometric i-t methods. The reported potentials or voltages tested by CP and i-t methods are all read after 0.5 h of test to ensure a stable reading. For the Faradaic efficiency test in overall water splitting, the drainage method was used. A constant current of 50 mA was applied to the two-electrode electrolyzer with electrode areas of 1.0 $\rm cm^{-2}$ for about 1.300 s. During the experiment, volumes of water displaced by evolved H₂ and O₂ were monitored. Faradaic efficiency was calculated by comparing the experimental gas production and theoretical gas production assuming ideal gas conditions.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.1c03089.

SEM images, XRD patterns, FT-IR spectra, XPS spectra, and Raman spectra of control samples; electrochemical polarization curves; electrochemical double-layer capacitance measurement in the non-faradaic region; post-test characterization (PDF)

AUTHOR INFORMATION

Corresponding Authors

Xinxin Xiao – Department of Chemistry, Technical University of Denmark, DK-2800 Kongens Lyngby, Denmark;
orcid.org/0000-0002-0240-0038; Email: xixiao@ kemi.dtu.dk

Christian Engelbrekt – Department of Chemistry, Technical University of Denmark, DK-2800 Kongens Lyngby, Denmark; @ orcid.org/0000-0003-3679-3666; Emaîl: cheng@kemi.dtu.dk

Authors

Fangyuan Diao – Department of Chemistry, Technical University of Denmark, DK-2800 Kongens Lyngby, Denmark

 Wei Huang – Department of Chemistry, Technical University of Denmark, DK-2800 Kongens Lyngby, Denmark;
 orcid.org/0000-0002-9654-5456

Georgios Ctistis – Department of Photonic Sensor Technology, Institut für Nanophotonik Göttingen, 37077 Göttingen, Germany

Hainer Wackerbarth – Department of Photonic Sensor Technology, Institut für Nanophotonik Göttingen, 37077 Göttingen, Germany

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- Yuan Yang Key Laboratory for Liquid-Solid Structural Evolution and Processing of Materials (Ministry of Education), Research Center for Carbon Nanomaterials, School of Materials Science and Engineering, Shandong University, Jinan 250061, P. R. China
- Pengchao Si Key Laboratory for Liquid-Solid Structural Evolution and Processing of Materials (Ministry of Education), Research Center for Carbon Nanomaterials, School of Materials Science and Engineering, Shandong University, Jinan 250061, P. R. China
- Jingdong Zhang Department of Chemistry, Technical University of Denmark, DK-2800 Kongens Lyngby, Denmark; O orcid.org/0000-0002-0889-7057

Complete contact information is available at: https://pubs.acs.org/10.1021/acsami.1c03089

Author Contributions

The manuscript was written through contributions of all authors. C.E. and X.X. supervised and reviewed this work. F.D. designed the experiments, analyzed data, and prepared the manuscript. W.H., Y.Y., and P.S. offered help in electrochemical and structural analyses. G.C. and H.W. performed Raman tests and structural analyses. All authors have given approval to the final version of the manuscript.

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ABBREVIATIONS

OER, oxygen evolution reaction NiFeP@NiP@NF, NiFeP catalyst coated on nickel phosphide rods on nickel foam H₂, hydrogen HER, hydrogen evolution reaction TMPs, transition metal phosphides NF. nickel foam NiFe PBA, NiFe Prussian blue analogue NiPO, nickel phosphate hydrate NiFe PBA@NiPO@NF, NiFe Prussian blue analogue formed on nickel phosphate hydrate rods grown on NF NiPO@NF, nickel phosphate hydrate rods constructed on the surface of nickel foam XRD, X-ray diffraction ICSD Coll. Code, Inorganic Crystal Structure Database Collection Code EDS, energy-dispersive spectroscopy FT-IR, Fourier transform infrared SEM, scanning electron microscope XPS, X-ray photoelectron spectroscopy RT, room temperature NiP@NF, prepared by phosphidation of NiPO@NF RuO2@NF, RuO2 paste on NF NiFe PBA@NF, NiFe PBA grown directly on nickel foam NiFeP@NF, prepared by phosphidation of NiFe PBA@NF R_{ct} , charge transfer resistance

CP, chronopotentiometry

Pt/C@NF, commercial 20 wt % platinum on graphitized carbon black pasted on nickel foam

ECSA, electrochemical surface area

 C_{dl} electrochemical double-layer capacitance

TEM, transmission electron microscopy

HRTEM, high-resolution TEM

RHE, reversible hydrogen electrode

LSV, linear sweep voltammetry

CV, cyclic voltammetry

EIS, electrochemical impedance spectroscopy

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Research Article

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Supporting Information

Bifunctional and Self-supported NiFeP-Layer-Coated NiP Rods for Electrochemical Water Splitting in Alkaline Solution

Fangyuan Diao¹, Wei Huang¹, Georgios Ctistis², Hainer Wackerbarth², Yuan Yang³, Pengchao Si³, Jingdong Zhang¹, Xinxin Xiao^{1*}, Christian Engelbrekt^{1*}

¹ Department of Chemistry, Technical University of Denmark, DK-2800 Kongens Lyngby, Denmark.

² Institut f
ür Nanophotonik G
öttingen e.V., Department of Photonic Sensor Technology, Hans-Adolf-Krebs-Weg 1, 37077 G
öttingen, Germany

³ Key Laboratory for Liquid-Solid Structural Evolution and Processing of Materials (Ministry of Education), Research Center for Carbon Nanomaterials, School of Materials Science and Engineering, Shandong University, Jinan 250061, P. R.

* Xinxin Xiao: xixiao@kemi.dtu.dk

* Christian Engelbrekt: cheng@kemi.dtu.dk

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Supplementary References

S1. Supplementary SEM images, XRD patterns, FT-IR spectra, XPS spectra, and Raman spectra of control samples



Figure S1. (a) SEM image and (b) XRD pattern of NF.



Figure S2. XRD pattern of NiPO@NF.



Figure S3. SEM images (a, b) and EDS results (c) of NiPO@NF.



Figure S4. (a–c) FT-IR and (d–f) Raman spectra of intermediate and final materials. Comparison between (a, d) NiPO@NF and NF, (b, e) NiPO@NF and NiFe PBA@NiPO@NF, and (c, f) NiFe PBA@NiPO@NF and NiFeP@NiP@NF. (g) Magnified CN-region of the Raman spectrum of NiFe PBA@NiPO@NF. (h) Magnified D-/G-band region of the Raman spectra of NiFeP@NiP@NF and NiFeP@NF.



 $\label{eq:Figure S5.} \ensuremath{\operatorname{SEM}}\xspace{0.5ex} \ensuremath{\operatorname{SE$

Note: High-quality growth of NiPO rods bunches is a crucial step for the final product. The morphology is influenced by the ions in the solution. Figure S4a and S4b show the NiPO on NF fabricated without NiCl₂ and FeCl₃, looking like bushes sparsely growing on the NF surface. However, the NiPO grew uncontrollably and blocked the porous structure of NF even if in the presence of a slight amount of Ni²⁺ in the solution. In comparison, the NiPO@NF fabricated in the solution with both NiCl₂ and FeCl₃ (Figure S3a and S3b) shows more uniform morphology.



 $\label{eq:Figure S6.} \ensuremath{\mathsf{SEM}}\xspace \ensuremath{\mathsf{sem}}\xspace \ensuremath{\mathsf{sem}}\xspace \ensuremath{\mathsf{NiFe}}\xspace \ensuremath{\mathsf{PBA}}\xspace \ensuremath{\mathsf{NiFe}}\xspace \ensuremath{\mathsf{NiFe}}\xspace \ensuremath{\mathsf{PBA}}\xspace \ensuremath{\mathsf{sem}}\xspace \ensuremath{\mathsf{NiFe}}\xspace \ensuremath{\mathsf{PBA}}\xspace \ensuremath{\mathsf{NiFe}}\xspace \ensuremath{\mathsf{NiFe}}\xspace \ensuremath{\mathsf{PBA}}\xspace \ensuremath{\mathsf{sem}}\xspace \ensuremath{\mathsf{max}}\xspace \ensuremath{\mathsfmax}}\xspace \ensuremath{\mathsfmax}\xspace \ensuremath{}\xspace \ensuremath{}\xspa$



Figure S7. (a) XRD patterns of NiFe PBA@NiPO@NF and NiPO@NF. (b) SEM image of NiFe PBA@NiPO@NF.



Figure S8. XPS survey spectrum (a), and high-resolution XPS spectra of Ni 2p (b), Fe 2p (c), K 2p (d), N 1s (e), and C 1s (f) of the NiFe PBA@NiPO@NF.



 $Figure \, S9. \, {\rm SEM} \ {\rm images} \ of \ NiFe P@NiP@NF \ with \ different \ magnifications.$



 $\label{eq:Figure S10.} {\bf SEM}\, images\, (a,b,c)\, and\, XRD\, pattern\, (d)\, of\, NiP@NF.$


Figure S11. (a-e) TEM and (f) HRTEM image of a single rod of NiFeP@NiP. EDX spectra are recorded locally at points 1 and 2 (d), with the K:Ni:Fe:P atomic ratio of 0.3:3.9:1:10 and 0.4:1.0:1:8.4, respectively.

Note: Because the rod and the outer layer are relatively thick and the NiFeP layer is easily oxidized in air, it is difficult to observe lattice fringes. A representative HRTEM image (Figure S11f) shows a fringe spacing of 0.246 nm, most likely corresponding to the (301) planes of Ni12P5. Unfortunately, we were not able to obtain more useful information from HRTEM.



Figure S12. High-resolution XPS spectra of C 1s (a) and N 1s (b) of NiFeP@NiP@NF.



Figure S13. High-resolution $\operatorname{Ni}2p\operatorname{XPS}$ spectra of the surface $\operatorname{NiP@NF}(blue)$ and

NiFeP@NiP@NF.

S2. Supplementary electrochemical polarization curves



Figure S14. (a) SEM images of NiFe PBA@NF; (b) Polarization curve of NiFe PBA@NF and NiFeP@NiP@NF; (c) SEM image of NiFeP@NF; (d) Polarization curve of NiFeP@NF and NiFeP@NiP@NF.



Figure S15. Polarization curves of NiFeP@NiP@NF, NiP@NF, NiPO@NF, NiFe PBA@NiPO@NF, RuO₂ on NF and NF without *iR*-correction in 1.0 M KOH.



Figure S16. Electrochemical OER performance measurements in 1.0 M KOH. (a) Polarization curves of NiFeP@NiP@NF-*t* obtained from the phosphidation of NiFe PBA@NiPO@NF-*t* (*t* = 1, 3, 6, 12 and 24 h). (b) Polarization curves of NiFeP@NiP@NF-*T* (*T* = 250, 350, 450 and 550 °C).

Note: The OER activity of NiFeP@NiP@NF-t (t = 1, 3, 6, 12 and 24 h) and NiFeP@NiP@NF-T (T = 250, 350, 450 and 550 °C) were investigated to find the optimal phosphidation conditions. As shown in Figure S11a, the sample soaked in the mixed solution of Ni²⁺/sodium citrate and K₃[Fe(CN)6] for 6 h delivers the superior activity. Less reaction time leads to the insufficient catalyst loading. However, if the reaction time is too long, the resulted thick layer comes along with high impedance and thus reduced catalytic activity.¹

Meanwhile, the phosphidation temperature applied should be moderate, high enough to proceed phosphidation while not too high to destroy the structure of the catalyst.²Among the samples with different phosphidation temperatures, NiFeP@NiP@NF-450 °C shows the best OER performance.



Figure S17. Long-term OER and HER stability test of NiFeP@NiP@NF at the current density of





Figure S18. Polarization curves of NiFeP@NiP@NF, NiP@NF, NiPO@NF, NiFe PBA@NiPO@NF, RuO $_2$ on NF and NF without iR correction in 1.0 M KOH.

S3. Electrochemical-double-layer capacitance measurement in non-faradaic region



Figure S19. Cyclic voltammograms in the region of 0.67-0.77 V vs. RHE for NiFeP@NiP@NF (a) and NiP@NF (b) under different scan rates. (c) The half of the peak current density difference $(\Delta J=J_a-J_c)$ at 0.72 V vs. RHE plotted against the scan rate. The fitted linear regression is used to estimate C_{dl}.



Figure S20. ECSA normalized OER (a) and HER (b) polarization curves for NiFeP@NiP@NF and NiP@NF.



S4. Post-test characterization

Figure S21. XRD patterns of the as-prepared fresh NiFeP@NiP@NF and the sample after 120 h OER stability test (a) and after 120 h HER stability test (b), where a1, b1 and b2 show the locally enlarged view of figure a and b; test condition: CP test at a current density of 10 mA cm⁻².



 $\label{eq:Figure S22.} SEM \, images \, of \, NiFe P@NiP@NF \, after \, 120 \, h \, \, OER \, (a, b) \, and \, HER \, (c, d); \, test \, condition: \\ CP \, test \, at \, a \, current \, density \, of \, 10 \, mA \, cm^{-2}.$



Figure S23. High-resolution XPS spectra of (a) Ni 2p, (b) Fe 2p, (c) O 1s, and (d) P 2p of the sample NiFeP@NiP@NF after 120 h OER (test condition: CP test at a current density of 10 mA cm ⁻²).



Figure S24. High-resolution XPS spectra of (a) Ni 2p, (b) Fe 2p, (c) O 1s, and (d) P 2p of the sample NiFeP@NiP@NF after 120 h HER (test condition: CP test at a current density of 10 mA cm⁻²).

S5. Supplementary summarizing tables

| Catalyst | η (mV) @ j [mA cm ⁻²] | Tafel slope [mV dec ⁻¹] | Loading [mg cm ⁻²] | Ref. |
|---|--------------------------------------|---|-----------------------------------|--------------|
| NiFeP@NiP@NF | $228@10\ 252@100$ | 60.7 | ~3 | This work |
| Ni-Fe _x P@NF | $254@50\ 267@100$ | 37 | ~8 | 3 |
| NiFeP@N, C doped carbon cloth | 270@100 | 47 | ~2.67 | 4 |
| Ni-P@carbon fiber paper | ~270@10 | 73 | 25.8 | 5 |
| $NiMoP_{2}$ nanowires @carbon cloth | 260@20 | 90.6 | ~5 | 6 |
| Ni-Co-Phollow nanobricks | 270@10 | 76 | 2.0 | 7 |
| N-doped carbon encapsulated $\operatorname{Co}_{x}\operatorname{Fe}_{1:x}P$ | 299@10 | 44 | 0.28 | 8 |
| nanoparticles | | | | |
| Nickelphosphite (Ni ₁₁ (HPO ₃) ₈ (OH) ₆) | 232@10 | 91 | ~3 | 9 |
| (Ni, Fe) \mathbf{S}_2 @Mo \mathbf{S}_2 @ carbon fiber paper | 270@10 | 43.21 | n/a | 10 |
| P, Al codoped porous NiO@NF | 310@100 | 36 | n/a | 11 |
| FeS/NiS@NF | 203@10 | 39 | n/a | 12 |
| Ni/NiFeMoO _x /NF | 255@10 | 35 | 1.8 | 13 |
| $\mathrm{CoS}_{\mathrm{x}}/\mathrm{Ni}_{3}\mathrm{S}_{2}@\mathrm{NF}$ | 280@20 | 105.4 | ~2.83 | 14 |
| FeNiP/N,P-modified carbon sheets | 318@10 | 103 | 0.25 | 15 |
| Fe doped V_2P&Ni_2P@NF | 201@10 | 75 | n/a | 16 |
| Fe2 doped Ni-Co-P nanoplates@carbon cloth (Fe1-NiCoP@CC) | 293@50 | 37.8 | 1.2 | 17 |

Table S1. Comparison of OER activity with reported non-noble OER catalysts in 1.0 M KOH.

| Catalyst | η (mV) @ j [mA cm ⁻²] | Tafel slope [mV dec ⁻¹] | Loading [mg cm ⁻²] | Ref. |
|--|--------------------------------------|--|-----------------------------------|-----------|
| NiFeP@NiP@NF | 105@10 | 97.9 | ~3 | This work |
| Ni-Fe _x P@NF | 119@10 | 80 | ~8 | 3 |
| NiFeP@N, C doped carbon cloth | 94@10 | 70 | ~2.67 | 4 |
| Ni-P@carbon fiber paper | 117@10 | 85.4 | 25.8 | 5 |
| NiMoP ₂ nanowires@carbon cloth | 199@100 | 112 | ~5 | 6 |
| Ni-Co-Phollow nanobricks | 107@10 | 46 | 2.0 | 7 |
| N-doped carbon encapsulated $\operatorname{Co}_{x}\operatorname{Fe}_{1\cdot x}\operatorname{P}$ | 139@10 | 57 | 0.28 | 8 |
| nanoparticles | | | | |
| Nickel phosphite (Ni ₁₁ (HPO ₃) ₈ (OH) ₆) | 121@10 | 102 | ~3 | 9 |
| (Ni, Fe)S $_2$ @MoS $_2$ @carbon fiber | 130@10 | 101.22 | n/a | 10 |
| | 199010 | 01 | . [. | 11 |
| P, Al codoped porous NiO@NF | 138@10 | 81 | n/a | |
| FeS/NiS@NF | 144@10 | 120 | n/a | 12 |
| Ni/NiFeMoO _x @NF | 117@100 | 76 | 1.8 | 13 |
| $\mathrm{CoS}_{\mathrm{x}}/\mathrm{Ni}_{3}\mathrm{S}_{2}@\mathrm{NF}$ | 204@10 | 133.32 | ~2.83 | 14 |
| FeNiP/N,P-modified carbon sheets | 181@10 | 111 | 0.25 | 15 |
| Fe doped V ₂ P&Ni ₂ P@NF | 66@10 | 37 | | 16 |
| Fe1 doped Ni-Co-P nanoplates@carbon cloth (Fe1-NiCoP@CC) | 60@10 | 51.1 | 1.2 | 17 |

Table S2. Comparison of HER activity with reported non-noble HER catalysts in 1.0 M KOH.

| Catalyst | Voltage (V) @ <i>j</i> [mA cm ⁻²] | Loading [mg cm ⁻²] | Ref. |
|---|--|-----------------------------------|-----------|
| NiFeP@NiP@NF | $1.57@10 \\ 1.64@20$ | ~3 | This work |
| Ni-Fe _x P@NF | 1.62@10 | ~8 | 3 |
| NiFeP@N, C doped carbon cloth | 1.54@10 | ~ 2.67 | 4 |
| Ni-P@carbon fiber paper | 1.63@10 1.73@20 | 25.8 | 5 |
| $NiMoP_2nanowires@carboncloth$ | 1.67@10 | ~5 | 6 |
| Ni-Co-Phollow nanobricks | 1.62@10 | 2.0 | 7 |
| $N\text{-}doped carbon\\ encapsulated Co_xFe_{1\cdot x}P nanoparticles$ | 1.66@10 | 0.28 | 8 |
| Nickel phosphite (Ni $_{11}$ (HPO $_3$) $_8$ (OH) $_6$) | 1.60@10 | ~3 | 9 |
| (Ni, Fe)S_2@MoS_2@carbon fiber paper | 1.56@10 | n/a | 10 |
| P, Al codoped porous NiO@NF | 1.59@10 | n/a | 11 |
| FeS/NiS@NF | 1.618@10 | n/a | 12 |
| Ni/NiFeMoO _x @NF | 1.63@100 (<i>iR</i> -corrected) | 1.8 | 13 |
| $CoS_x/Ni_3S_2@NF$ | 1.863@50 | ~2.83 | 14 |
| FeNiP/N,P-modified carbon sheets | 1.71@10 | 1.0 | 15 |
| $Fe \ doped \ V_2 P \& Ni_2 P @ NF$ | 1.56@10 | n/a | 16 |
| Fe1-NiCoP@CC Fe2-NiCoP@CC | 1.61@10 | 1.2 | 17 |

Table S3. Comparison of water splitting activity with representative non-noble bi-functional catalysts in alkaline solution.

| Sample | $R_s[\Omega]$ | $R_{ct}\left[\Omega ight]$ | CPE |
|------------------|---------------|----------------------------|---|
| NiFeP@NiP@NF | 2.25 | 2.37 | $Y_{0}: 425 \text{ mMho*s^N} $ N = 0.784 |
| NiFe PBA@NiPO@NF | 2.39 | 8.17 | Y:126 mMho*s^N N = 0.846 |
| NiP@NF | 2.66 | 10.9 | Y:513 mMho*s^N 0 = 0.82 |
| NiPO@NF | 2.43 | 22.3 | Y:32.0 mMho*s^N 0 = 0.777 |
| RuO2@NF | 2.29 | 62.8 | Y : 13.4 mMho*s^N N = 0.798 |
| NF | 2.54 | 380 | Y: 6.00 mMho*s^N 0 = 0.699 |

Table S4. EIS fitting results for OER at 1.50 V vs. RHE with the equivalent circuit model in Figure S13.

Table S5. EIS fitting results for HER at -0.20 V vs. RHE with the equivalent circuit model in Figure S13.

| Sample | $R_s[\Omega]$ | $R_{ct}\left[\Omega ight]$ | CPE |
|------------------|---------------|----------------------------|--|
| NiFeP@NiP@NF | 2.44 | 8.26 | Y_:19.1 mMho*s^N N = 0.706 |
| NiFe PBA@NiPO@NF | 2.67 | 24.5 | Y : 0.182 mMho*s^N N = 0.863 |
| NiP@NF | 2.534 | 12.5 | $Y_0: 2.43 \text{ mMho*s^N} $ N = 0.802 |
| NiPO@NF | 2.27 | 38.8 | Y_0:0.292 mMho*s^N N = 0.851 |
| Pt/C@NF | 4.79 | 0.996 | $Y_{0}: 16.8 \text{ mMho*s^N} $ N = 0.744 |

| NF | 2.76 | 51.3 | Y_:0.248 mMho*s^N |
|----|------|------|-------------------|
| | | | N = 0.834 |

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Chapter 4

Exploration of structure and oxygen evolution reaction performance of CoFe Prussian blue analogue and its three derivatives

Prussian blue analogue (PBA) with a general formula of $A_xM[M'(CN)_6]_{1-yYy}$ nH₂O (where A represents the alkali metal ions like Na⁺ and K⁺, M and M' correspond to different transition metal elements (e.g. Fe, Co, Ni, Zn, and Cu), and γ represents the [M'(CN)_6] vacancy), is a kind of porous coordination polymers (PCPs). The framework of PBA crystal is constructed by repeatable M-C=N-M' units. There are wide choices of the transitional metal ions (M), hexacyanometallates ([M'(CN)_6]) and the species (A) hosted in the interstitial space for different PBAs. These prepared PBAs can be transformed into other active materials like metal oxides, metal phosphides, metal sulfides, alloy particles, and metal@C composites by heat treatment in different conditions or hydrothermal methods to fabricate active OER electrocatalysts. However, studies on the influence of species (A) in the interstitial space on the morphology evolution during heat treatment and OER performance of PBA derivatives are rarely reported.

In this work, a kind of CoFe PBA (K1.1Co[Fe(CN)6]0.84Y0.16 \cdot nH2O) was first synthesized. Then the K⁺ were replaced by NH4⁺ with a hydrothermal method in urea aqueous solution, forming U-CoFe PBA ((NH4)1.87Co[Fe(CN)6]0.82Y0.18 \cdot mH2O). Products of CoFe PBA and U-CoFe PBA under heat treatment at 400 °C, Ar atmosphere were studied. It is found that the products after heat treatment were different from the pristine PBAs in terms of morphology and crystalline structure. Electrochemical tests of OER performance were performed on CoFe PBA, U-CoFe PBA, and their derivatives after heat treatment (Ar-CoFe PBA and Ar-U-CoFe PBA). Ar-U-CoFe PBA exhibited the best OER performance ($\eta_{10} = 305$ mV) and excellent stability in 1.0 KOH. The morphology of Ar-U-CoFe PBA after the stability test was characterized by TEM, indicating considerable stability of the electrocatalyst.

This work has been summarized as a manuscript for a journal, co-authored by Fangyuan Diao, Mikkel Rykær Kraglund, Huili Cao, Kai Gao, Yuan Yang, Xiaomei Yan, Pengchao Si, Qingfeng Li, Christian Engelbrekt, and Xinxin Xiao.

This chapter is given below with the format of an article for a journal.

Structure and Oxygen Evolution Reaction Performance of CoFe Prussian Blue Analogue and Three Derivatives

Fangyuan Diao^a, Mikkel Rykær Kraglund^b, Huili Cao^a, Kai Gao^a, Yuan Yang^c, Xiaomei Yan^a, Qingfeng Li^b, Pengchao Si^c, Christian Engelbrekt^{a*}, Xinxin Xiao^{a*}

^a Department of Chemistry, Technical University of Denmark, DK-2800 Kongens Lyngby, Denmark.

^b Department of Energy Storage and Conversion, Technical University of Denmark, DK-2800 Kongens Lyngby, Denmark.

^c Key Laboratory for Liquid-Solid Structural Evolution and Processing of Materials (Ministry of Education), Research Center for Carbon Nanomaterials, School of Materials Science and Engineering, Shandong University, Jinan 250061, P. R. China.

*Corresponding authors: Christian Engelbrekt (cheng@kemi.dtu.dk); Xinxin Xiao (xixiao@kemi.dtu.dk).

Abstract: Prussian blue analogues (PBAs) are an important group of framework-like coordination polymers with an inherent ordered structure and abundant and tunable metal ion sites. PBAs and their derivatives represent a large group of functional materials for various electrochemical applications, including electrochemical oxygen evolution reaction (OER). In this work, it is found that all K⁺ in the interstitial space of CoFe PBA can be replaced by NH4⁺ in a heated aqueous urea solution (U-CoFe PBA), altering the nature of CoFe PBA. Heat treatment of PBAs in Ar with a moderate temperature can effectively generate CoFe alloy particles or create defects on the remaining cubic PBA structure, a versatile strategy to modulate the OER performance. The sample after urea and heat treatment (Ar-U-CoFe PBA) performs best in OER, registering overpotentials of 270 and 305 mV at 1 and 10 mA cm⁻², respectively, and exhibits remarkable stability.A single-cell alkaline electrolyzer with an Ar-U-CoFe PBA anode and a Pt/C cathode requires an initial cell voltage of 1.66 V to achieve 100 mA cm⁻² at 80 °C and an activation energy of 14.4 kJ mol⁻¹, as well as showing excellent operational stability with negligible degradation after 100 h. The excellent OER performance of Ar-U-CoFe PBA is ascribed to the optimized chemical states of Co and Fe, a large surface area, and the amorphous and defect-rich structure of the PBA cubes.

Keywords: Prussian blue analogues; PBA derivatives; Oxygen evolution reaction; Electrolyzer

1. Introduction

Prussian blue analogues (PBAs) represent a family of materials constructed by metalcyanide frameworks sharing the chemical formula A_xM[M'(CN)₆]_{1-y} y_y nH₂O (where A represents the alkali metal ions like Na⁺ and K⁺, M and M' correspond to different transition metals (e.g. Fe, Co, Ni, and Cu), and y represents the [M'(CN)6] vacancy), which are simplified as MM'PBAs.^{1,2} The rich variety of metal elements and their ratios enable a large number of PBA family members, featuring a wide range of properties and applications.³ For example, CoFe PBAs with a face-centered cubic structure show photomagnetic effect, which is sensitive to the species of alkali metal ions.^{4,5} PBAs are widely explored active materials of secondary batteries of alkali metal ions (e.g. Li⁺, Na⁺, and K⁺), alkaline earth metal ions, and other multivalent ions (e.g. Mg²⁺, Ca²⁺, Zn²⁺, and Al³⁺), because their open channels and interstitial space (3.2 Å in diameter for the open <100> channels; 4.6 Å in diameter for the interstitial space) constructed by M'-C=N-M could allow the insertion/de-insertion offoreign cations.^{3,6} Some small ions or molecules can also be accommodated in the interstitial space of PBA. For example, PBAs are good candidates for NH₄⁺-ion aqueous rechargeable batteries, which are attracting growing attention for large-scale electricity storage due to their advantage of low cost and high safety.^{7,8} Wessells et al. indicated that NH₄⁺ intercalates into PBA at a higher potential than Na^+ and K^+ because of the larger ion size of NH_{4^+} leading to a lower Gibbs free energy.9 Prussian blue (PB) and PBAs behave well in gas absorption applications with gases like H₂, CO₂, and NH₃¹⁰⁻¹³ Takahashi et al. found that PB and another two PBAs (CoCo PBA and CuFe PBA) can capture ammonia in ambient air at interstitial and vacancy sites, and the absorbed ammonia prefers to transform into NH₄⁺ in the presence of H₂O with prolonged exposure time.¹³ The above literature implies that the alkali metal ions of PBAs can be exchanged with other cations.

PBAs and their derivatives are also regarded as promising candidates for oxygen evolution reaction (OER) catalysts, featuring low-cost, simple synthesis, ease of scale-up, adjustable metal active sites, etc.^{14,15} Lee and coworkers used experimental measurements and density functional theory calculations to construct a volcano plot of the OER activity of isomorphous $Na_xM[Fe(CN)_6]_{1-y}$ y nH₂O (MFe PBA, M=V, Co, Ni, and 110

Fe), concluding that NiFe PBA and CoFe PBA exhibit better OER performance.¹⁶ Han et al. studied the performance of Co₄(Fe(CN)₆)_{2.67} (H₂O)_{15.33} growing on fluorine-doped tinoxide (FTO) glass in a wide pH range (1 < pH < 13), showing excellent activity, stability, and corrosion resistance even in strong acid condition (pH= 2).¹⁷ Heat treatment is a commonly used methods to fabricate PBA derivatives, leading to a range of oxides, sulfides, phosphides, and alloys through adjusting the atmosphere, temperature, and other experimental parameters. Heat treatment can also induce defects to the PBAs. For example, Zeng et al. reported that the heat treatment with an additional saltencapsulation pre-step could improve the OER performance because salt encapsulation can covert NiFe PBA cubes into an irregular nanoparticle-connected and hollow structure to expose more active sites for the catalytic reaction.¹⁸ To transform PBAs into metal nitrides, Kang et al. performed calcination at 450 °C in NH₃ atmosphere to achieve nitridation.^{19,20} However, the influence of the intercalated species in the interstitial space of PBAs on the structural and compositional evolution and the corresponding OER performance after heat treatment is rarely reported.

In this contribution, we study CoFe PBA synthesized via a facile co-precipitation method and its three derivatives including a urea-treated product (U-CoFe PBA), heat-treated product (Ar-CoFe PBA), and heat-treated U-CoFe PBA (Ar-U-CoFe PBA). Through comprehensive characterization, it is found that a hydrothermal step with aqueous urea solution can effectively replace K⁺ in the interstitial space of CoFe PBA with NH₄⁺. This exchange leads to completely different behavior of the heat-treated derivatives and different alkaline OER performance. Ar-CoFe PBA and Ar-U-CoFe PBA show superior activity to CoFe PBA and U-CoFe PBA, while Ar-U-CoFe PBA shows higher stability over Ar-CoFe PBA, the derivative without urea treatment.

2. Experimental

2.1. Chemicals and Materials

All chemicals were used as received without further purification unless otherwise mentioned. Sodium citrate dehydrate (Na₃C₆H₅O₇·2H₂O, \geq 99%), cobalt (II) nitrate hexahydrate (Co(NO₃)₂·6H₂O, \geq 98%), urea (NH₂CONH₂, \geq 99.0%), potassium hexacyanoferrate(III) (K₃[Fe(CN)₆], \geq 99%), 2-propanol ((CH₃)₂CHOH, anhydrous, \geq 99.5%), hydrochloric acid (HCl, 37 wt%, 1.2 g mL⁻¹ at 25 °C), and NafionTM perfluorinated ion-exchange resin (10 wt% in H₂O) were purchased from Sigma-Aldrich. Ethanol

absolute (\geq 99.5%) was provided by VWR Chemical BDH. Carbon black (75 m² g⁻¹, \geq 99.9%) and 10 wt% platinum on carbon black (Pt/C) were bought from Alfa Aesar by Therm o Fisher Scientific (Germany). 1.0 M potassium hydroxide (KOH, pH=14) solution was purchased from Fisher Chemical. Aemion+ TM High IEC membrane (AF2-HLE8-40-X, thickness: 40 µm) was supplied by Ionomr Innovations, which was immersed in 1.0 M KOH for 24 h before usage. Aemion+ TM High IEC ionomer (AP2-HNN8-00-X, Ionomr Innovations) was received in powder. Nickel foam (thickness: 300 µm) was purchased from Suzhou Jiashide Metal Foam Co., Ltd., China, which was cleaned with ethanol, 1.0 M HCl solution, and water successively before usage. Ultrapure water was prepared with arium® pro VF Ultrapure Water System (Sartorius AG, Germany, 18.2 MΩ·cm).

2.2. Preparation of CoFe PBA and its derivatives

i) Preparation of CoFe PBA. CoFe PBA cubes were synthesized by a facile coprecipitation method.²¹ 100 mL aqueous solution of 2.0 mmol K₃[Fe(CN)6] was slowly poured into 100 mL aqueous solution containing 3.0 mmol Co(NO₃)₂ 6H₂O and 4.5 mmol sodium citrate under stirring. The obtained solution was stirred for another 20 min and then aged in an oven at 40 °C for 24 h. Finally, the precipitate was collected via centrifugation, washed with water three times, and dried in a vacuum oven at 80 °C for 24 h.

ii) Preparation of U-CoFe PBA. 0.300 g CoFe PBA was dispersed in a 90 mL aqueous solution containing 0.901 g urea. The mixed solution was sonicated for at least 20 min and transferred to a 150 mL Teflon-lined autoclave and treated at 150 °C for 6 h. After the autoclave cooled naturally, the U-CoFe PBA powder was collected and washed with water three times by centrifugation. The sample was finally dried in a vacuum oven at 80 °C for 24 h.

iii) Heat-treatment of CoFe PBA and U-CoFe PBA. The obtained CoFe PBA and U-CoFe PBA were treated in a tube furnace at 400 °C for 2 h with a heating rate of 2 °C min⁻¹ under Ar atmosphere. After natural cooling to room temperature, samples were collected and labelled as Ar-CoFe PBA and Ar-U-CoFe PBA, respectively. Control samples treated at other temperatures (200, 300, and 600 °C) were named as Ar-CoFe PBA T °C and Ar-U-CoFe PBA T °C, where T represents the heat-treatment temperature.

2.3. Characterization methods

Powder X-ray diffraction (XRD) patterns were acquired with a Huber G670 Guinier camera using Cu Ka1 radiation ($\lambda = 1.54056$ Å) with 40 kV and 40 mA. X-ray photoelectron spectroscopy (XPS) results were collected on a Thermofisher Scientific Nexsa XPS system. Fourier transform infrared (FT-IR) spectra were collected on a Bruker Alpha-P FT-IR spectrophotometer. The material morphology was characterized with a scanning electron microscope (SEM, FEI Quanta FEG 250 Analytical ESEM). Transmission electron microscopy (TEM) images, high-resolution TEM (HRTEM) images, and the corresponding energy dispersive spectroscopy (EDS) analysis were collected with a Tecnai T20 G2 at 200 kV equipped with a TVIPS XF416 4k × 4k camera. Thermal gravimetric analysis (TGA) was measured at a heating rate of 2 °C min⁻¹ in N₂ and heated up to 700 °C on a thermogravimetric analyzer (Mettler Toledo). The specific surface area was measured using nitrogen adsorption at 77 K by the Brunauer-Emmett-Teller (BET) method with a Micromeritics ASAP 2020.

2.4. Electrochemical measurements

Primary electrochemical tests of the catalysts were carried out in a three-electrode cell containing O₂-saturated 1.0 M KOH at room temperature on a CHI 760C electrochemical workstation (CH Instruments, Inc. USA), or an Autolab potentiostat (Eco Chemie, the Netherlands). A carbon rod and an Hg/HgO (1.0 M KOH) electrode were used as the counter electrode and the reference electrode, respectively. All potentials were calibrated to the reversible hydrogen electrode (RHE) ($E_{vs. RHE} = E_{vs. Hg/HgO} + 0.098 + 0.059 \text{ pH}$). The catalyst ink was prepared by dispersing 4.0 mg of the sample and 2.0 mg of carbon black in a mixture of 25 µL Nafion solution (10 wt% in water), 250 µL water, and 750 µL 2propanol. After ultrasonication for 1 h, 10 µL of the catalyst ink was drop-cast onto the polished rotating disk glassy carbon electrode (RDE, disk area: 0.1963 cm²) and dried in the air, leading to a final catalyst loading of ~0.20 mg cm⁻². Linear sweep voltammetry (LSV) and cyclic voltammetry (CV) curves without iR compensation were collected at a scan rate of 5 mV s⁻¹ after CV shas stabilized. The overpotential (η) at a specific current density (i) is calculated by the equation: $\eta = E(i) - 1.23$ V, where the E(i) represents the potential at the current density of i in mA cm⁻². Electrochemical impedance spectroscopy (EIS) measurements were carried out at the potential of 1.60 V in the frequency range of 10 kHz - 0.01 Hz, with an amplitude of 5 mV. LSV and CV curves are presented as collected without *i*R compensation unless specified.

The operational stability of OER was preliminarily studied with chronopotentiometry (CP) at 10 mA cm⁻² for 20 h on RDE at 1600 rpm to remove generated gas bubbles. Ar-CoFe PBA and Ar-U-CoFe PBA were also pasted on nickel foam (mass loading: 2.0 mg cm⁻², without the addition of carbon black) for a 40 h CP test at 10 mA cm⁻² in 1.0 M KOH at room temperature. The samples after stability tests were dried in vacuum for further XPS and TEM analysis.

A two-electrode water electrolysis test was performed in a circular single-cell electrolyzer. 1.0 M aqueous KOH solution was circulated throughout the cell at a flow rate of 80 mL min⁻¹. The electrolyte temperature was controlled by heating elements and thermocouples in the endplates. The Aemion+ electrolysis membrane was used to separate the anode and cathode chambers. Ar-U-CoFe PBA (~ 8.6 mg cm⁻²) and Pt/C (~ 3.7 mg cm⁻²) on the Ni foam, both prepared by a spray coating method, were employed as the anode and cathode, respectively. Specifically, the catalyst ink was prepared by adding 0.04 g catalyst into a mixed solution of 1.40 g 2-propanol and 1.00 g 1 wt% ionomer solution (volume ratio of ethanol: H₂O=1:1) under sonication at room temperature to obtain a homogenous ink. The total solid content (catalyst and ionomer, with a weight ratio of 4:1) in the catalysts ink was 2.05 wt%. The catalyst ink was sprayed with an airbrush paint sprayer (Art. 17-372, BILTEMA) on the Ni foam placed on a hotplate at 120 °C. Polarization curves at various operational temperatures of 40, 60, and 80 °C, alongside CP curves at 100 mA cm⁻² and 80 °C over a time course of 100 h, were obtained.

3. Results and discussion

3.1. Synthesis and structural characterization



Scheme 1. Schematic illustration of the synthesis route for CoFe PBA, U-CoFe PBA, Ar-CoFe PBA, and Ar-U-CoFe PBA.

CoFe PBA and its three derivatives are fabricated following the route as illustrated in **Scheme 1**. CoFe PBA is synthesized by the co-precipitation of cobalt nitrate and potassium hexacyanoferrate,²² experiencing the reaction between Co^{2+} and $[\text{Fe}(\text{CN})\epsilon]^{3+}$ in the solution to form the CoFe PBA precipitate. During this process, citrate ions are also involved by coordinating with Co^{2+} , posing control over the nucleation and crystal growth.²¹ After a reaction time of 24 h at 40 °C, a deep purple precipitate is collected by centrifugation, displaying a uniformly cubic morphology (side length: 127 ± 9 nm) and smooth surfaces as confirmed by SEM (**Figure S1a**) and TEM (**Figure 1a**). The selected area electron diffraction (SAED) pattern of an ensemble of CoFe PBA cubes shows a polycrystalline feature (**Figure 1b**), with circles from the inside to the outside that are attributed to the plane (2 0 0), (2 2 0), and (4 0 0), respectively. These planes are in accordance with peaks at 17.6, 25.1, and 35.7° of the corresponding XRD pattern (**Figure 1**).

2a) (Inorganic Crystal Structure Database (ICSD) Collection Code: 164830).²³ The lattice parameter of CoFe PBA is calculated to be 10.06 Å from the XRD pattern, which is consistent with the lattice fringe spacing measured on the HRTEM image (Figure 1c). With the assistance of EDS (Figure S2), the final formula of CoFe PBA is determined to be K1.1Co[Fe(CN)6]0.8y0.2 nH2O. The chemical bonds in CoFe PBA are further examined by FT-IR (Figure 2b). The broad bands at around 3387 and 1608 cm⁻¹ correspond to the O-H stretching mode and H-O-H bending vibration from water, respectively.²⁴ The band at 3624 cm⁻¹ can be explained by the -OH stretching mode in Metal-OH (Metal refers to Co and Fe in CoFe PBA, -OH is from absorbed H2O).^{25,26} This observation further confirms the presence of water molecules in CoFe PBA. The band at 2087 cm⁻¹ is assigned to the stretching vibration of the CN groups in Fe-CN-Co units. In the far-IR region, two bands representing Fe-CN and Co-CN flexural vibration absorption appear at 592 and 471 cm⁻ ¹, respectively.²⁷

U-CoFe PBA, a brown powder, is obtained by the hydrothermal treatment of CoFe PBA in an aqueous urea solution at 150 °C. Such a hydrothermal procedure does not destroy the cubic shape of the pristine PBA, as indicated by SEM (Figure S1b) and TEM (Figure 1d) images. U-CoFe PBA registers the same particle size $(130 \pm 9 \text{ nm})$ and smooth surfaces as the pristine PBA. With the similar powder XRD pattern and SAED pattern, U-CoFe PBA shares similar crystalline characteristics with CoFe PBA. Notably, the XRD peaks of U-CoFe PBA move to a smaller angle in comparison with CoFe PBA, relative to the expansion of its cell parameter (a=10.07 Å). The HRTEM image of a single U-CoFe PBA cube (Figure 1f) further demonstrates its crystalline structure. The atomic ratio of Co to Fe in U-CoFe PBA (Co:Fe = 1:0.8) obtained by EDS analysis is identical to that of CoFe PBA (Co:Fe = 1:0.8) (Figure S2 and S3). In contrast to the crystallography, the differences between U-CoFe PBA and the pristine CoFe PBA are further revealed by EDS, XPS and FT-IR spectra. In comparison to the EDS spectrum of CoFe PBA, U-CoFe PBA finds the disappearance of the characteristic peaks of K around the energy range of 3-4 keV. The disappearance of K in U-CoFe PBA is further validated by the XPS spectra (Figure S4a). Furthermore, a new peak located at around 1412 cm⁻¹ appears in the FT-IR spectrum of U-CoFe PBA (Figure 2b), suggesting that the hydrothermal process introduces new species into U-CoFe PBA when removing K⁺ from the interstitial space in order to maintain charge neutrality. During the hydrothermal process at 150 °C, urea

reacts with water, producing CO_2 and NH_3 (Eq.1). NH_3 combines with H_2O to form $NH_3 \cdot H_2O$, which dissociates in water to form NH_{4^+} and OH^- (Eq.2).

$$CO(NH_2)_2 + H_2O \rightarrow CO_2 + 2NH_3 \tag{1}$$

$$NH_3 + H_2O \rightarrow NH_3 \cdot H_2O \leftrightarrow NH_4^+ + OH^-$$
(2)

Ultimately, NH₄⁺ in the solution could replace potassium ions in the interstitial space of CoFe PBA. NH₄⁺ is also likely to replace partial zeolitic water molecules, as indicated in the TGA curves (**Figure S5**) showing that U-CoFe PBA registers a smaller weight loss by 3.3 wt% around 150 °C than that of CoFe PBA.^{28,29} No urea is observed in U-CoFe PBA. The characteristic FT-IR peaks of urea are mainly located at 1400-1700 cm⁻¹ (**Figure S6**), including the peak of C=O at about 1675 cm⁻¹, and C-N at about 1455 cm⁻¹, quite different from that of U-CoFe PBA.^{30,31} Instead, new bands are located at around 3220 and 1412 cm⁻¹ of the FT-IR spectrum of U-CoFe PBA, which are assigned to triply degenerate stretching vibration and bending vibration of NH₄⁺, respectively, indicating the incorporation of NH₄⁺ in the U-CoFe PBA structure.^{13,32–35} In the N 1s XPS spectra of CoFe PBA (**Figure S4b**), a new peak around 402.5 eV corresponding to NH₄⁺ further supports this.^{36,37} The proposed structure of U-CoFe PBA is illustrated in **Figure 2c**. The formula of U-CoFe PBA is determined to be (NH₄)1.9Co[Fe(CN)6]0.8Y0.2 mH₂O by EDS analysis (**Figure S3**).

Another two derivatives, Ar-CoFe PBA and Ar-U-CoFe PBA, are obtained by the heat treatment of CoFe PBA and U-CoFe PBA under Ar flow at 400 °C for 2 h, respectively. Ar-CoFe PBA maintains the cubic PBA structure as shown in the SEM and TEM images (Figure S1c and Figure 2g). Nanoparticles of approximately 20 nm in diameter, can be found on the surface of the Ar-CoFe PBA cubes by TEM (Figure 1i and Figure S7). The HRTEM image of Ar-CoFe PBA (Figure 1h) exhibits a clear lattice fringe with the spacing of 0.51 nm, corresponding to the (2 0 0) plane of CoFe PBA crystal. The associated fast Fourier transform (FFT) pattern (inset of Figure 2h) indicates the angular relationships of different planes, which are also in agreement with the cubic crystal structure. Although the peaks downshift, which represents a larger cell parameter (a=10.25 Å), main peaks on the XRD pattern of Ar-CoFe PBA (Figure 2a) are consistent with CoFe PBA. These results indicate that the cubes of Ar-CoFe PBA maintain the PBA feature after heat treatment. An HRTEM image of the nanoparticle attached to the surface of the cube (inset of Figure 1i) shows lattice fringes spacing of about 0.205 nm, while EDS (Figure S7b and S7c) shows mainly Co and Fe (no K and N), and a higher

Co/Fe atomic ratio than CoFe PBA. Besides this, the XRD pattern of Ar-CoFe PBA witnesses the appearance of a new peak at around 45.2° compared to CoFe PBA, which is in accordance with the pattern of CoFe alloy (ICSD Coll. Code of 102381).¹⁸ Therefore, it can be deduced that the Co and Fe combine to form small CoFe alloy nanoparticles after losing CN ligands during the heat treatment. The FT-IR spectrum of Ar-CoFe PBA (**Figure 2b**) registers the disappearance of broad bands in the range of 3700–3000 cm⁻¹ of CoFe PBA, suggesting the loss of water molecules. Two bands at around 2072 and 2169 cm⁻¹ correspond to the stretching of CN ligands in the Fe^{II}-CN-Co³⁺ and Fe^{III}-CN-Co²⁺, respectively.^{27,38,39} Based on the above analysis, the heat treatment process at 400 °C is believed to effectively remove the water molecules, and a part of CN groups of Fe-CN-Co units in CoFe PBA, leading to under-coordinated Co and Fe that form CoFe alloy nanoparticles embedded in the cubes.



Figure 1. Morphology characterization of the samples. TEM images, SAED patterns, and HRTEM images of CoFe PBA (a-c) and U-CoFe PBA (d-f). TEM image (g), HRTEM image and the corresponding FFT pattern of the lattice on the cube (h), and HRTEM image of the nanoparticle on

the surface (i) of Ar-CoFe PBA. TEM images (j, k) and the magnified HRTEM images (l) of Ar-U-CoFe PBA. Insets of c, f, h, and i are the magnified HRTEM images of the corresponding samples.

The TEM image of Ar-U-CoFe PBA (Figure 1) shows the maintained cubic structure, with an average particle size of 117 ± 9 nm. Nanoparticle-like dark spots form in the cubes during heat treatment (Figure 1k). Besides this, some areas (diameter: ≤ 15 nm) display clear lattice fringes and other areas of the cube are disordered (Figure 1). The XRD pattern of Ar-U-CoFe PBA (Figure 2a) also shows an amorphous structure, without evident peaks. Therefore, Ar-U-CoFe PBA consists of a largely amorphous structure with sporadic nanocrystals. The FT-IR spectrum of Ar-U-CoFe PBA in Figure 2b sees the disappearance of the band at around 1412 cm⁻¹, indicating the release of NH₄⁺ from the interstitial position of the sample during heat treatment. Comparison of Ar-U-CoFe PBA T °C (T=200, 300, 600) samples (**Figure S8b**) indicates that the release of NH_{4^+} happens at 200-300 °C. Ar-U-CoFe PBA 300 °C maintains the crystalline structure of CoFe PBA, and Ar-U-CoFe PBA 600 °C displays a completely different XRD pattern from CoFe PBA (Figure S8d). Thus, the PBA structure is stable up to 300 °C and is completely deformed at 600 °C (Figure S9b). 400 °C is selected as an optimal temperature with moderate deformation of the PBA. EDS mapping of Ar-U-CoFe PBA 400 °C (simplified as Ar-U-CoFe PBA unless otherwise stated) (Figure S10) shows the homogeneous dispersion of Co, Fe, N, and C in a single cube, while the atomic ratio of Co, Fe, and N is around 1:0.8:3.9 - a higher N content than in Ar-CoFe PBA (Co:Fe:N = 1:0.8:2.8) (Figure S11 and S7a). The broad band at around 1850-2240 cm⁻¹ in the FT-IR spectrum of Ar-U-CoFe PBA contains four peaks (Figure 2b), which are assigned to the stretching vibration of the remaining disordered Fe^{II}-CN-Co²⁺ and Fe^{III}-CN-Co²⁺.^{26,40} Besides, there is only one peak in the N 1s spectra of Ar-U-CoFe PBA at around 398.1 eV, originating from the cyanide groups (Figure S12), further confirming the removal of NH4^{+,41,42} The d-spacings of these clear lattice fringes in Ar-U-CoFe PBA as shown in Figure 11 are 0.494 and 0.25 nm, which well match with planes (200) and (400) of cubic CoFe PBA. The reduction of their d-spacing is attributed to the rearrangement of Fe-CN-Co units and the lack of K⁺ or NH4⁺ filling the interstitial space. The heat treatment process at 400 °C in Ar atmosphere on U-CoFe PBA can partially remove CN from the Fe-CN-Co units, causing the collapse of its crystalline structure and leading to the amorphous characteristic of Ar-U-CoFe PBA. Besides, the heat treatment process at 400 °C also removes the coordinated H₂O in U-CoFe PBA. These reactions could create a lot of edges and defects in the cube. In



conclusion, Ar-U-CoFe PBA is a composite of disordered Fe-CN-Co units and PBA nanocrystals as illustrated in **Figure 2d**.

Figure 2. (a) XRD patterns, and (b) FT-IR spectra of CoFe PBA, U-CoFe PBA, Ar-CoFe PBA, and Ar-U-CoFe PBA. Illustrated crystal structure of U-CoFe PBA (c) and illustrated composition of an amorphous Ar-U-CoFe PBA cube (d).

Chemical valence states of Co and Fe on the surface of these 4 samples are further investigated by XPS. The Fe 2p high-resolution XPS spectra of CoFe PBA and U-CoFe PBA (**Figure 3a**) are similar in shape and position of the peak. The two peaks at 708.5 and 721.3 eV of CoFe PBA and U-CoFe PBA are ascribed to Fe^{II} 2p_{3/2} and Fe^{II} 2p_{1/2}, respectively. In Co 2p spectra (**Figure 3b**), two doublets, corresponding to Co²⁺ 2p_{3/2} and Co²⁺ 2p_{1/2} at around 780.8 and 796.4 eV and Co³⁺ 2p_{3/2} and Co³⁺ 2p_{1/2} at 782.4 and 797.6 eV, can be observed for both CoFe PBA and U-CoFe PBA. Electron transfer happens from the antibonding eg* orbital of Co²⁺ to the bonding t_{2g} orbital of Fe^{III} to maximize the ligand field stabilization energy, while the CoFe PBA is prepared with K₃[Fe(CN)6](III) and $Co^{2+4,43,44}$ The hydrothermal process which replaces K⁺ with NH₄⁺ doesn't alter the chemical state of Fe and Co. Therefore, the band at around 2087 cm⁻¹ on their FT-IR spectra is derived from Fe^{II}-CN-Co^{2+/3+} units in CoFe PBA and U-CoFe PBA (Figure 2b). The chemical valences of Fe and Co in the two heat-treatment derivatives Ar-CoFe PBA and Ar-U-CoFe PBA are different from their precursors. The high-resolution spectra of Fe 2p of Ar-CoFe PBA and Ar-U-CoFe PBA exhibit peaks representing Fe^{II} (708.4 and 721.2 eV) and Fe^{III} (710.8 and 723.6 eV) (Figure 3a), respectively. Besides this, a larger portion of Fe exhibits a higher chemical valence (Fe^{III}) on the surface of Ar-U-CoFe PBA (Fe^{III} =68 at%) compared to Ar-CoFe PBA (Fe^{III} =37 at%), which is believed to be beneficial to the OER performance.⁴⁵ There are two spin-orbit peaks at 781.7 and 796.9 eV in the high-resolution Co 2p XPS spectra of Ar-CoFe PBA and Ar-U-CoFe PBA (Figure 3b), representing a mixed oxidation state of Co²⁺ and Co³⁺, similar to previously reported Co 2p XPS spectra of Co₃O_{4.46-49} The chemical state change of Fe and Co is due to a thermally activated electron transfer along the Fe-CN-Co linkage, which usually occurs in CoFe PBAs containing alkaline ion in the lattice.^{5,50} One additional peak in the Co 2p XPS spectra of Ar-CoFe PBA at 778.3 eV is assigned to metallic Co in the cobalt-rich CoFe alloy nanoparticles on the surface. These results are consistent with the previous discussion on FT-IR spectra and TEM images analysis.



Figure 3. High-resolution XPS spectra of (a) Fe 2p and (b) Co 2p of CoFe PBA, U-CoFe PBA, Ar-CoFe PBA, and Ar-U-CoFe PBA.

3.2. OER performance and analysis

Electrocatalytic OER performance of CoFe PBA, U-CoFe PBA, Ar-CoFe PBA, and Ar-U-CoFe PBA is initially evaluated in 1.0 M KOH at room temperature with a standard three-

electrode setup. The catalyst loading is optimized (Figure S13) with a medium loading of 0.2 mg cm^{\cdot 2} displaying the best performance, which is adopted for all the remaining testing on the RDE. Figure 4a presents the *i*R-corrected (85 % *i*R compensation) LSV curves. Ar-U-CoFe PBA exhibits the best OER performance among the four samples with the smallest onset potential of ~ 1.46 V and a fast current rise with the applied potential. Ar-U-CoFe PBA requires overpotentials of 270 and 305 mV to obtain 1 and 10 mA cm⁻², respectively, 280 and 316 mV for Ar-CoFe PBA, whereas 369 and 422 mV for U-CoFe PBA, 339 and 387 mV for CoFe PBA, separately. In comparison to their derivatives, U-CoFe PBA and CoFe PBA, requiring much higher overpotentials to deliver the same current density, are not active for electrocatalytic OER in alkaline condition. The comparison of the OER performance of Ar-U-CoFe PBA T °C (T= 300, 400, and 600) by LSV is shown in Figure S14, with Ar-U-CoFe PBA 400 °C (simplified as Ar-U-CoFe PBA unless otherwise stated) registering the highest current density at the sample applied potential. This is consistent with the above structure analysis of those control samples as 400 °C increases the defects of CoFe PBA and generates CoFe alloy nanoparticles, while preserving the cube structure of CoFe PBA. The OER activity of Ar-U-CoFe PBA and Ar-CoFe PBA is comparable with other reported catalysts with similar morphology or composition such as porous CoFe PBA nanocubes fabricated by calcinating CoFe PBA in N₂ at 200 °C for 1 h (η_{10} =316 mV)⁵¹, FeCo oxide derived from CoFe PBA (Co₃[Fe(CN)₆]₂, $\eta_{10}=310 \text{ mV})^{52}$, and other electrocatalysts listed in **Table S1**.

To further analyze the OER kinetics, Tafel plots are profiled by plotting the overpotential (η) vs. log current density (*j*). Tafel slope (b) can then be determined by linear fitting of these Tafel plots with the Tafel relationship of η and j ($\eta = a + b \times \log j$). The OER mechanisms in alkaline electrolytes are considered as the following reaction steps:^{45,53}

| $M + OH^- \rightleftharpoons$ | $MOH + e^{-}$ | $\operatorname{Step} 1$ |
|--------------------------------|-------------------|--------------------------|
| МОН + ОН⁻ < | $MO + H_2O + e^-$ | $\operatorname{Step} 2$ |
| $MO + OH^- \rightleftharpoons$ | $MOOH + e^{-}$ | $\operatorname{Step} 3$ |
| M00H + 0H [−] < | $M00^{-} + H_20$ | $\operatorname{Step} 4$ |
| $MOO^- \rightleftharpoons$ | $M + O_2 + e^-$ | $\operatorname{Step}{5}$ |

The reaction rate of OER is influenced by multiple reaction steps including continuing OH⁻ adsorption, O-H bond breaking, and O₂ desorption. The measured Tafel slopes can be used to analyze the possible rate-determining step (RDS).^{45,54,55} As shown in **Figure 4b**, Tafel plots of samples in this work mainly consist of two regions of the Tafel slope,

one around 40 mV dec⁻¹ at the low overpotential and the other one at the high overpotential tending to be higher to about 100 mV dec⁻¹. Based on the case study proposed by Shinagawa et al.⁴⁵, we speculate that Step 5 is likely to be the RDS for OER. Besides, a small Tafel slope implies a favourable surface structure and composition for OER, which indicates the intermediate forming at the early steps remains fast.⁴⁵ Ar-U-CoFe PBA possesses a smaller Tafel slope (36.1 mV) than those of Ar-CoFe PBA (38.3 mV dec⁻¹), CoFe PBA (51.3 mV dec⁻¹), and U-CoFe PBA (56.8 mV dec⁻¹) at the low overpotential. The Tafel slopes of Ar-U-CoFe PBA, Ar-CoFe PBA and CoFe PBA increase to 74.9, 100 and 94.1 mV dec⁻¹, respectively, at the high overpotential range up to 0.45 V. Therefore, Ar-U-CoFe PBA shows considerable OER kinetics.



Figure 4. OER performance in 1.0 M KOH electrolyte using three electrode (a, d) and twoelectrode (e, g, f) system. (a) *i*R-corrected LSV curves and (b) corresponding Tafel plots of CoFe

PBA, U-CoFe PBA, Ar-CoFe PBA, and Ar-U-CoFe PBA at room temperature. (c) Nitrogen adsorption (dot) -desorption (circle) isotherms of CoFe PBA, U-CoFe PBA, Ar-CoFe PBA, and Ar-U-CoFe PBA. (d) Stability test at 10 mA cm⁻² of Ar-CoFe PBA and Ar-U-CoFe PBA on RDE for 20 h at 124

room temperature. (e) CP test at 100 mA cm⁻² and 80 °C for about 100 h. The noises at the start and end are due to the polarization curves test. (f) Polarization curves at 40, 60, and 80 °C before (dot) and after (circle) the CP stability test in a course of about 100 h, as shown in (e). (g) Cartoon and the digital photo of the alkaline electrolyzer used for the two-electrode test.

EIS is an important characterization method to explore the electrochemical resistance during OER. **Figure S15** displays Nyquist plots of the four samples, which are simulated by the proposed equivalent circuit as inserted in the figure. Nyquist plots of heat-treated samples including Ar-U-CoFe PBA (3.8Ω) and Ar-CoFe PBA (4.5Ω) show visibly smaller semicircular diameters, which represents charge transfer resistance (R_{ct}) at the electrodeelectrolyte interface, in contrast to those of U-CoFe PBA (41.0Ω) and CoFe PBA (19.6Ω). Overall, Ar-U-CoFe PBA possesses the best electrocatalytic OER performance, i.e., the smallest onset potential, Tafel slope, and R_{ct}, among the four samples.

Electrochemical active surface area (ECSA) of the electrode is studied by the measurement of double-layer capacitance (Cdl) calculated from CV in the non-faradaic potential region (**Figure S16** and **S17**).⁵⁶ However, it is found that Cdl here is not a feasible parameter to correlate the OER performance of our materials. Instead, BET measurement was used for the measurement of the specific surface area (**Figure 4c**). The specific surface area of U-CoFe PBA is around $313 \text{ m}^2 \text{ g}^{-1}$, which is $81 \text{ m}^2 \text{ g}^{-1}$ larger than that of CoFe PBA ($222 \text{ m}^2 \text{ g}^{-1}$). This is likely due to the limited surface etching during the hydrothermal procedure. After heat treatment, the specific surface area of Ar-CoFe PBA decreases remarkably to ~66 m² g⁻¹, which could be explained by the growth of alloy nanoparticles on the surface of PBA ($277 \text{ m}^2 \text{ g}^{-1}$) is slightly less than that of U-CoFe PBA ($313 \text{ m}^2 \text{ g}^{-1}$), and much larger than that of Ar-CoFe PBA, implying the different structural evolution during heat treatment leading to less aggregation. A large surface area, usually regarded as an advantage of catalysts, provides more sites for the catalytic reaction.^{57,58}

Figure S18 displays CV curves in the potential window of 0.80-1.60 V, showing the preoxidation/reduction behaviour of electrocatalysts (scan rate: 5 mV s⁻¹), which can reflect the OER performance.^{16,59,60} CoFe PBA exhibits two pairs of peaks at ~1.137/1.110 V (midpoint redox potential: Eu₂= 1.124 V; peak separation=27 mV) and ~1.460/1.453 V (Eu₂= 1.457 V; peak separation=7 mV) on its CV curve, originating from the redox reaction of a high spin system Co^{2+/3+} and the low spin Fe^{II}(CN)₆⁴/Fe^{III}(CN)₆³⁻, respectively.⁶¹ U-CoFe PBA displays a pair of peaks at ~1.327/1.268 V (Eu₂= 1.298 V, but with a larger peak separation: 59 mV) representing the oxidation and reduction of the $Co^{2+/3+}$ at 5 mV s⁻¹ (**Figure S19**). Another redox pair at a higher potential representing redox reaction of $Fe^{III}(CN)6^{3-}/Fe^{II}(CN)6^{4-}$ on U-CoFe PBA is likely to be overlapped with the OER region. The higher $E_{1/2}$ and the smaller peak separation of U-CoFe PBA over CoFe PBA is believed to be caused by the NH₄⁺ node in interstitial sites, requiring higher energy to pass through the channels and holes compared with K⁺ in PBA's structure.⁶² Further, U-CoFe PBA registers considerably small redox current density at the same catalyst mass loading, indicating a limited number of electrochemical active surface area, despite the higher BET area. Ar-CoFe PBA has a pair of redox peaks at ~1.189/1.108 V ($E_{1/2}$ = 1.149 V; peak separation=81 mV) regarded as the joint redox wave of the Co and Fe species in the CoFe PBA with a pair of redox peaks at ~1.188/1.098 V ($E_{1/2}$ = 1.143 V; peak separation=90 mV). The redox peaks in CV curves are in accordance with the chemical state of Co and Fe by XPS analysis for the four samples and the influence of replacement of K⁺ with NH₄⁺.

Based on the above results and analysis, the improved OER performance of Ar-U-CoFe and Ar-CoFe PBA is very likely due to the chemical state change of Co and Fe during heat treatment. The iron species in $\text{Fe}^{II}(\text{CN})6^3$ /Fe^{II}(CN)6⁴ seem to be inert in OER due to the strong coordination of C=N. Also, heat treatment efficiently causes removal of partial CN groups and thus the reorganization of the material, liberating CoFe alloy nanoparticles in Ar-CoFe PBA and causing an amorphous structure containing enriched defects in Ar-U-CoFe PBA. Therefore, Ar-CoFe and Ar-U-CoFe PBA have lower onset potential than CoFe PBA and U-CoFe PBA. The smaller Tafel slopes and R_{ct} values of Ar-CoFe and Ar-U-CoFe PBA indicate their excellent OER kinetics.

The long-term operational stability of Ar-U-CoFe PBA and Ar-CoFe PBA is characterized by the CP method (**Figure 4d**). Ar-U-CoFe PBA shows excellent stability at 10 mA cm⁻² without visible potential shift for a time period of 20 h. The overpotential required by Ar-CoFe PBA at the same condition exhibits a slight increase of ~7 mV. Samples pasted on the nickel foam exhibit a similar trend during 40 h CP tests (**Figure S20**). **Figure S21** exhibits that the long-term OER test destructs the cubic structure of Ar-CoFe PBA greatly, turned into typical transition metals (like Ni, Fe, and Co) (oxy)hydroxides' layered structure.^{63,64} In sharp contrast, Ar-U-CoFe PBA remains its initial cubic shape after the long-term OER test, as indicated in **Figure S22**. Layered structure of metal (oxy)hydroxides, smaller than those on Ar-CoFe PBA, can also be observed at the outmost of the cube. HRTEM images of both samples after long-term test (Figure S21d and S22d) show some spots with a lattice fringe spacing determined to be 0.297 nm, which can be ascribed to the (2 2 0) plane of CoFe oxide (ICSD Coll. Code of 17714). Elemental chemical states analysis of Ar-U-CoFe PBA and Ar-CoFe PBA after 40 h stability test by XPS is displayed in Figure S23. High-resolution XPS spectra of Fe 2p and Co 2p of these two samples (Figure S23a, b) exhibit similar shapes and both contain Co^{2+} , Co^{3+} , Fe^{2+} , and Fe³⁺, indicative of the similar chemical environment of Co and Fe on the surface. Highresolution XPS spectra of O 1s (Figure S23c) are composed of three peaks attributed to M-O, M-OH, and absorbed water (M represents Co and Fe), respectively. Based on the TEM and XPS analysis, the surface of Ar-CoFe PBA and Ar-U-CoFe PBA is converted to CoFe (oxy)hydroxides and oxides during continuous OER.^{29,65} Besides, both XPS (Figure S23d) and EDS (Figure S24) indicate that there is no element N on the surface, indicative of the complete dissolution of CN groups during the stability test. This phenomenon is previously reported using PBAs as OER catalysts.^{25,66} Ar-U-CoFe PBA presents better stability than Ar-CoFe PBA, largely attributed to its amorphous structure. In other words, a large amount of disordered Fe-CN-Co units and PBA nanoparticles in Ar-U-CoFe PBA hamper the morphology transformation and provide superior stability.

Finally, a single-cell electrolyzer is assembled as **Figure 4g**, with Ar-U-CoFe PBA pasted on Ni foam as the anode and a Pt/C based cathode. The electrolyzer requires a cell voltage of 1.66 V to achieve 100 mA cm⁻² at 80 °C and exhibits excellent stability with a negligible cell voltage increase of ~0.01 V after the 100 h test (**Figure 4e**). At 40 °C and 60 °C, it needs higher initial cell voltages of 1.76 and 1.70 V, respectively, to deliver 100 mA cm⁻², separately requiring higher cell voltage increases of 0.09 V and 0.05 V after the stability test as shown in the polarization curves before and after the long-term test in **Figure 4f**. The apparent activation energy of OER for a catalyst can be determined by the Arrhenius plot: $\log(j) = -0.434E_a/(RT) + \text{const}$, where R represents the Boltzmann constant (8.315 J g⁻¹ mol⁻¹ K⁻¹) and E_a is the activation energy (J g⁻¹ mol⁻¹).^{67,68} Based on the derived Arrhenius plots at the cell voltage of 1.70 V (**Figure S25**), the initial E_a is 14.4 kJ mol⁻¹, which slightly increases to 19.2 kJ mol⁻¹ after the stability test, further indicating good activity and stability of Ar-U-CoFe PBA towards OER. Note that the E_a obtained here is from a full electrolyzer, and such values are comparable to other reported OER catalysts
like FeCoW oxyhydroxides (49 kJ mol $^{-1}$), CoOx (11.1 kJ mol $^{-1}$), and NiFeOx (25 kJ mol $^{-1}$). 69

4. Conclusions

Overall, we have explored the composition, crystalline structure, and morphology of CoFe PBA and three derivatives including U-CoFe PBA, Ar-CoFe PBA, and Ar-U-CoFe PBA. It is concluded that K⁺ in the interstitial space can be completely replaced by NH⁴⁺ without destroying the cubic structure and changing the chemical state of Fe and Co by a hydrothermal procedure in the aqueous urea solution. Heat treatment of CoFe PBA and U-CoFe PBA at high temperatures (200-600 °C) in an Ar atmosphere can introduce defects by removing H₂O, NH₄⁺, and CN groups, thus influencing the materials' phase and composition. When heated at 400 °C, CoFe alloy nanoparticles grow on the surface of CoFe PBA, while U-CoFe PBA's framework collapses and becomes amorphous with PBA nanocrystals dispersing in large amounts of disordered Fe-CN-Co units. Electrochemical OER performance of these four samples in alkaline solution varies, showing that heattreatment derivatives behave favourably over the pristine PBA due to the moderated chemical states of Co and Fe for OER. Ar-U-CoFe PBA outperforms Ar-CoFe PBA in terms of electrochemical activity and operational stability, exhibiting a promising anode material in an assembled alkaline electrolyzer. This work is meaningful to the development of new species of PBAs and their derivatives and their application in the electrocatalysis of water oxidation.

Declaration of competing interest

The authors declare no competing financial interest.

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Supporting Information:

Structure and Oxygen Evolution Reaction Performance of CoFe Prussian Blue Analogue and Three Derivatives

Fangyuan Diao^a, Mikkel Rykær Kraglund^b, Kai Gao^a, Huili Cao^a, Yuan Yang^c, Xiaomei Yan^a, Qingfeng Li^b, Pengchao Si^c, Christian Engelbrekt^{a*}, Xinxin Xiao^{a*}

^a Department of Chemistry, Technical University of Denmark, DK-2800 Kongens Lyngby, Denmark.

^b Department of Energy Storage and Conversion, Technical University of Denmark, DK-2800 Kongens Lyngby, Denmark.

^c Key Laboratory for Liquid-Solid Structural Evolution and Processing of Materials (Ministry of Education), Research Center for Carbon Nanomaterials, School of Materials Science and Engineering, Shandong University, Jinan 250061, P. R. China.

*Corresponding authors: Christian Engelbrekt (cheng@kemi.dtu.dk); Xinxin Xiao (xixiao@kemi.dtu.dk).

S1. Materials design and characterization



Figure S1. SEM images of (a) CoFe PBA, (b) U-CoFe PBA, (c) Ar-CoFe PBA, and (d) Ar-U-CoFe PBA.



 ${\bf Figure\,S2.\,EDS\ analysis\ of\ CoFe\ PBA\ for\ the\ corresponding\ inserted\ TEM\ image.}$



Figure S3. EDS analysis of U-CoFe PBA for the corresponding inserted TEM image.



Figure S4. XPS spectra of (a) K 2p and (b) N 1s of CoFe PBA and U-CoFe PBA.



Figure S5. TGA curves of (a) CoFe PBA and (b) U-CoFe PBA.



 ${\bf Figure\,S6.\,FT-IR\,\,spectrum\,of\,the\,\,solid\,urea.}$



Figure S7. EDS analysis of Ar-CoFe PBA for the corresponding inserted TEM images of three different positions.



Figure S8. FT-IR spectra (a, b) and XRD patterns (c, d) of Ar-CoFe PBA T °C and Ar-U-CoFe PBA T °C (T=200, 300, 600).



Figure S9. SEM images and EDS analysis of (a1, a2) Ar-CoFe PBA 600 °C and (b1, b2) Ar-U-CoFe PBA 600 °C.



Figure S10. Elemental mapping of Ar-U-CoFe PBA cube.



Figure S11. EDS analysis of Ar-U-CoFe PBA for the corresponding inserted TEM image.



Figure S12. XPS spectra of N 1s of Ar-CoFe PBA and Ar-U-CoFe PBA.

Note: Thermogravimetric analysis (TGA) curves (**Figure S5**) of CoFe PBA and U-CoFe PBA measured in the N₂ atmosphere provide rich information about their evolution during heat treatment. CoFe PBA suffers from a large mass loss of 13.7% below 150 °C in **Figure S5a**, which is attributed to the elimination of surface absorbed and zeolitic water molecules. As the temperature increases from 150 to 350 °C, the mass loss of 3.7% is mainly assigned to the removal of the coordinating H₂O. The mass loss between 350 °C and 540 °C could be ascribed to the decomposition of Fe-CN-Co in CoFe PBA. For U-CoFe PBA, the TGA curve (**Figure S5b**) shows a weight loss of 10.4% below 156 °C corresponding to the removal of surface absorbed and zeolitic water molecules. With the temperature increasing to 295 °C, it exhibits a large mass loss of 12.6%, which is due to 144

the release of coordinating H₂O and NH₄⁺. The disappearance of the peak at around 1412 cm⁻¹ on the FT-IR curve of Ar-U-CoFe 300 °C (**Figure S8b**) confirms the release of NH₄⁺. All coordinating H₂O could be removed at 400 °C for CoFe PBA and U-CoFe PBA as **Figure 2b** indicates. Ar-CoFe PBA 300 °C and Ar-U-CoFe PBA 300 °C still keep the crystal structure as CoFe PBA and U-CoFe PBA, which means the structure stability until 300 °C. However, after the heat treatment at 600 °C, the characteristic peaks on FT-IR spectra disappear, and the XRD phases are dominated by CoFe alloy for both Ar-CoFe PBA and Ar-U-CoFe PBA (**Figure S8c** and **S8d**). Besides this, the cubic morphology is deformed for both CoFe PBA and U-CoFe PBA as shown in **Figure S9**. Thus, the selected 400 °C is a moderate temperature, which can effectively remove water molecules, NH₄⁺, and a part of CN groups and maintain their cubic morphology.

S2. OER performance and characterization of samples after stability test



Figure S13. LSV curves of Ar-U-CoFe PBA with different loadings on the RDE.



Figure S14. LSV curves of Ar-U-CoFe PBA T $^{\circ}$ C where T represents 300, 400, and 600 $^{\circ}$ C, respectively.



Figure S15. Nyquist plots of CoFe PBA, U-CoFe PBA, Ar-CoFe PBA, and Ar-U-CoFe PBA. Inset is the equivalent circuit model of the experiment.







Figure S17. Half of the current density (ΔJ =Ja-Jc) at 0.95 V vs. RHE plotted against the scan rate, and a linear fitting was applied to estimate double-layer capacitance (C_{dl}).

Note: Double-layer capacitance (Cd) calculated from CV measurements at different scan rates in the non-faradaic potential region as shown in **Figure S16 and S17** was commonly used to evaluate the electrochemical active surface area (ECSA) of the electrode.^{1,2} However, CdI can be greatly influenced by the electrolyte, electrode materials (structure, elemental kinds, oxidation state, etc.), and the extent of the absorption process.³⁻⁵ For this experiment, it was performed in 1.0 M KOH in the potential range of 0.9-1.0 V vs. RHE. NH4⁺ in the U-CoFe PBA might influence the absorption of OH⁻ in the electrolyte, which leads to the CdI of U-CoFe PBA being much smaller than CoFe PBA. Besides this, the chemical states of Co and Fe in Ar-CoFe PBA and Ar-U-CoFe PBA are different from those in CoFe PBA and U-CoFe PBA. This may be the reason for a smaller CdI of Ar-CoFe PBA and Ar-U-CoFe PBA than CoFe PBA and U-CoFe PBA. These distinctions of samples make it difficult to compare ECSA by CdI. As the samples in this work are all fine powders, the Brunauer–Emmett–Teller (BET) method is utilized to evaluate the specific surface area.



Figure S18. CV curves of CoFe PBA, U-CoFe PBA, Ar-CoFe PBA, Ar-U-CoFe PBA performed in the potential range of 0.80-1.60 V vs. RHE at 5mV s⁻¹.



Figure S19. CV curves performed in the potential range of 0.80-1.60 V vs. RHE at different scan rates (5, 10, 20, 50, and 100 mV s⁻¹). a. CoFe PBA, b. U-CoFe PBA, c. Ar-CoFe PBA, d. Ar-U-CoFe PBA.



Figure S20. Stability test of Ar-CoFe PBA (a) and Ar-U-CoFe PBA (b) pasted on the Ni foam at 10 $mA cm^{-2}$ for 40 h at room temperature.



 $\mathbf{Figure~S21.}\ \mathrm{TEM}\ \mathrm{and}\ \mathrm{HRTEM}\ \mathrm{images}\ \mathrm{of}\ \mathrm{Ar-CoFe}\ \mathrm{PBA}\ \mathrm{after}\ 40\ \mathrm{h}\ \mathrm{OER}\ \mathrm{stability}\ \mathrm{test}.$



Figure S22. TEM and HRTEM images of Ar-U-CoFe PBA after 40 h OER stability test.



Figure S23. XPS spectra of Ar-CoFe PBA and Ar-U-CoFe PBA after 40 h OER stability test: (a) Fe 2p, (b) Co 2p, (c) O 1s, and (d) N 1s.



Figure S24. EDS analysis of Ar-CoFe PBA after 40 h OER stability test (a) and Ar-U-CoFe PBA after 40 h OER stability test (b). Inset is the area for the EDS test.



Figure S25. The corresponding Arrhenius plots at the cell voltage of 1.70 V based on the polarization curves in Figure 4f.

Table S1. Comparison of OER activity of electrocatalysts with a similar shape or composition withCoFe PBA and its derivatives.

| Materials | Overpotential at 10 mA cm ⁻² | Tafel slope (mV·dec ⁻¹) | Electrolyte | Ref. |
|--|--|--|-------------|-----------|
| Ar-U-CoFe PBA | 305 | 36.1 | 1 M KOH | This work |
| Ar-CoFe PBA | 316 | 38.3 | 1 M KOH | This work |
| CoFe PBA | 387 | 51.3 | 1 M KOH | This work |
| U-CoFe PBA | 422 | 56.8 | 1 M KOH | This work |
| Microporous CoFe PBA- | 316 | 49.6 | 1 M KOH | 6 |
| 200 by calcinatingCoFe | | | | |
| PBA in N_2 at 200 $^{\circ}\!\mathrm{C}$ for 1 | | | | |
| h | | | | |
| CoFe PBA hollow cages | 330 | 57 | 1 M KOH | 7 |
| CoFe PBA in-situ | 290 | 39.72 | 1 M KOH | 8 |
| growing on the surface | | | | |
| of vanadiumnitride | | | | |
| (VN) particles | | | | |
| Bare CoFe PBA without | 398 | 78.35 | 1 M KOH | |
| VN | | | | |
| Core-shell PBAs with | 271 | 53.7 | 1 M KOH | 9 |
| compositional | | | | |
| heterogeneity (Ferich | | | | |
| shell and Co rich core) | | | | |
| Nickel-cobalt bimetal | 300 | 80 | 1 M KOH | 10 |
| phosphide nanocages | | | | |
| FeCo oxide derived | 310 | 55.5 | 1 M KOH | 11 |
| from FeCo PBA | | | | |
| (Fe ₃ [Co(CN) ₆] ₂) | | | | |
| CoFe oxide derived | 314 | 66.6 | 1 M KOH | |
| from CoFe PBA | | | | |
| (Co ₃ [Fe(CN) ₆] ₂) | | | | |
| Amorphous Co-Ni-B-O | 300 | 60 | 1 M KOH | 12 |
| nanosheets by chemical | | | | |
| reduction of CoNi PBA | | | | |
| Co-based nanocubes | 302 | 74.37 | 1 M KOH | 13 |
| containing a low | | | | |

| amount of ruthenium | | | | |
|---|-----|------|---------|----|
| oxide (RuO ₂ /Co ₃ O ₄) | | | | |
| Co-Fe-fluoride porous | 250 | 38.3 | 1 M KOH | 14 |
| nanocubes derived from | | | | |
| CoFe PBA | | | | |
| Mesoporous | 280 | 69.6 | 1 M KOH | 15 |
| Co ₃ N@amorphousN- | | | | |
| doped carbon | | | | |
| nanocubes | | | | |
| Dodecagon N-doped | 309 | 67 | 1 M KOH | 16 |
| PdCoNi carbon-based | | | | |
| nanosheets | | | | |

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Chapter 5 Conclusions and prospectives

The fabrication of active and robust electrocatalysts based on abundant and non-precious metals is still a big challenge for overall water electrolysis. PBAs with abundant metallic atom centers and CN groups forming a 3D framework have been applied in many fields like batteries, supercapacitors, gas absorption, drug delivery, and catalysis. They are also versatile precursors to fabricate efficient OER and HER electrocatalysts. In this thesis, two groups of PBA derivatives were developed by engineering the morphology and composition, both displaying good activity and stability in alkaline conditions.

In the first work, NiPO rods with an average width of about 1.51 µm and a length of tens of micrometers were grown on the Ni foam by a hydrothermal method in a microwave synthesizer. A layer of NiFe PBA (thickness: 120-160 nm) was successively grown on the surface of the NiPO rods through a facile coprecipitation method, in which Ni²⁺ on NiPO reacts with [Fe(CN)6]³⁻ at the start to form the close contact between NiFe PBA layer and NiPO rods. After an efficient phosphidation step of NiFe PBA@NiPO@NF, NiFeP@NiP@NF was successfully synthesized. It displayed excellent electrocatalytic OER and HER performance, requiring overpotentials of 227 and 105 mV, respectively, to deliver 10 mA cm⁻². An electrolyzer with NiFeP@NiP@NF as both cathode and anode required a cell voltage of 1.64 V to deliver 20 mA cm⁻² and continuously worked for 120 h without obvious degradation. Good activity and stability benefit from the rational design of the catalyst structure. NiFeP derived from NiFePBA works as the active material and provided numerous active sites and modified electronic structure for OER and HER. NiP from NiPO provides a large surface to NiFeP. Besides, the rod structure could prevent structural degradation and delamination caused by produced gas bubbles. Intimate contact between NiFeP, NiP, and Ni foam could effectively reduce the resistance losses and improve reaction rates.

In the second work, the composition, crystalline structure, and morphology of CoFe PBA and its derivatives including U-CoFe PBA, Ar-CoFe PBA, and Ar-U-CoFe PBA were explored. It was found that K⁺ in the CoFe PBA's interstitial spaces could be completely replaced by NH₄⁺ produced by aqueous urea solution at 150 °C, leading to a slightly larger cell parameter than that of CoFe PBA. The evolution of U-CoFe PBA in an Ar atmosphere at 400 °C was different from that of CoFe PBA because of this replacement. CoFe alloy nanoparticles grew on the surface of CoFe PBA cubes due to the removal of CN in some Fe-CN-Co units. In comparison, the framework of U-CoFe PBA collapsed because of the loss of NH₄⁺ and the removal of CN in some Fe-CN-Co units, leading to amorphous cubes of disordered Fe-CN-Co units and dispersed PBA. Besides, the chemical states of Co and Fe were changed by the heat treatment. Results of OER performance tests showed that heat-treatment derivatives ($\eta_{10, Ar-U-CoFe PBA}=305$ mV, $\eta_{10, Ar-CoFe PBA}=316$ mV) were more active than their precursors ($\eta_{10, U-CoFe PBA}=422$ mV, $\eta_{10, Ar-CoFe PBA}=387$ mV). Ar-U-CoFe PBA was more stable than Ar-CoFe PBA due to its composition and structure, and it was a promising anode catalyst for an alkaline electrolyzer. This work is believed to be meaningful for the development of new PBAs and their derivatives for usage in electrocatalytic OER and other fields.

In summary, two kinds of active, stable, and non-precious electrocatalysts from PBAs (NiFe PBA and CoFe PBA) for OER and HER in alkaline conditions have been developed. Through different material design strategies, favorable morphology, electronic structure, and composition have been obtained for OER and HER. New findings in material syntheses, such as growing NiPO rods on NF, U-CoFe PBA with NH₄⁺, and amorphous Ar-U-CoFe PBA cubes, found in this thesis are meaningful for other researchers who are interested in PBAs or electrocatalysis.

Based on this project, some perspectives are also proposed as follows:

1) Structural and compositional evolution during electrochemical tests are mainly studied by ex-situ methods like TEM and XPS. In comparison, in-situ methods like Raman spectroscopy, X-ray absorption spectroscopy, and TEM can provide more convincing evidence to explain materials' evolution and OER mechanisms.¹⁻⁴ For example, a bimetallic carbide (O, N-NiFeCx-350 °C) transformed from NiFe PBA was tested by insitu Raman spectra under a constant current density of 1 mA cm⁻². The formation of NiFeOxHy on the material's surface was directly confirmed by continuously in-situ Raman observation for 800 s.¹ Lee et al. conducted in-situ X-ray absorption fine structure (XFAS) analysis to determine the valence state variation of metals in different PBAs (PB, CoFe PBA, and NiFe PBA) with the anodic scan from 1.0 to 1.6 V vs. RHE.² These methods could also provide more information if applied to our synthesized samples.

2) The structure-performance relationship of the synthesized samples should be carefully investigated by theoretical simulation methods to uncover the OER mechanism. DFT calculation is widely used in understanding composites or doped materials.^{5–7} For example, Hu et al. used DFT calculation to indicate the favorable electronic states of Co atoms neighboring Fe in Fe-CoP.⁶ Lin et al. synthesized a hierarchical electrocatalyst with Ni₃C nanoparticles on NiFe PBA nanosheets and performed DFT calculations to uncover the electronic distribution of atoms on the interface of the two materials to explain its excellent OER performance.⁸ For the optimized samples mentioned in chapter 3 (NiFeP@NiP@NF) and chapter 4 (Ar-U-CoFe PBA), it is necessary to use theoretical simulation methods to deeply understand the advantage of their structure and composition.

3) CN groups are important and characteristic of PBAs. Great attention should be paid to reactions that may involve them. Besides, more attempts at clarifying the function and evolution of NH₄⁺ should be given after it has been introduced into CoFe PBA. For example, analysis of the gas product of PBAs during the heat treatment by gas chromatography can provide more information about PBAs' evolution and their derivatives. Heat treatment of CoFe PBA with NH₄⁺ in a small and sealed device may produce a different product from the one treated in Ar flow because NH₄⁺ can take part in reactions instead of leaving with the Ar flow.

PBAs and their derivatives are variable in composition and structure and was applicable in a lot of fields. It is meaningful to understand them and to explore more derivatives with new methods to improve their performance for different applications.

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Appendix

Supporting information on applying the NiFeP@NiP@NF and Ar-U-CoFe PBA prepared in Chapter 3 and Chapter 4, respectively, in an alkaline electrolyzer, is given in this section. It includes the introduction of the electrolyzer, results of related tests, and materials characterization after tests. These tests were performed at DTU Energy under the supervision of Prof. Qingfeng Li and Dr. Mikkel Rykær Kraglund.

The test platform mainly consists of three parts: the electrolyzer, the power supply, and the monitor (or control software) as shown in Figure A1. As displayed in Figure A2, the electrolyzer comprises the electrolysis cell, tanks storing the electrolyte, reference electrodes, gas sensors, pumps, tubes for circulating the electrolyte and transporting the produced H₂ and O₂, heating elements, thermocouples, etc. Two stainless steel parts (Figure A3b and e) sandwich the PTFE gaskets, electrodes, and the diaphragm (Figure A3c), which are tightened by screws to get an electrolysis cell as Figure A3a shows. For the NF and NiFeP@NiP@NF, a Zirfon UTP 500 (Agfa-Gevaert Group) separator and 30 wt% KOH aqueous solution were utilized. For Ar-U-CoFe PBA, Aemion+ electrolysis membrane (Ionomr Innovations) and 1 M KOH aqueous solution were used (more information is found in Chapter 4).

The electrolysis cell with Ni foam as both cathode and anode requires the cell voltage of 1.91 V to reach 100 mA cm⁻² at 80 °C, and the cell voltage increases to 1.96 V after 16 h CP test (Figure A4b). The electrolysis cell with NiFeP@NiP@NF as both cathode and anode requires a low cell voltage of 1.605 V to deliver 100 mA cm⁻² at 80 °C at the start. After about 115 h CP test, the cell voltage shows a negligible increase of 0.01 V. It requires 1.84 and 2.05 V to deliver 500 and 1000 mA cm⁻², respectively, at 80 °C (Figure A5b). The degradation of the cell is not obvious after about a 14-day CP test as shown in Figure A5b. CV curves of the two electrolysis cells in Figure A4a and Figure A5a provide more information about cell performance at different temperatures (40, 60, and 80 °C). It indicates that the NiFeP@NiP@NF shows potential as a bifunctional electrocatalyst in alkaline condition. SEM images of the NiFeP@NiP@NF after CP test on the cathode and anode are shown in Figure A6. The rods are kept on the cathode (Figure A6a). However, there are no rods on the anode (Figure A6b), which would attribute to the corrosion during OER.

A-1 Introduction of the alkaline electrolyzer



Figure A1. Digital photo of the testing platform, including a PC/monitor, power supplies, and the electrolyzer.



Figure A2. Digital photo of the electrolysis cell during operation.


Figure A3. a. Digital photo of the assembled alkaline electrolyzer. b. Digital photo of the top view of the stainless steel part. c. Digital photo of the parts including the electrodes, diaphragm, and PTFE gaskets. d. Illustration of the assembly of the electrodes. e. Digital photo of the top view of assembled electrodes. Electrodes used in this electrolyzer have an area of 1×1 cm⁻². Zirfon UTP 500 and Aemion+electrolysis membrane are used as the diaphragm in 30 wt% KOH and 1 M KOH solution, respectively.



A-2 Performance tests with the electrolyzer

Figure A4. a. CV curves of electrolyzer with the Ni foam as both the anode and cathode tested at 40, 60, and 80 °C. b. CP test at 100 mA cm⁻², 80 °C for about 16 h. The noises at the start are due to the polarization curves test. The electrolyte is 30 wt% KOH aqueous solution.



Figure A5. a. CV curves of the electrolyzer with NiFeP@NiP@NF as both the anode and cathode tested at 40, 60, and 80 °C before and after CP test with conditions as shown in b. b. CP test at 100, 500, and 1000 mA cm², 80 °C for about 330 h. The noises in the figure at the start or end of different current density changes are due to the polarization curves test. The electrolyte is 30 wt% KOH aqueous solution.

A-3 Electrodes' characterization after CP test



 $\label{eq:Figure A6} Figure A6. {\tt SEM} \ images of NiFe P@NiP@NF after CP test \ in \ Figure \ A5b. \ a. \ Cathode. \ b. \ Anode.$