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**AMORPHOUS ALLOY: A POTENTIAL
ELECTROCATALYST IN WATER
SPLITTING**

CAI WEIZHENG

**SCHOOL OF CHEMICAL AND BIOMEDICAL
ENGINEERING**

2019

**AMORPHOUS ALLOY: A POTENTIAL
ELECTROCATALYST IN WATER
SPLITTING**

CAI WEIZHENG

School of Chemical and Biomedical Engineering

A thesis submitted to the Nanyang Technological University
in partial fulfilment of the requirement for the degree of

Doctor of Philosophy

2019

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research, is free of plagiarised materials, and has not been submitted for a higher degree to any other University or Institution.

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Authorship Attribution Statement

This thesis contains material from 2 papers published in the following peer-reviewed journals in which I am listed as an author.

Chapter 2 is published as W. Cai; R. Chen; H. Yang; H. B. Tao; H.-Y. Wang; J. Gao; W. Liu; S. Liu; S.-F. Hung; B. Liu, Amorphous vs Crystalline in Water Oxidation Catalysis: A Case Study of NiFe Alloy. Nano Letters 2020, 4278–4285.

The contributions of the co-authors are as follows:

- B.L. conceived and designed the project. W.C. synthesized and characterized the materials and performed the electrochemical experiments. W.C., C.R., H.Y., H.T., H.W., J.G. and S.L. analyzed the electrochemical data. W.L. performed the HAADF-STEM and elemental mapping measurements. S.H. performed the XAS. B.L. wrote the manuscript. All authors reviewed and contributed to the manuscript.

Chapter 3 is published as W. Cai; H. Yang; J. Zhang; H.-C. Chen; H. B. Tao; J. Gao; S. Liu; W. Liu; X. Li; B. Liu, Amorphous Multimetal Alloy Oxygen Evolving Catalysts. ACS Materials Letters 2020, 624-632.

The contributions of the co-authors are as follows:

- B.L. conceived and designed the project. W.C. synthesized and characterized the materials and performed the electrochemical experiments. W.C., H.Y., H.T., J.G., S.L. and X.L. analyzed the electrochemical data. W.C., J.Z. and H.T. conducted the fitting of microkinetic model. W.L. performed the HAADF-

STEM and elemental mapping measurements. H.C. performed the XAS. B.L. wrote the manuscript. All authors reviewed and contributed to the manuscript.

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Abstract

Catalytic water splitting to produce hydrogen gas driven by renewable electricity is regarded as one of the most promising methods for the sustainable energy conversion, but its efficiency is greatly restricted due to the high overpotential required for the anodic water oxidation half reaction. To accelerate the sluggish four-electron transfer kinetics for the oxygen evolution reaction (OER), it has attracted numerous attention on developing earth-abundant materials as efficient electrocatalysts.

Amorphous catalysts are reported to have better activities of water oxidation than their crystalline counterparts, but little is known about the underlying origin, which retards the development of high-performance amorphous oxygen evolution reaction (OER) catalysts. In the first work, to gain an in-depth understanding of the structure-performance relationship for OER on amorphous alloy catalysts, we present a room temperature wet-chemical technique to prepare an amorphous nickel-iron alloy catalyst for water oxidation. And crystalline nickel-iron alloy catalysts without changing composition can be obtained via thermal annealing of amorphous catalyst in N₂ atmosphere. Through theoretical analysis including cyclic voltammetry and electrochemical impedance spectroscopy studies, and following by experimental methods of isotope (¹⁸O) labeling studies and in situ X-ray absorption spectroscopy (XAS) on both amorphous and crystalline nickel-iron alloy catalysts, it was demonstrated that the amorphous nickel-iron alloy catalyst could be electrochemically activated to expose active sites by applying a positive anodic potential because of the short-range ordering of the amorphous structure.

This process greatly increased the number of active sites and thus significantly improved the water oxidation activity. Additionally, the amorphous nickel-iron alloy catalyst with Ni to Fe atomic ratio of 3:1 could reach a water oxidization current density of 10 mA/cm² at an overpotential of 265 mV (*iR* corrected) on a glassy carbon electrode, which is 100 mV smaller as compared to the crystalline counterpart. Additionally, by coating the as-prepared amorphous nickel-iron alloy catalyst onto a nickel foam, long term OER stability in 1 M KOH at 80 °C and 500 mA/cm² could be achieved, rendering the amorphous nickel-iron alloy catalyst practically feasible for high performance water electrolysis.

To gain an in-depth understanding of the electronic-performance relationship for OER on amorphous alloy catalysts, we develop the amorphous multimetal alloy catalyst with different electronic structures toward oxygen evolution reaction. In the second work, we provide a room temperature solution technique to synthesis the homogeneously dispersed, amorphous multimetal alloy catalysts. Based on analysis of HAADF-STEM, XPS valence band, electrochemical simulation, and using methanol as a probing molecule to measure binding energy, we success to modulate the 3d electronic structure of amorphous multimetal alloy and thus tune the adsorption energies for oxygenated intermediates. It is demonstrated that near optimal adsorption energy is achieved for oxygenated intermediates by adding high-valence metal (molybdenum) resulting in significantly improved water oxidation activity. Additionally, the amorphous nickel-iron-molybdenum alloy catalyst could reach a water oxidization current density of 10 mA/cm² at an overpotential of 220 mV on a glassy carbon electrode, which is the best OER catalyst as compared to recently reported works.

Additionally, by coating the as-prepared amorphous nickel-iron-molybdenum alloy catalyst onto nickel foam as anode coupled with a crystalline nickel boron catalyst as the hydrogen-evolving cathode, long term OER stability at 80 °C in 6 M KOH and 500 mA/cm² could be achieved with input voltage around 1.48 V (1.63 V in 1 M KOH at room temperature), making the amorphous nickel-iron-molybdenum alloy catalyst practically feasible for high performance water electrolysis.

In this thesis, we revealed the mechanism of amorphous catalyst outperforming much better OER performance than the crystalline counterpart using both in situ and ex situ measurements, demonstrating that the amorphous nickel iron alloy catalyst could be electrochemically activated to expose active sites under an anodic potential due to the short-range ordering structure. And we further successfully designed the OER catalyst, which showed the highest activity over the world, based on the deep comprehension of electronic-performance relationship for OER on the amorphous alloy.

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List of Publications

- (1) **W. Cai**; H. Yang; J. Zhang; H.-C. Chen; H. B. Tao; J. Gao; S. Liu; W. Liu; X. Li; B. Liu, Amorphous Multimetal Alloy Oxygen Evolving Catalysts. ACS Materials Letters 2020, 624-632.
- (2) **W. Cai**; R. Chen; H. Yang; H. B. Tao; H.-Y. Wang; J. Gao; W. Liu; S. Liu; S.-F. Hung; B. Liu, Amorphous vs Crystalline in Water Oxidation Catalysis: A Case Study of NiFe Alloy. Nano Letters 2020, 4278–4285.
- (3) S. Liu; H. B. Yang; S.-F. Hung; J. Ding; **W. Cai**; L. Liu; J. Gao; X. Li; X. Ren; Z. Kuang; Y. Huang; T. Zhang; B. Liu, Elucidating the Electrocatalytic CO₂ Reduction Reaction over a Model Single-Atom Nickel Catalyst. Angewandte Chemie International Edition 2020, 59 (2), 798-803.
- (4) Z. Yu; Y. Y. Chun; J. Xue; J. Z. Y. Tan; W. K. Chan; **W. Cai**; Y. Zhang; T. T. Y. Tan, Balancing the thickness of sensitizing and inert layers in neodymium-sensitized tetralayer nanoconstructs for optimal ultraviolet upconversion and near-infrared cross-linked hydrogel tissue sealants. Biomaterials Science 2020, 8 (10), 2878-2886.
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Nomenclature

$^{\circ}\text{C}$	degree Celsius
θ	diffraction angle
α	dispersion parameter
α_a	transfer coefficient of anodic
α_c	transfer coefficient of cathodic
η	overpotential
ν	scan rate
σ	the charge density for monolayer coverage
μL	microlitre
*	active site
$\theta(\text{E})$	surface intermediate coverage
θ_{O^*}	the surface coverage of O^*
θ_{OH^*}	the surface coverage of OH^*
θ_{M^*}	the surface coverage of empty sites
ΔG	Gibbs free energy
3D	three dimensional
a-BSCF	amorphous quaternary Ba-Sr-Co-Fe oxide
a-LNF	Amorphous Fe doped LaNiO_3
b	Tafel slope
A	CPE coefficient
B.E.	binding energy

BET	Brunauer–Emmett–Teller
C_0	concentration of oxidized species
C_{ads}	the relaxation of charge associated with the adsorbed intermediates
C_{dl}	double layer capacitance
cm	centimeter
CPEs	constant phase elements
C_R	concentration of reductive species
CUSs	coordinative unsaturated sites
CV	cyclic voltammetry
C_s	ideal specific capacitance
DFT	density functional theory
E	applied potential
e^-	electron
C	Coulomb
E^0	standard theoretical potential
E_1^0 (V)	calculated potential of first OER step
E_2^0 (V)	calculated potential of second OER step
E_3^0 (V)	calculated potential of third OER step
E_4^0 (V)	calculated potential of fourth OER step
E_c	corrected potential
ECSA	electrochemical surface area
EDX	energy dispersive X-ray spectroscopy
E_{eq}	equilibrium potential

E_F	Fermi level
EIS	electrochemical impedance spectroscopy
E_m	measured potential
E_o	potential under which no obvious adsorption occurs
ET	electron transfer
eV	electron volt
EXAFS	extended X-Ray absorption fine structure
F	Faraday constant
FESEM	field emission scanning electron microscopy
FRA	frequency response analysis
GC	glassy carbon
h	hours
HADDF	high-angle annular dark-field imaging
HER	hydrogen evolution reaction
HPLC	high performance liquid chromatography
HRTEM	high resolution transmission electron microscope
i_c	charging current
ICP-AES	inductively coupled plasma atomic emission spectroscopy
ICP-MS	inductively coupled plasma mass spectrometry
j	current density
j_0	exchange current density
K_1^0	equilibrium constant of first step OER

K_2^0	equilibrium constant of second step OER
k_1^0	rate constant of first step OER
k_2^0	rate constant of second step OER
k_3^0	rate constant of third step OER
k_a	anodic rate constant
k_c	cathodic rate constant
L	liter
LSV	linear sweep voltammetry
mA	milliamper
MOR	methanol oxidation reaction
mV	millivolt
n	the number of the transferred electrons
nm	nanometer
O^*	adsorbed O intermediates
OER	oxygen evolution reaction
OH^*	adsorbed OH intermediates
OOH^*	adsorbed OOH intermediates
P_{step}	potential step
PTFE	polytetrafluoroethylene
R	universe gas constant
RDS	rate-determining step
Ref	reference
RHE	reversible hydrogen electrode
R_p	interfacial charge transfer resistance

R_s	solution resistance
SCE	saturated calomel electrode
SEAD	selected area (electron) diffraction
SEM	scanning electron microscop
STEM	scanning transmission electron microscope
T	temperature
TEM	high resolution transmission electron microscope
U-I	volt-current
V	volt
v_1	reaction rate for the first step of OER reaction
v_2	reaction rate for the second step of OER reaction
v_3	reaction rate for the third step of OER reaction
XAS	X-ray absorption spectroscopy
XANES	X-ray absorption near edge structure
XPS	X-ray photoelectron spectroscopy
XRD	X-ray Diffraction
Z_{CPE}	impedance of CPEs

Chapter 1 Introduction

1.1 Background of Electrochemical Oxygen Evolution Reaction

Over the last decades, energy consumption grows more and more quickly in today's society. However, fossil fuels, the main part of the current energy structure, are nonrenewable and produce a huge amount of pollution, while causing serious environmental and economic problems.¹⁻⁴ Therefore, it is urgent and significant to develop renewable and clean energy resources to fulfill the enormous energy demand in the future. Hydrogen gas, with the highest energy mass density and without any pollution after combustion in air, is regarded as the most promising energy resource in the future.^{5,6} However, the traditional method of producing hydrogen by methane reforming generates many byproducts including carbon dioxide which is the greenhouse gas.⁷⁻⁹ Therefore, electrochemical water splitting plays an essential role in producing clean hydrogen fuels to meet the increasing demands on renewable energy resources.¹⁰⁻¹⁴ Unfortunately, due to the slow kinetics of the oxygen evolution reaction(OER) involving four-electron transfer step, there is a requirement of a high overpotential to drive the oxygen evolution reaction, leading to massive energy consumption on the anode.¹⁵⁻¹⁹ To overcome this sluggish four-electron transfer process, tremendous efforts have been put into both theoretically and experimentally to study this interface charge transfer process.^{20,21} Numerous reaction pathways of the four-electron transfer process have been established on various systems.²²⁻²⁵

Furthermore, diverse descriptors have been exploited to construct the relationships between catalytic activity and common properties of materials, such as Norskov reported descriptors of $\Delta G_{O^*} - \Delta G_{HO^*}$, and other similar descriptors are usually based on adsorption of intermediates. Finally, these theoretical studies provide fundamental guidance for designing efficient electrocatalysts for OER.²⁶⁻²⁸ Among the various electrocatalysts, noble metal-based IrO_2 and RuO_2 have been discovered with the most efficient electrocatalytic activity by offering a small overpotential and low Tafel slope in both alkaline and acidic media.^{29,30} However, two significant weaknesses impede the application of these materials on a large scale. One is the small production in the world with 35.5 tons of Ru and 3 tons of Ir every year.³¹ Another reason is the instability during the long term water splitting process. It has been demonstrated that RuO_2 and IrO_2 are dissolved as RuO_4^{2-} and IrO_4^{2-} in electrolytes under high applied potential.^{29,30,32,33} To vanquish the difficulty, copious non-noble metal-based materials have been developed. The transition metal-based oxides and hydroxides are the central issues in the last decades, such as perovskites, rutiles, spinels, layer double hydroxides et al.³⁴⁻³⁸ Other metal-based crystalline catalysts including metal chalcogenides,³⁹⁻⁴³ nitrides,⁴⁴⁻⁴⁸ phosphides⁴⁹⁻⁵³ were also developed as OER catalysts showing remarkable activities usually due to high conductivity. Besides, nonmetal based catalysts are also exploited in spite of the much worse performance and instability.^{54,55} However, owing to far worse catalytic activity compared to noble metals, rational strategies have been extensively investigated to make a considerable improvement in intrinsic activity, number of active sites and stability.

Nanoengineering is the most widely used approach, by offering obviously at least two merits: one is creating a great increase of specific surface area resulting in a high number of surface active sites. Another is the modification of the electronic properties leading to improved intrinsic activity. It has been reported that single layer nickel hydroxides, spinel cobalt oxides quantum dots, perovskites nanoparticles, et al showed much better activity than the bulk materials.⁵⁶⁻⁶² Defect engineering is also an attractive method of enhancing the catalytic activity, it has been reported that the intrinsic OER catalytic activities usually correlates with the unsaturated coordination atoms on the surface. Therefore, electrocatalysts are rationally designed by doping with other elements, creating oxygen vacancies by reduction or oxidation, regulating the lattices by mechanical treatments, and creating edges, kinks, holes by various physical and chemical ways. For example, the reported acid-etched layered double Ni(OH)₂ with rich defects demonstrated a better OER performance by lowering the overpotential to 300 mV and Tafel slope of 41 mV/dec.⁶³ And single-crystalline Co₃O₄ reported by with abundant oxygen vacancies on the (111) facets gave a small Tafel slope of 49 mV/dec and overpotential of 220 mV.⁶⁴ Lattice tensile strained NiFe LDHs reported by Zhou Daojin revealed an applied potential of only 1.44 V vs RHE to drive the water oxidation.⁶⁵ Besides, substrate engineering is usually used to improve the stability and conductivity of the electrocatalysts. Carbon fiber cloth, nickel foam, carbon paper, other carbon derived materials^{66,67}, CeO₂, TiO₂ are the most widely used supports or substrates. By casting the catalysts onto the supports or in situ synthesizing on the supports, most of the catalysts perform outstanding

stability and activity in a large current density, which provides continuous enthusiasm on the development of supported catalysts for potential large scale applications.⁶⁸⁻⁷⁰ On the other hand, amorphous materials, in contempt of the higher catalytic activity than their crystalline counterparts, received limited attention, due to the uncontrollable structures, scant methods of synthesis and ambiguous mechanisms on OER. A reported work of Liu Junze demonstrated that amorphous cobalt hydroxide showed enhanced OER activity attributed to the high density of active sites.⁷¹ An in situ generated amorphous CoFePi ascribed the higher activity to the unique 3D structure and amorphous-crystalline interface.⁷² In fact, most of the reported works assigned the enhanced performance to the increased active sites but there is no deep understanding the mechanism, which impeded the development of amorphous materials as high efficient OER catalysts. Here, in the thesis, at first, we have done a systematic literature review of the OER including both theoretical and experimental studies. Then by synthesizing the amorphous alloy using a room temperature reduction method, we successfully figured out the fundamental mechanism on OER for amorphous alloy revealing that the amorphous structure could be activated to expose more active sites under applied potential during the OER process. Based on the understanding of the unique structure and basic law of oxygen evolution reaction, we rationally designed an amorphous NiFeMoB system with the optimal binding energy to the intermediates demonstrating the best OER catalytic activity so far reported in the literature.

1.2 Kinetics and Mechanism of the Oxygen Evolution Reaction

1.2.1 Kinetics of the oxygen evolution reaction

To initiate the investigation on oxygen evolution reaction and the design of electrocatalysts, it is significant to figure out the fundamental thermodynamics and kinetics of electrocatalytic reactions. An electrocatalyst is typically a catalyst facilitating the electrochemical reaction involving the charge transfer process.^{14,28,73,74} In detail, the behaviors of the catalyst on their surface are associated with the adsorption and desorption of intermediates accompanied by the charge transfer between the electrode and reactants.^{11,15,18,75} Among the various electrocatalytic parameters to evaluate the performance of OER, Three parameters are generally used: overpotential, exchange current density and Tafel slope.^{14,17,76,77}

Overpotential. For a typical oxygen evolution reaction, the smallest potential of 1.23 V (vs RHE) is thermodynamically required to drive the generation of oxygen in the water splitting system.^{19,78,79} The existence of overpotential results from the additional applied potential over than thermodynamically equilibrium of 1.23 V to overcome the barriers of reaction kinetics. According to the reported work based on the thermodynamics and the Nernst equation^{80,81}, the applied potential can be described as

$$E = E^0 + \frac{RT}{nF} \ln \frac{C_O}{C_R} \quad (1.1)$$

$$\eta = E - E^0 \quad (1.2)$$

where E is the applied potential, E^0 is the theoretical potential. R is the universe gas constant. T is reaction temperature. n is the number of the transferred electrons. F is Faraday constant. C_O is the concentration of oxidized species. C_R is the concentration of reductive species. Notably, η represents the overpotential obtained at a specified current density (such as 1 mA/cm², 10 mA/cm², 100 mA/cm², 500 mA/cm²).^{76,79} Therefore, a lower overpotential means the better design of the catalyst.

Exchange current density. Another important parameter is exchange current density, which is a measure of apparent total current density include both the anodic and cathodic current density in the chemical equilibrium state of a reversible reaction. The overall current density is generally expressed as:

$$j = nFk_a[C_R] \exp\left(\frac{\alpha_a nF\eta}{RT}\right) - nFk_c[C_O] \exp\left(\frac{-\alpha_c nF\eta}{RT}\right) \quad (1.3)$$

Where j is the overall current density. n is the number of the transferred electrons. F is the Faraday constant. k_a and k_c are the rate constants of anodic and cathodic reaction. C_O and C_R are the concentration of reduction and oxidation matters. α_a , α_c represent the transfer coefficient of anodic, cathodic half-reaction. R is the universe gas constant. T is reaction temperature. η is the overpotential. At equilibrium conditions where η is 0 and j is 0, the anodic and cathodic currents are equal to each other, here the exchange current density is defined as the absolute value of anodic or cathodic current density:

$$j_0 = nFk_a[C_R] = nFk_c[C_O] \quad (1.4)$$

A higher exchange current density usually reflects the better performance for a target reaction. Unfortunately, it is difficult to obtain the value of exchange current density because we can only obtain the overall current density from the experiment data and the estimated value always accompanies a large error. Therefore, this parameter in spite of the good definition is rarely used to evaluate the activity of catalysts.

Tafel slope. Tafel slope of b is defined as how the applied potential responds to the rate of charge transfer. According to the simplified Butler-Volmer equation^{82,83}:

$$j = j_0 \left[\exp\left(\frac{\alpha_a n F \eta}{RT}\right) - \exp\left(\frac{-\alpha_c n F \eta}{RT}\right) \right] \quad (1.5)$$

In the OER process, the overall current density is mainly contributed from anodic electrode under high over potential where the cathodic part can be neglected and this expression doesn't consider the effect of mass transport.^{84,85} Accordingly, b can be obtained by simplifying the Bulter-Volmer equation to Tafel equation as

$$j = j_0 \exp\left(\frac{\alpha_a n F \eta}{RT}\right) \quad (1.6)$$

Translate the equation into logarithm form we can define the Tafel slope as

$$b = \frac{\partial \eta}{\partial \log(j)} = \frac{2.303RT}{\alpha n F} \approx \frac{60}{\alpha n} (mV/dec) \quad (1.7)$$

In this respect, a smaller Tafel slope usually indicates a better performance of the catalyst with a smaller over potential to increase the current density, which means faster kinetics on the reaction. According to the relationship of equation (1.2) and

(1.7), it can be concluded that using the overpotential η rather than applied potential E shows no influence on the measurement of Tafel slope and is often considered as the more conventional and convenient protocol for multistep reactions.^{85,86} In the simplified analysis of the four-step oxygen evolution reaction, the value of α could be regarded as 0.5 for the charge transfer step with a single electron transferred as RDS (rate determine step). Therefore, if the first charge-transfer step with one electron transferred is the RDS, the Tafel slope can be calculated as 120 mV/dec. However, if the RDS involves the second, third, fourth step with two, three, four electrons transferred, it is difficult to acquire the value of Tafel slopes due to the complexity of the α . The specific values are given based on the different pathways as shown in chapter 1.2.2. This analysis provides theoretical support to figure out the rate determine step of a real OER according to the measured Tafel slope.

1.2.2 Proposed reaction pathways of oxygen evolution reaction

Oxygen evolution reaction involves the transfer of four electrons in the half-reaction of water oxidation on the anode to produce a molecule of oxygen gas. There are a lot of researchers have put forward feasible mechanisms on the pathway for oxygen evolution reaction under both acid and alkaline. It should be noted that most of the mechanisms include the same intermediates such as OH^* , O^* , OOH^* (* is the active site), while the differences concentrate on the formation of oxygen, the general and widely accepted reaction pathway for oxygen evolution was proposed by Bockris and Otagawa.⁸⁷

Figure 1.1 Mechanistic general scheme of the catalyst, where M is the active site on the surface.

According to this reaction pathway, the initial step involves the adsorption of OH^- ions and then discharges an electron to form an adsorbed hydroxide layer ($M-OH$), equation 1.8 (Tafel slope 120mV/dec). In the subsequent step, the adsorbed OH reacts with OH^- then discharge an electron to form an oxide layer ($M=O$), equation 1.9 (Tafel slope 40mV/dec). In the third step, the oxide layer reacts with OH^- then

discharge an electron to form an oxyhydroxide layer (M-OOH), equation 1.10 (Tafel slope 24mV/dec). The last step involves a reaction of oxyhydroxide and OH^- then discharge an electron to release oxygen and back to the initial state, equation 1.11 (Tafel slope 15mV/dec). However, it has to be mentioned that these values of the Tafel slope are usually not unique for a given pathway with the surface coverage of the intermediates that may well vary with potential. Therefore, it is typically a big issue to distinguish the specific reaction pathway in a particular system. So as shown in Figure 1.1-1.6, there are a lot of mechanistic schemes have been proposed for various electrocatalysts of different nature in both acidic and alkaline media based on both the experimental and theoretical data.^{22-25,88,89}

Reaction pathway on metal oxide-based materials. Figure 1.2 provides a typical mechanistic scheme of cobalt-based materials to describe the valence state change during the oxygen evolution reaction. The Co^{2+} active site adsorbed an OH^- to form $\text{Co}^{3+}\text{-OH}$ with one electron transferring, accompanied with the second electron transferred, the valence state of Co further shifted to +4 in the terms of $\text{Co}^{4+}\text{-OH}$, however, unlike the typically mentioned pathway, this work took the neighboring OH in $\text{Co}^{4+}\text{-OH}$ to bond each other evolving an oxygen molecule as the third step. And the strong $\text{Co}^{4+}\text{-OH}$ binding was attributed to the absence of electrons in the d_{z^2} orbitals. A similar pathway of the cobalt-based catalyst was also confirmed in many other reported work.^{90,91} These works paid attention to the oxygen vacancies on the surface of oxides, which were regarded as the active sites, and usually give a route to create more oxygen vacancies to improve the OER performance. Here, for example, Xu

Wenjing et al used the ligand assisted poly reduction method to acquire oxygen vacancies enriched porous cobalt oxides exhibiting a decreased overpotential of 306 mV for OER.⁹² And a plasma engraving strategy was conducted on the cobalt oxides by Lei Xu to create more oxygen vacancies on the surface to offer a ten-times increased specific activity than the pristine Co_3O_4 .⁹³

Figure 1.2 Reaction pathway on metal oxide-based materials. Mechanistic scheme of the amorphous quaternary Ba-Sr-Co-Fe oxide (a-BSCF) in alkaline. Reproduced with permission.²⁵ Published by The Royal Society of Chemistry.

Reaction pathway on metal hydroxide and oxyhydroxide surface. Figure 1.3 displays the typical reaction pathway on the NiFe layer double hydroxides, which were regarded as the most promising OER electrocatalysts. The proposed pathway was based on in situ XAS measurements and cyclic voltammetry analysis of $\text{Ni}_{65}\text{Fe}_{35}(\text{O}_x\text{H}_y)$ catalyst.²⁴ It showed that there no catalytic activity under applied potential range from 1.0 to 1.4 V vs RHE with the active site remained the initial state of $(\text{Ni}^{2+}\text{Fe}^{3+})$. With the applied potential over than 1.4 V vs RHE, the active site

chemical adsorbed OH^- and transferred an electron with metal oxidation as $(\text{Ni}^{3+}\text{Fe}^{3+})\text{-OH}$. In the second step, further discharge of OH^- happened with the higher oxidized state of $(\text{Ni}^{4+}\text{Fe}^{3+})\text{-O}$. This work put forward a consecutive step of $(\text{Ni}^{+4-\delta}\text{Fe}^{3+})\text{-O}^{-2+\delta}$ considering the charge redistribution between metal sites and oxy ligand. And the special state was observed by in situ O-K-edge data. The third carried out under potential over 1.5 V proved by detecting the O-O bond coupling in the terms of $(\text{Ni}^{+4-\delta}\text{Fe}^{3+})\text{-O}^{-2+\delta}\text{-OH}$. Finally, the active site reduced to the initial chemical state $(\text{Ni}^{2+}\text{Fe}^{3+})$ with the fourth electron discharged. This result pointed out that only the surface species of NiOOH participated in the oxygen evolution reaction but can't distinguish the active site between Ni and Fe. This reaction pathway took the electronic of active sites as a concerned point and the oxygen evolution on the catalyst surface accompanied by a redistribution of charges. And it had been discovered the electronic interaction between metal atoms with charge redistribution in a huge amount of Ni and cobalt-based catalyst with the incorporation of Fe leading to enhanced OER performance,⁹⁴⁻⁹⁷ in spite of the unclear active sites. This interesting phenomenon attracted continuous interests in exploiting the real active site.

Figure 1.3 Reaction pathway on metal hydroxide and oxyhydroxide surface. Mechanistic scheme of the $\text{Ni}_{65}\text{Fe}_{35}(\text{O}_x\text{H}_y)$ catalyst in alkaline. Reproduced with permission.²⁴

Reaction pathway with lattice oxygen participation. The pathway reported in Figure 1.4 was different from the typical one mentioned above by emphasizing the participation of lattice oxygen with the surface oxygen vacancy in alkaline media.²³ Here, the black symbol of O was the lattice O and the purple symbol of O was from electrolytes. It is clear to observe the OH^- discharged on the lattice oxygen site rather than the metal site with the emerging of surface oxygen vacancies at the first electron transfer step. The second electron transfer step happens accompanied with the oxygen molecule desorption and OH^- adsorption on the metal site. Then in the third step, another OH^- discharged on the metal site by occupying the surface oxygen vacancy. Finally, the formed OH site discharged the fourth electron transferred and re-formed as the lattice oxygen, back to the initial state. The similar pathway was further investigated by Grimaud, A. et al.⁹⁸ They used the ^{18}O -isotopic labeling method

studied the pH-dependent oxygen evolution reaction of Perovskite $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$ ($x = 0, 0.5$ and 1) and $\text{Pr}_{0.5}\text{Ba}_{0.5}\text{CoO}_{3-\delta}$, further pointed out that these oxides were able to generate oxygen gas from the lattice oxygen with non-concerted proton-electron transferred step in the reaction pathway. These findings offered another point to design such kind of OER electrocatalysts by tuning the metal-oxygen bond strength.

Figure 1.4 Reaction pathway with lattice oxygen participation. Mechanistic scheme of the perovskite oxide catalysts in alkaline media. Reproduced with permission.²³ Copyright © 2016 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

Reaction pathway in acidic media. The OER mechanism in acidic media was usually studied on Ir and Ru based catalyst due to the fact that the other materials drastically dissolved in acidic media. Figure 1.5 displayed the possible routes for the OER accompanied by the dissolution of iridium on Ir and IrO_2 . The blue arrows showed the mechanism of the intermediates adsorption on the surface, while the green route occurred at low overpotential and red route occurred at high overpotential.

Unlike the OH^- adsorption in alkaline media, the oxygen resource was H_2O in acidic media. The reaction pathway was similar to the pathway discussed above (Figure 1.1) and reported by many works.^{99,100} However, it should be noted that the process of dissolution was different at low and high overpotential. It can be seen at low overpotential that the iridium dissolved in terms of Ir^{3+} after decomposition of the intermediate of $\text{HIr}^{4+}\text{O}_2\text{OH}$ into O_2 and $\text{HIr}^{3+}\text{O}_2$ on the surface, which was observed by mass spectroscopy. But at high overpotential, the iridium dissolved in terms of IrO_4^{2-} after the transformation of the intermediate of $\text{HIr}^{4+}\text{O}_2\text{OH}$ into IrO_3 on the surface. This result in fact indicated the short-term stability in acidic media. Besides, Figure 1.5b detailed investigated the reaction pathway and the effect of the addition of H_2O_2 of OER on IrO_x based on the theoretical DTF calculation and in situ electrochemical evanescent wave spectroscopy and inlet electrochemical mass spectroscopy. The result further confirmed the inevitable intermediated state of Ir^{4+} indicating the pathway of blue arrows proposed in Figure 1.5b. Based on the understanding of the dissolution of noble based catalysts, several kinds of approaches had been applied including composing the noble metal into the stable TiO_2 , constructing the mixed rutile structure of Ru-IrO_x .^{33,101} All in all, The studies of reaction pathway for various catalyst systems in both alkaline and acidic media based on both in situ experiments and theoretical calculation provided possible strategies to design OER catalyst with high performance and long-term stability.

Figure 1.5 Reaction pathway in acidic media. (a) Mechanistic scheme of the Ir-based materials in acidic media. Reproduced with permission.⁸⁸ (b) Mechanistic scheme and the interaction with H₂O₂ of iridium oxide. Reproduced from Ref.⁸⁹ with permission from the PCCP Owner Societies.

1.2.3 Insight of the descriptors toward the trends of activity

As the discussion in sections 1.2.1 and 1.2.2, all of the proposed mechanistic schemes of reaction pathway were associated with the OH^{*}, O^{*}, OOH^{*} intermediates. In light of this, a lot of research had been focused on the ideas of a universal descriptor which demonstrated the catalytic activity trends on the variety of OER catalytic materials.^{15,28} Besides, it has been demonstrated by numerous experimental data in the last decades that the so-called Sabatier principle (Figure 1.6) is an extremely useful principle for heterogeneous catalysis, which declares that the best catalyst required the active site binding to the key intermediate neither too weakly nor too strongly.^{10,75} According to the fact that the oxygen evolution reaction was usually carried out under a high anodic potential, the reaction always proceeded on the oxidized surface. Additionally, Bockris and Ottagawa, based on their abundant

electrochemical work, stated that the catalytic performance of OER was associated with the intermediates of OH binding on the catalyst surface.¹⁰² Deeper theoretical thermodynamic research from Marc T.M. Koper concluded that the catalytic activity was correlated to the O^* adsorption energy.^{18,75} And kinetic simulation on catalyst surface by DFT from Norskov also made significant contributions to this point in OER reaction.¹⁵ Therefore, based on the reaction mechanism of OER and the Sabatier principle from heterogeneous catalysis,¹⁰ it can be inferred that a too strong adsorption OOH^* or too weak adsorption of O^* limit the activities of most catalysts. As shown in Figure 1.7-1.10, a lot of descriptors were established on various kinds of materials toward the trends in electrocatalytic activity^{26-28,103-106} based on both theoretical and experimental database of OOH^* and O^* adsorption energies on oxides surface.²⁸ Most of the obtained catalytic activity followed volcano-type plot with the change of enthalpy ($OOH^* - O^*$), toward the OER on oxides based structures (rutile, spinel, and perovskite). And these results were consistent with the reported experimental data. Besides, other descriptors based on OH^* , O^* displayed similar conclusions. The catalyst with the highest activity was at the top of the volcano.

Figure 1.6 Schematic representation of the qualitative Sabatier principle. ¹⁰⁷Copyright © 2015 Published by Elsevier Inc.

Activity trends towards OER for single-crystalline oxides. The trends towards OER for perovskites were systematically studied by Jens K. Nørskov and Jan Rossmeisl as shown in Figure 1.7a.²⁸ Here, based on the abundant database of calculated energies binding to O and OH on these oxide surface, the descriptor of $(\Delta G_{O^*} - \Delta G_{HO^*})$ was introduced, constructing a universal description of the activity trends toward oxygen evolution reaction. The plot gave the increased activity of single crystal as LaMnO_3 , LaFeO_3 , LaCoO_3 , SrFeO_3 , SrNiO_3 , LaNiO_3 , SrCoO_3 , in agreement with the reported experiment data of Bockris et al. and Y. Matsumoto et al.^{108,109} It should be noted that the calculated results took all of the oxide structure as crystal and used the reaction proposed and discussed in chapter 1.2.2. Other oxides included rutile, anatase and Mn_xO_y were displayed in Figure 1.7b. The plot gave the increased activity of crystalline structure as ReO_2 , VO_2 , CrO_2 , MoO_2 , PtO_2 , RuO_2

permission.²⁸ Copyright © 2011 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim (c) Activity trends for various metal oxides. From Ref.¹⁰⁶ Reprinted with permission from AAAS.

Activity trends towards OER for lattice oxygen participated system. Chapter 1.2.2 had discussed the reaction pathway on the lattice oxygen participated oxide surface. Here activity trends toward OER for lattice oxygen participated system were reported as emerging from the studies of Alexie M. Kolpak.²⁶ As shown in Figure 1.8a, and b, the negative reaction free energy plotted against Gibbs energy of intermediates of O^* , where the shadow indicated the similar volcano type based on both adsorbate evolution mechanism and lattice-oxygen participation mechanism. However, the lattice-oxygen participation mechanism displayed smaller overpotentials at the top of the volcano plot than that of the adsorbate evolution mechanism for lanthanum based perovskites due to the relatively constant value for transformation from $(V_O + OO^*)$ to $(V_O + OH^*)$. The study further indicated the importance of energy binding to oxy intermediates in the lattice-oxygen participated system too.

Figure 1.8 Activity trends towards OER for lattice oxygen participated system. (a) Activity trends for lanthanum-based perovskites based adsorbate evolution

mechanism and (b) lattice-oxygen participation mechanism, respectively, plotting against the standard free energy of ΔG_{O^*} . Reproduced with permission.²⁶ Copyright © 2018, American Chemical Society.

Activity trends towards OER for metals in a non-oxygen environment. Jumras Limtrakul and Vinich Promarak¹⁰⁵ studied the trends activity toward the particular system of metalloporphyrin frameworks (Figure 1.9) where the well-defined same frameworks with various metals as active sites include Cr, Mn, Fe, Co, Ni, Cu, Zn, Ru, Rh, Pd, Ag, Ir, Pt and Au. It should be noted that the metal center bonded to non-oxygen elements such as N, Cl, I, F, et al in this kind of structure. So it is clear to distinguish the influence from different crystalline surfaces. These results also plotted the theoretical overpotential against the free Gibbs energy of ($O^* - OH^*$) giving the decreased activity as metalloporphyrin frameworks with the metal center of Ir, Co, Rh, Ni, Pd, Ag, Zn, Au. Further study on the halogen substitutions also showed the decreased activity of Ir-F, Co-F, Rh-F. It can be concluded that the activity trends toward OER followed the volcanic plot with the descriptor of ($\Delta G_{O^*} - \Delta G_{HO^*}$) even in the same chemical environment without oxygen for various metals furnishing instruction on the design of non-oxides based metal catalysts.

Figure 1.9 Activity trends towards OER for metals in a non-oxygen environment. Volcanic plot for transition metals plotted as a function of $\Delta G_{\text{O}^*} - \Delta G_{\text{HO}^*}$. Reproduced from Ref.¹⁰⁵ with permission from the PCCP Owner Societies.

Activity trends towards OER for the non-metal system. Figure 1.10 displays the activity trends towards OER on different sites of the armchair and zigzag graphene nanoribbons by plotting the overpotential against the Gibbs free energy of ($\text{O}^* - \text{OH}^*$). It should be noted that almost all of the active sites showed increased active activity at the left of the volcano plot. The phenomenon could be interpreted by the charge redistributing on the planar graphite due to the strong electronegativity of nitrogen in the carbon plane. Volcanic type plot derived from the descriptor of ($\Delta G_{\text{O}^*} - \Delta G_{\text{HO}^*}$) further ascertained the significance of the intermediates binding energy on the surface sites. Although these carbon-based materials usually showed bad stability for oxygen evolution reaction, the activity trends induced by different active sites also gave a useful reference for design nonmetal OER electrocatalysts.

Figure 1.10 Activity trends towards OER for the non-metal system. Activity trends for different sites of the armchair and zigzag graphene nanoribbons plotted against the standard free energy of the $\Delta G_{O^*}^0 - \Delta G_{OH^*}^0$. Reproduced with permission.¹⁰⁴ Copyright © 2014 Elsevier Inc. All rights reserved.

The scaling relationship in the oxygen intermediates based descriptor. A confusing phenomenon could be obviously concluded from all of these above descriptors^{26, 28, 104, 105} that even the electrocatalyst at the top of the volcano plot showed a significant value rather than zero of overpotential for oxygen evolution reaction. These behaviors are attributed to the so-called scaling relationship. In general, the binding energy of O^* to the metal usually shows the near double value of OH^* to metal due to the double bond between O and metal compared with the single bond between OH and metal (Figure 1.11a). Meanwhile, the binding energy of OOH^* to the metal usually showed constant value over OH^* . A proximate equation for transition metals could be described as:

$$\Delta G_{OOH^*} - \Delta G_{OH^*} = 2.8 \text{ eV} \quad (1.13)$$

$$\Delta G_{O^*} = 1.65 \cdot \Delta G_{OH^*} + 0.58 \text{ eV} \quad (1.14)$$

Experimental and theoretical data based on various kinds of transition metals were shown in Figure 1.11b and c. The scaling relationship revealed that the optimal overpotential at the top of the volcanic plot can't reach the value of zero. The results offer an increasing interest to break through the limitation by establishing the electrocatalytic on two sites assisting each other rather than on a single site. Although there were limited experimental results collected to design and develop to overcome the scaling relationship. The theoretical calculations proved that breaking such scaling relationship resulting in a greatly enhanced catalytic activity, however, remained to be carried out in experiments.¹¹⁰

Figure 1.11 The scaling relationship in the oxygen intermediates based descriptor. (a) Schematic representation of the scaling relations for ΔE_{O^*} , ΔE_{OH^*} , ΔE_{OOH^*} as a function of ΔE_{O^*} . (b) Scaling relations between ΔE_{O^*} and ΔE_{OH^*} and (c) ΔE_{OH^*} and ΔE_{OOH^*} . Reproduced with permission.²⁷ Copyright © 2013, American Chemical Society.

1.3 Electrocatalysts Design for Oxygen Evolution Reaction

1.3.1 Catalysts from noble metal-based rutile, pyrochlore, and hollandite

Based on the understanding of the above fundamental mechanism and descriptors, a huge amount of materials had been developed and designed to overcome the higher overpotential of OER. For example, numerous interests were concentrated on several classes of crystal structures: metal dioxides, spinels, perovskites, rock salts, layer hydroxides and pyrochlores.^{29,30,34-38,111} A typical example was shown in Figure 1.12a, here rutile based materials showed the tetragonal crystalline structure where the metal ion coordinated by six oxygen and oxygen showed the trigonal planer coordination. The rutile-type materials such as RuO_2 ,¹¹²⁻¹¹⁵ IrO_2 ,¹¹⁶⁻¹¹⁹ TiO_2 ,^{119,120} were typical kinds of metal dioxides for water oxidation, especially the precious RuO_2 , IrO_2 showed the best activity in both acid and base electrolytes. However, it had been studied that the rutiles, especially RuO_2 , exhibited meaningful dissolution¹⁰¹ under applied potential during oxygen evolution reaction in terms of RuO_4^{2-} and IrO_4^{2-} as mentioned in chapter 1.2.3. The mixed RuIrO_x oxides were reported to an effective way to both improve the catalytic activity and hinder the dissolution of Ru and Ir, in which Ir acted as an Ir protective skeleton to balance the stability and activity.¹²¹ The core-shell $\text{RuO}_2@\text{IrO}_2$ in Figure 1.12b was a typical example of designed mixed oxides, which showed a 3-fold current density than the pure IrO_2 at the potential of 1.48 V vs RHE. And it seemed that the stability of the mixed oxides mainly resulted from the more

precious IrO_2 . More exquisite investigation on the dissolution was conducted on the crystallinity of IrO_2 .¹²² By calcining the Ir at 250, 350, 450, 550 °C, increased stability was observed, the author attributed the higher stability to the strong lattice oxygen and less surface hydroxylation. Furthermore, the incorporation of Ti into the strong lattice structure at the high temperature offered more stability by forming various oxides species on the surface.¹²³ However, an ambiguous fact that the amorphous and amorphous-crystalline mixed IrO_x exhibited more stably to catalysis water splitting. The reason for the enhanced stability still remained unclearly for the amorphous structure. Otherwise, for system design, a kinetic study by Rossmeisl¹⁵ suggested that the overall reaction rate of oxygen evolution is mainly decided by the adsorption strength of intermediates on the Ru and Ir sites. The unsaturated Ru and Ir sites announced the linear relationship between binding energies of intermediates on the surface.¹²⁴ And associated with the Sabatier principle, the universal relationship between binding strength to oxygen and catalytic rate could offer guidance to design the best catalyst on this kind of oxide surface. And the type of analysis was also extended to the other kinds of structures.^{97,125,126} Other crystalline structure of hollandite was displayed in Figure 1.12c and d as an example, the Ir centers, coordinated by six oxygen, showed lower valence states by the high occupied d orbital leading to vigorous binding energy to the intermediates. These similar effects were also discovered in pyrochlore and other noble metal-based electrocatalysts, indicating the regulation induced from the alkali metal ions.^{29,127} It should be

mentioned that the influence of alkali metal ions to the active centers was studied in other catalysts and electrolytes.

Figure 1.12 Catalysts from noble metal-based rutile, pyrochlore, and hollandite. (a) Atomic model of rutile (110) metal dioxide surface, and (b) TEM images of RuO_2 , $RuO_2@IrO_2$, IrO_2 . Reproduced with permission.³⁰ © 2017 Published by Elsevier B.V.. (c) Crystal structure of $K_{x \approx 0.25}IrO_2$ and IrO_2 , and (d) related TEM images. Reproduced with permission.²⁹ © 2017 Published by Elsevier B.V..

1.3.2 Catalysts from spinel

Aside from the precious electrocatalysts, another important family of OER catalyst was the spinel structure-based materials, which was usually composed of first-row transition metal elements in group 2 and group 13 with the formula of AB_2O_4 . A and B typically were regarded as two kinds of crystallographic sites so-called octahedral with six oxygen coordinated and tetrahedral with four oxygen coordinated. The model of crystalline structure and HRTEM images of the typical morphologies were shown in Figure 1.13a and b. The difference between the sites usually resulted in different d-band splitting according to the crystal field theory,¹²⁸ where the octahedral center usually displayed lower energy orbitals of t_{2g} while the tetrahedral center displayed the e_g as lower energy orbitals. Therefore, the difference of orbitals arrangement was known to lead to different binding strength to oxygen, resulting in different catalytic activity.

Figure 1.13 Atomic models and morphology of spinel. (a) Crystal structure of spinel and orbital splitting of transition metals in an octahedral and tetrahedral geometry. Reproduced with permission.³⁶ © 2019 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. (b) Aberration-corrected HAADF-STEM images of LT-LiCoO₂. Reproduced with permission.³⁷ Copyright © 2014, Springer Nature.

The most famous spinels for OER were usually iron based¹²⁹⁻¹³¹ such as CoFe₂O₄¹³², CuFe₂O₄, NiFe₂O₄, MnFe₂O₄, cobalt based^{133,134} such as CoCo₂O₄, NiCo₂O₄, MnCo₂O₄. Besides, it had attracted a lot of interest in discovering the active sites in spinel responsible for oxygen evolution. Co₃O₄ was regarded as the most simplified structure to study the two kinds of sites. So substituting the tetrahedral Co²⁺ or octahedral Co³⁺ by another metal ion provided an effective method of comparing the difference between two sites for oxygen evolution reaction. Although the incorporation of transition metals tended to occupy both of the tetrahedral and octahedral sites or only part of octahedral sites, Zn and Al were discovered completely to substitute the tetrahedral and octahedral sites in Co₃O₄ respectively.¹³⁵ It had been found that the trend of OER activities in the order of CoAl₂O₄ > Co₃O₄ > ZnCo₂O₄ in alkaline with the facts that Zn and Al oxides showing little OER catalytic activity. The Tafel slope of 56 mV/dec for the CoAl₂O₄ indicated the rate determine step of deprotonation after the first step while the Tafel slope of 113 mV/dec for the ZnCo₂O₄ indicating the rate determine step at first OH⁻ adsorption step, suggesting weak adsorption of OH⁻ on the octahedral sites. Furthermore, the in situ Co K-edge EXAFS spectra for CoAl₂O₄ and Co₃O₄ displayed significantly decreased of Co-O bond under applied potential while showing no change for ZnCo₂O₄, which not only

confirmed the tetrahedral Co initiated CoOOH as active sites but also seemed to point out the $\text{Co}^{2+}/\text{Co}^{3+}$ rather than $\text{Co}^{3+}/\text{Co}^{4+}$ transformation during the oxygen evolution reaction.

Although there were other reported works supported the octahedral sites as active sites,^{36,136} most of the works mention the formation of CoOOH on the spinel surface accompanied by a surface reconstruction. A detailed investigation on the spinel surface by Shuo Zhang³⁷ disclosed that an amorphous layer of $\text{Li}_x\text{Co}_2\text{O}_{4-\delta}(\text{OH})_\delta$ was generated on spinel $\text{Li}_2\text{Co}_2\text{O}_4$ under electrochemical oxygen evolution with the appearance of Co^{4+} . The operando Co K-edge XANES proved the appearance of Co^{4+} by increased exciting energy and the amorphous layer on the spinel surface after OER was observed by HAADF-STEM images. The author attributed the amorphous transformation to the appearance of Co^{4+} . With the delithiation in the structure under increased applied potential, oxygen vacancies formed on the surface and the valence state of Co shifted to the high 4+, then a self-reconstruction occurred by hydroxyl adsorption on the defects. Finally, there was a 20 mV decrease of overpotential at the current density of 10 mA/cm^2 . And long term durability study by L. Calvillo revealed that these obvious activated 3 nm amorphous layer formed on the aged spinel surface while the bulk kept on the crystalline structure after electrochemical oxygen evolution, these complicated amorphous layers tended to lose metal ions under applied potential causing the loss of OER performance.¹³⁷ The similar oxy amorphous layers were also observed by many other works, suggesting the importance of amorphous structure for enhanced oxygen evolution reaction.¹³⁸ And the relationships among the stability,

OER catalytic activity and the amorphous layer were still remained to be figured out in the future.

1.3.3 Catalyst from perovskite

Perovskites are another kind of OER catalysts with the general formula ABO_3 , in which one or more alkaline or rare-earth metals occupy A sites and transition metals occupy the B sites. In an ideal cubic unit cell, A is usually a larger metal cation in 12-fold cuboctahedral coordination, B is usually small metal cation in 6-fold octahedral coordination. The typical crystalline structure and TEM images were shown in Figure 1.14a and b. The various sizes of the cations usually lead to the change of coordination number of the A, B sites, which offered a strategy to design the OER catalysts by regulating the binding energy of active sites to oxy intermediates.³⁵

Figure 1.14 Atomic models and morphology of perovskite. (a), (b) Crystal structures of perovskites and perovskite hydroxides, and SEM, TEM images of Co-Sn-Ti nanotube. Reproduced from Ref.³⁵ with permission from The Royal Society of Chemistry.

The famous study on such structure was accomplished by Suntivich et al,¹³⁹ which established a clear relationship between the occupancy of e_g orbital of the transition active site and binding energy of oxy intermediates on the surface, causing the changes of activities for perovskites. The descriptor based on the fact that the e_g orbital of the transition active site participated in the bonding to oxy intermediates, therefore, the occupancy showed a great impact on the binding energy oxy intermediates on the surface sites.¹⁴⁰ By examining the catalytic performance of more than 10 transition metal oxides systematically. A volcano-shaped diagram was acquired by plotting the OER catalytic activity versus the occupied electron on 3d orbital suggesting the peak of OER performance with the nearly unit e_g occupancy, which guided to the highest catalytic activity of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF) with the comparable overpotential as IrO_2 at the normalized activity of 10 A/g_{ox}. In terms of this observation, these results combined the binding strength of oxy intermediates and electronic states of transition metal active sites. The filling number of the e_g orbital was developed as a really effective descriptor accounting for the electrocatalytic oxygen evolution activity for perovskites. For example, according to the descriptor, Yuqiao Guo et al engineering the electronic state of calcium manganese oxide to obtain 0.81 occupied e_g orbital of Mn, exhibiting the 100 times enhanced oxygen evolution activity over the pristine catalyst.¹⁴¹

However, the above descriptor of e_g occupancy was established on the ex situ and initial state of the bulk catalysts. Therefore, a further study was reported by Emiliana Fabbri on the dynamic surface and electronic state of the active sites during the oxygen evolution reaction for perovskites.¹⁴² As mentioned in chapter 1.2, with the applied potential increasing, not only the OH^- oxidation on the catalytic surface to evolve as oxygen, the lattice oxygen on the surface of catalyst could also participate in the reaction. The phenomenon had been observed by in situ XAS measurement indicating a surface self-reconstruction during the OER process. The above unit e_g occupied materials $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF) seemed to be a better precursor to generate a the oxy (hydroxide) layers on the surface more easily, which could be the real active species for oxygen evolution reaction, as discussed in the rutiles and spinels in chapter 1.2.3 and 1.3.1. The unit e_g occupied catalysts, in fact, presented numerous oxygen vacancies on the surface accounting for the flexible structure leading to better OER activity. Other examples of pristine structures were also observed to generate the oxygen vacancies by alkaline metal ion leaching. Up to date, most of the developed models and mechanisms established on the facts that the oxygen evolution activity was correlated to the adsorption of intermediates on the initial electrode. The self-reconstructed surface oxy (hydroxide) layers should be put more attention, where the layers usually showed the amorphous states indicating more interest in the amorphous for OER.

Another significant challenge for the high active e_g occupied materials $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF) was the stability under applied potentials. In fact,

usually, the high activity was accompanied by low durability which could be due to the self-reconstructed surface induced by oxygen vacancies. A $\text{SrSc}_x\text{Nb}_y\text{Co}_{1-x-y}\text{O}_{3-\delta}$ perovskite (SSNC1) was studied by Wei zhou for high activity and durability oxygen evolution reaction.¹⁴³ The $\text{SrSc}_x\text{Nb}_y\text{Co}_{1-x-y}\text{O}_{3-\delta}$ perovskites exhibited the enhanced performance by offering near 5.8 times of current density than the $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF) at an overpotential of 0.35 V and little degrade was observed after 17 hours OER operating at 0.7 V vs Ag/AgCl (3 M NaCl) in 0.1 M KOH. This long term stability was attributed to the unchanged surface for $\text{SrSc}_x\text{Nb}_y\text{Co}_{1-x-y}\text{O}_{3-\delta}$ perovskites (SSNC1) after OER. The HRTEM of the aged catalyst displayed no obvious self-reconstructed structure on the surface. It can be speculated that there was a single or ultrathin oxy (hydroxide) layer formed on the surface during OER based on the above discussed. Therefore, self-reconstructed oxy (hydroxide) layers were not only responsible for the high activity but also constituting for the stability under applied potential for perovskites.

1.3.4 Catalyst from layer double hydroxides

The family of layered hydroxides including $\text{M}(\text{OH})_2$ and MOOH (M could be Ni, Fe, Co, Mn, etc) usually exhibits considerable high activity for oxygen evolution, as shown in Figure 1.15a, b, c. It is usually a layer structure with the unit layer of AcB, where A and B represent the layers of OH^- and c is the layer of metal ions, then two of the AcB layers construct as a double-layer structure in terms of $[\text{AcB Z AcB}]$ where Z is the layer of other ions or neutral molecules. The typical examples are nickel-based

and cobalt-based layer double hydroxides. It should be noted that the kinds of Z show a significant influence on the kind layer double hydroxide. For example, the beta phase (β -MOOH) usually uses protons as Z layers and the gamma phase (γ -MOOH) usually uses alkali ions or water molecules as Z layers. With the increased interest in water splitting, these layer double hydroxides and oxyhydroxides^{94,96,97,144-147} had been regarded as a kind of promising catalyst for OER due to their excellent property in alkaline media.

Figure 1.15 Atomic models and morphology of layer double hydroxides. (a), (b), (c) Structural models for the OER active (Ni, Fe) OOH catalysts. Reproduced with permission.³⁸ Copyright (2018) National Academy of Sciences Proc. (d) FE-SEM and TEM images of N-rGO_{ae} spray-coated on CFP, Ni(OH)₂ electrodeposited on the N-rGO_{ae}/CFP. Reproduced with permission.³⁴ Copyright © 2017, Springer Nature.

Due to the flexible structure double layer under anodic potential, the early researcher carried out abundant works on the dynamic change of the structure during oxygen evolution reaction. H. Bode et al^{146,148,149} proposed and proved the phased transformation by giving the bode scheme for nickel hydroxide. The initial β -Ni(OH)₂ with the layer spacing of 4.7 Å charged into an increased layer spacing of 4.8 Å in the terms of β -NiOOH as shown in the following equation:

With the continuous charging process, the larger water molecules inserted into the layers accompanied by the formation of γ -NiOOH with the layer spacing over than 7 Å, further charging of the γ -NiOOH led to the α -NiOOH phase which similar to γ -NiOOH but with more ions and molecules between the layers. These charged products were accompanied with valence state of Ni from 2+ to 3+, and could be charged directly back to the initial phase of β -Ni(OH)₂. The early researchers attributed the high OER activity of nickel hydroxide into the β -Ni(OH)₂ by phase transformation, however, Alexis T. Bell et al¹⁴⁶ discovered that pure β -Ni(OH)₂ aged in Fe free electrolytes exhibited a considerably poor OER activity although the β -NiOOH and γ -NiOOH formed as the domain phase undercharging and overcharging. In contrast, pure β -Ni(OH)₂ aged in Fe contained electrolytes exhibited a substantially higher catalytic oxygen evolution activity in the phases of β -Ni(Fe)OOH and γ -Ni(Fe)OOH. More evidence from Shannon W. Boettcher stated that cyclic

voltammetry on Fe free β -Ni(OH)₂ still displayed⁹⁷ two redox peaks of Ni suggesting the enhanced activity resulted from Fe incorporation rather than phased transformation. Interestingly, it had been found that the β -NiOOH phase showed lower activity than the γ -Ni(Fe)OOH phase, which was the amorphous structure. This result was consistent with the self-reconstruction of the surface in chapter 1.3.1~1.3.3 demonstrating the important influence of the amorphous structure for oxygen evolution reaction.

The most important question in such kind of materials was related to nickel-iron layer double hydroxide, which could be the most active OER catalyst according to reported materials in alkaline in experiments.^{97,150-152} It is pointed out that the incorporation of Fe in nickel hydroxide exhibited a dramatic increase of activity, and numerous work had been put into the investigation of the role of iron for improved intrinsic catalytic activity based on the above discussion of phase transformation for nickel hydroxide. As reported by Chen, J. Y. *et al.*, under long term water splitting, tetravalent irons were discovered in the NiFe hydroxide catalyst with the ratio of Ni/Fe near 3, however, the little signal of Fe⁴⁺ existed for the OER process in the Fe oxide. Although it remains unclear that the active site for OER was originated from the observed Fe⁴⁺ species, these experiments emphasize the important role of Fe enhancing the OER activity in NiFe based electrocatalysts by offering the high 4+ valence state.¹⁵¹ Besides, a combination of the experiment with calculation, the role of Fe was further studied by Goldsmith, Z. K. *et al.*¹⁵² It had been shown that the Fe⁴⁺ and high valence states of Ni formed at the redox peak with the increased applied

potential before the onset of oxygen evolution on Ni_3FeO_x surface. The theoretical results indicated that the conduction band minimum was changed due to incorporated Fe, in which, $\beta\text{-NiOOH}$ favored the oxidation of Fe^{3+} to Fe^{4+} meanwhile Fe^{4+} enhanced the electronic conductivity of Ni-Fe structure. However, Shannon W. Boettcher et al pointed out the more than 30-fold increased conductivity was not enough to explain the dramatic enhancement in the activity by the lower thickness-dependent TOF than pure $\beta\text{-Ni(OH)}_2$ on Au and glassy carbon. Although a theoretical DFT for OER on Fe and Ni site was conducted respectively, by Alexis T. Bell,⁹⁴ suggesting Fe tended to be the active site by giving a lower overpotential. The answer was still not trusted because of ignoring Fe^{4+} . Another experimental fact offered by Peter Strasser¹⁵³ revealed that there were lower valence states of Ni in Ni-Fe materials than in pure Ni materials under applied potential. The author inferred that the low-level oxidation Ni could be served as the active sites, with the role of Fe was to increase the proportion of low oxidation Ni under applied potential. Therefore, although it is still not very clear which metal acted as the active sites yet, the incorporation of Fe could greatly enhance the conductivity, offer high valence states of Fe^{4+} centers and reduce the oxidation level of Ni under applied potential. A similar phenomenon was observed in cobalt-based materials too, therefore, further investigation of the active site was still a significant subject. Generally, most of Ni, Fe, Co-based layer double hydroxide showed good stability over than tens of hours, due to the stable oxy(hydroxide) in strong alkaline media even under high overpotential. Less stability under the severe condition of 80 °C was tested by Chen Rong et al,

stating the instability resulting from the diffusion of proton acceptors into the interlayers.¹⁵⁴

1.3.5 Catalyst from metal chalcogenides, nitrides, phosphides

Besides, other metal-based crystalline catalysts including metal chalcogenides,³⁹⁻⁴³ nitrides,⁴⁴⁻⁴⁸ phosphides⁴⁹⁻⁵³ were also developed as OER catalysts showing remarkable activities. The variety of the above-mentioned materials represented the kind of non-oxides for oxygen evolution reaction. In fact, metal chalcogenides, nitrides and phosphides acted as excellent OER catalysts usually by in situ transforming into oxides, hydroxides, oxyhydroxides on the surface and some even in bulk under applied potential. However, it had been reported that most of the metal chalcogenides, nitrides and phosphides exhibited better performance than the pure oxides and hydroxides phases. It can be inferred by experiments and theoretical calculations that 1) these kinds of pre-catalysts could transform to the hydroxides sometimes amorphous mix oxyhydroxides with a higher surface area. 2) often the core-shell structure of surface oxides-bulk chalcogenides, nitrides and phosphides offered a better conductivity than oxides. 3) another advantage was the synergistic electronic interaction between the N, P, S, Se, O and metal sites which could optimize the binding energy to the intermediates.

For example, cross columnar NiTe/NiS reported by Ziqian Xue¹⁵⁵ demonstrated only an overpotential of 257 mV to drive the oxygen evolution reaction at a current density of 100 mA/cm². The XPS and XAS provided the evidence of oxidized surface

and meanwhile revealed the strong electronic interaction on the interface induced by Te and S tuning the binding energy to intermediates finally enhancing the catalytic activity. Besides, a typical material of NiS/Ni₂P/carbon cloth was acquired by Xin Xiao¹⁵⁶ expressed an outstanding performance by offering the overpotential of 265 mV at 20 mA/cm². The electrochemical surface area test indicated the increased ECSA of NiS/Ni₂P/carbon cloth than pure NiS/CC and Ni₂P/CC suggesting that mixed chalcogenides and phosphides could further enhance the surface area for active sites. And it should be noted that the ECSA was acquired after surface activation under applied potential. A detailed phase transformation study on the surface of NiS was obtained by MinohLee.¹⁵⁷ It showed that the activated NiS/nickel foam drove the oxygen evolution at 10 mA/cm² with an overpotential of 256 mV, which was near 100 mV less than the activated pure oxidized nickel foam and near 80 mV less than bare nickel foam. Further investigation indicated that about 700 nm thickness of hydroxides/oxyhydroxides layer was observed on the surface, and the layer seemed to display as an amorphous structure. The XPS of S 2p displayed a weak signal suggesting the dissolution of S and the increased binding energy of Ni 2p further confirmed the oxidation of NiS providing abundant active sites for enhanced OER. It demonstrated that the formation of the amorphous hydroxide layers was usually due to the S (Se, P, Te, N) etching into electrolytes. Similar phenomenon were also discovered by many other researchers for lots of materials including Fe₃S₄@NiS,¹⁵⁸ NiSe₂/FeSe₂,¹⁵⁹ CoSe,¹⁶⁰ CoP,¹⁶¹ NiP,¹⁶² FeP/NiP.¹⁶³ CoNiN¹⁶⁴ CoN₄.⁴⁴ Since the main active sites in these catalysts were regarded as the metal centers, as discussed in

above chapters, multi-metals of Ni, Co, Fe chalcogenides, nitrides and phosphides were mostly synthesized to drive water oxidation, and on the other hand, due to the non-oxide structure of these kinds of pre-catalysts, often they were used to conduct hydrogen evolution reaction too and finally act as whole water splitting electrocatalysts. Interestingly, it was more commonly to prepared the transition metal chalcogenides, nitrides and phosphides on a conductive substrate such as nickel foam, carbon cloth, commercial alloy, carbon paper, which could be accounted for the conductivity of the core-shell structure. Vulcanization, selenization, phosphating, nitriding of the nickel foam or commercial alloy under annealing by reductants containing S, Se, P were the common methods. A typical example was the self-reconstruction 3D NiP foam reported by Xiaoguang Wang,¹⁶⁵ the purchased nickel foam was washed thoroughly by water and acetone, and dilute hydrochloric acid was used to remove the surface oxide layers, then the clean and dried nickel foam was annealed in a tube furnace under a nitrogen atmosphere with the red P at the upstream side at 250 °C. The 3D NiP foam was obtained after 3 hours consisting of Ni₂P skeletons covered with NiP_{0.8}-NiP₂ nanosheets. The OER performance demonstrated more than 300 mV decrease of overpotential at 200 mA/cm² than the pure nickel foam. Additionally, another route was the direct way that transition metal chalcogenides, nitrides and phosphides were synthesized on the carbon cloth and carbon paper at one step. For instance, β -NiS/carbon cloth was directly fabricated by hydrothermal method.¹⁶⁶ The commercial carbon cloth was pre-treated by concentrated hydrochloric acid to obtain a hydrophilic surface, then put into a Teflon-lined autoclave contain the

solution of nickel acetate and thiourea. By sealing and heating in a furnace at 180 °C for 48 hours, the β -NiS/carbon cloth was gained. Nanopowders of transition metal chalcogenides, nitrides and phosphides were transformed from the oxides, hydroxides precursors under annealing by reductants too. The transition metal nitrides were the typical kind materials synthesized by annealed at ammonia atmosphere,⁴⁴ as reported by Pengzuo Chen, the metallic Co_2N sample was acquired by annealing the β - $\text{Co}(\text{OH})_2$ precursor in a tube furnace under ammonia atmosphere at 380 °C for 2 hours. Interestingly, by substituting the precursor to α - $\text{Co}(\text{OH})_2$ but keeping the same other conditions, the black Co_3N was obtained, and further study by using Co_3O_4 as the precursor and changing the temperature to 420 °C, metallic Co_4N sample was finally prepared. The results of OER performance revealed the increased activity in the order of increased Co ratio which was interpreted by the enhanced intrinsic conductivity in Co_4N electrocatalyst. And it can be concluded that all of these fabricated transition metal chalcogenides, nitrides and phosphides demonstrated a conductive core even the surface was completely oxidized under applied potential, which was a good design for overcoming the bad conductivity of metal oxides and hydroxides.

1.4 Amorphous Materials as Efficient Electrocatalysts

1.4.1 Development of amorphous electrocatalysts

The amorphous or non-crystalline structure is a kind of solid without the long-range ordered atomic arrangement which is a typical equilibrium state for crystal in condensed matter physics and materials science. As discussed in chapter 1.3, most of

the crystalline electrocatalysts undergo a surface reconstruction during oxygen evolution under applied potential. And the transformed surface layers usually exhibit amorphous features. However, it still remains unclear how the amorphous structure affects the oxygen evolution reaction and lack of direct study on the pristine amorphous electrocatalysts rather than the in situ transformed amorphous electrocatalysts. Therefore, we decide to put attention into the amorphous structures. And we develop a significant project on designing the pristine amorphous electrocatalysts to figure out the mechanism for their oxygen evolution performance.

Figure 1.16 Morphology and catalytic performance of various amorphous catalysts. (a) The TEM images of $\text{Co}_3(\text{OH})_2(\text{HPO}_4)_2$ pre-catalyst after the OER and HER stability tests. And (b) The OER and HER polarization curve recorded for $\text{Co}_3(\text{OH})_2(\text{HPO}_4)_2$ on nickel foam. Reproduced with permission.¹⁶⁷ © 2019 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. (c) High-resolution TEM image and EDS mapping of the a-Mo-Ni₃S₂ nanosheets. And (d) HER polarization curves, Tafel plots of the a-Mo-Ni₃S₂. Reproduced from Ref.¹⁶⁸ with permission from The Royal Society of Chemistry. (e) TEM, HRTEM, HAADF-STEM images and the corresponding EDS mapping of amorphous NiMoP. And (f) OER polarization curves, Tafel plots. Reproduced with permission.¹⁶⁹ © 2019 Elsevier B.V. All rights reserved. (g) TEM image and HRTEM images after the pretreatment of the AH-CO. (h) LSV curves and TOFs of the catalysts. Reproduced with permission.¹⁷⁰ © 2018 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

Recently, various amorphous materials had attracted increasing interest for electrocatalysis,¹⁷¹⁻¹⁷³ particularly in water oxidation,¹⁷⁴⁻¹⁷⁷ which exhibited better catalytic activities in terms of overpotential as compared to their crystalline counterparts. For instance, the first kind of amorphous material was the in situ transformed amorphous oxyhydroxide electrocatalysts. Here, a cobalt-based amorphous electrocatalyst was reported by Matthias Driess.¹⁶⁷ The amorphous $\text{CoO}_x(\text{OH})$ was in situ transformed from Lazulite cobalt phosphate $\text{Co}_3(\text{OH})_2(\text{HPO}_4)_2$ during the continuous process of hydrogen evolution reaction and oxygen evolution reaction under applied potential. The features of the transformed amorphous structure are displayed in Figure 1.16a (in the inset you can see the diffuse electron scattering ring). Figure 1.16b compares the activity both HER and OER, it is clear that the activated amorphous catalyst demonstrated better performance compared to the

crystalline $\text{Co}_3(\text{OH})_2(\text{HPO}_4)_2$. The author attributed the enhanced activity to the improved ECSA (electrochemical surface area) without further interpretation. Other similar works as discussed in chapter 1.3 in which most of the crystalline electrocatalysts such as RuO_2 , Co_3O_4 , BSCF, NiP, in situ transformed the surface layer into amorphous by etching of inactive elements such as Li, S, P or self-reconstructed the oxygen vacancies. These generated amorphous layers were regarded as the active species catalytic the water oxidation, however, they lack deep understanding of the mechanism of OER.

The direct amorphous electrocatalysts without further treatment were further studied by other researchers in the oxygen evolution reaction. For instance, an as-prepared amorphous catalyst was fabricated by Chunzhong Li,¹⁶⁸ in which, the Mo doped amorphous Ni_3S_2 on nickel foam was prepared by the rapid solid-phase melting at low temperature. Figure 1.16c displayed the well-defined amorphous structure and Figure 1.16d compared the HER performance where amorphous catalyst revealed a much better catalytic activity than the crystalline counterpart. The enhanced activity was explained by the introduction of Mo rather than the structural difference. Further work reported by Hui Zhao¹⁶⁹ as shown in Figure 1.16e and f, the amorphous NiMoPO_x was synthesized by thermal reducing the NiMoO_4 using NaH_2PO_2 . The crystalline NiMoO_4 transformed into amorphous NiMoPO_x with the incorporation of P element resulting in a much advanced OER performance with a small overpotential of 297 mV at 15 mA/cm^2 outperforming than the NiMoO_4 . In this work, however, the better performance was simply assigned as the reduced Ni particles on the oxide

surface, lacking the distinguishing between amorphous and crystalline catalysts. The lack of further study on the pristine amorphous electrocatalyst for OER could be due to the difficulty in the characterization of the structure, not to mention the dynamic structure during oxygen evolution. It can be concluded that in such kind of materials, the bulk state was the disequilibrium state with the metallic feature, after electrocatalytic reaction or under applied potential, the surface layers were transformed into another kind of amorphous materials of oxyhydroxides or mixed phase. To a certain extent, the disorder configuration intuitively offered more active sites, but hard to distinguish the origin of the active sites.

Crystalline double hydroxide layers can be charged into oxyhydroxide under applied anodic potential intrinsically, therefore, it could be considered as a good testing material to study the role of amorphous structure for oxygen evolution reaction. Recently, Juzhe Liu¹⁷⁰ developed the amorphous cobalt hydroxide nanocages (Figure 1.16g, h) as an outstanding electrocatalyst exhibiting an overpotential of 280 mV at 10 mA cm⁻², much lower than the crystalline counterparts. Based on the analysis of in situ XAS and ex situ HRTEM, XPS, EPR, the increased number of oxygen vacancies were observed in the amorphous than crystalline structure, which was favorable for OER. Unlike the crystalline structure, the amorphous cobalt hydroxide with disordered atom distribution and numerous defects provided more unsaturated cobalt resulting in the high density of active sites. However, the thin layer of the amorphous feature was observed beside the crystalline one. Although the author revealed an overall conclusion that the amorphous structure could be more flexible transferred to

the catalytic active state. It can be inferred that the huge difference in the rough calculated TOF can't account for the amorphous structure on the surface for both amorphous and crystalline catalysts, so the main reasons could be the increased number of active sites which not only on the surface. But little works were further put into the investigations.

Additionally, the deep understanding of the mechanism of phase transformation still remained unclear for the oxygen evolution reaction. Other work in hydrogen evolution reaction without phase transformation as reported by Xuedong Bai,¹⁷⁸ amorphous NiB alloy exhibited outstanding catalytic hydrogen evolution performance and kept stable at a wide range of pH, showing comparable activity to the noble metal Pt. This work attributed the good catalytic efficiency to the unique amorphous structure and the tunable electronic states due to stable amorphous alloy state without transformation into oxyhydroxide layers. It in fact can be concluded that higher electrocatalytic activity could result from the pure unique amorphous structure rather than the transformed layers. Otherwise, the electrocatalytic performance of amorphous catalysts NiP, CoP, NiCoP, obtained by electroless deposition, showing more considerable water splitting activity than the conventional crystalline materials as electrocatalysts.¹⁷⁹ In conclusion, all of the amorphous catalysts had been reported with a disordered structure lacking crystallinity exhibiting a higher performance.¹⁶⁷⁻¹⁷⁰ However, it is still lacking a deep understanding on the mechanism of amorphous structure favoring oxygen evolution reaction.

1.4.2 Method of obtaining amorphous materials

The traditional preparation of amorphous solid is usually associated with the rapid quenching process requiring a cooling rate of at least 10^5K/s in a protective atmosphere or vacuum, which is hard to be conducted at the laboratory. In recent decades, as shown in Figure 1.17-1.21, a series of simple methods have been developed to prepare stable amorphous materials for water splitting catalysis.^{170,180-185} These kinds of methods can be conducted at more moderate conditions such as room temperature, without requiring special equipment.

Coordinating etching and co-precipitating for amorphous hydroxides and oxyhydroxides. As discussed in chapter 1.3, most of the crystalline electrocatalysts displayed a surface reconstruction to form amorphous oxyhydroxide layers, the kind of transformation usually induced by the ions etching on the surface, such as Li, S, P or oxygen vacancies reorganization on the surface with the assistance of OH^- and a water molecule. Those results inspired researchers to develop amorphous hydroxides by ions etching. As reported by Juzhe Liu,¹⁷⁹ amorphous cobalt hydroxide nanocages could be synthesized in a coordinating etching and precipitating process. The amorphous phase was successfully obtained by the etching and precipitating process in a solution containing Co^{2+} and surfactant with Cu_2O as a template. After a certain time, the Cu dissolved into solution and Co got into the cage shape structure forming an amorphous hydroxide material. Figure 1.17a and b further compared the structure between the as-prepared amorphous hydroxides and surface phase transformed

crystalline hydroxide, where the pure amorphous hydroxides showed more unsaturated Co sites, indicating a high degree of transformed active sites in an amorphous catalyst for the catalytic oxidation reaction. The top-down strategy was also applied in perovskites to synthesize amorphous Fe-doped LaNiO_3 in Figure 1.17c and d. In a typical process, the bulk-phase LaNiO_3 was immersed in a solution containing Fe^{3+} and La^{3+} , causing continual etching of LaNiO_3 , under violent ultrasonication. Amorphous Fe-doped LaNiO_3 was finally obtained with the large bulk-phase LaNiO_3 collapsed into nanoparticles. Especially, the same composition of amorphous Fe-doped LaNiO_3 was prepared by a bottom-up method of co-precipitation of La^{3+} , Ni^{2+} , Fe^{3+} ions as a comparison, both displayed the well-defined amorphous structure, however, the bottom-up method of co-precipitation required a high reaction rate and the amorphous structure was not stable.

Figure 1.17 Coordinating etching and co-precipitating for amorphous hydroxides and oxyhydroxides. (a) Transformation processes diagram of the AH-Co and CH-Co. And (b) HRTEM images of the CH-Co after the pretreatment. Reproduced with permission.¹⁷⁰ © 2018 WILEY - VCH Verlag GmbH & Co. KGaA, Weinheim. (c) Schematic illustration of the top-down and bottom-up strategies, and (d) SEM, TEM images of a-LNF(t-d), and R-space of Ni K-edges, Fe K-edges in a-LNF(b-u) and a-LNF(t-d) samples. Reproduced with permission.¹⁸³ © 2019 WILEY - VCH Verlag GmbH & Co. KGaA, Weinheim.

Electroless plating. Due to unstable amorphous structure, electroless plating on a substrate was developed as an effective approach to synthesize amorphous alloy. The typical route of preparing amorphous alloy was displayed in Figure 1.18a and b. Here, the Cu substrate was cleaned firstly by HCl to remove the surface oxides layers, and pretreated by SnCl₂ to activate the surface, following by electroless plating of NiP in a bath containing Ni²⁺ and hypophosphite for 10 min under strong stirring. The method of electroless plating was widely used in fabricating NiP, CoP, FeP, NiB, CoB, FeB and their mixed materials. The ratio of metal to P or B could be controlled by tuning the temperature and time for plating. However, the process of electroless plating was not stable and usually offered a very low efficiency. So some heavy metal ion had been used as a catalyst to catalyze the electroplating. For example, a silver-catalyzed electroless plating technology was developed to synthesize the amorphous NiB on titania support, reported by Zhijie Wu.¹⁸⁶ In a typical process, titania was pretreated in a solution containing AgNO₃, NH₄OH, NaBH₄ and HCHO at 313 K for 4 hours to formed the substrate of Ag/TiO₂. Then the electroless plating was conducted in solution consisted of NiSO₄, C₂H₄(NH₂)₂, NaBH₄, KBH₄ at 313 K. In general, the

commonly used reductants for electroless plating were the NaBH_4 , KBH_4 , NaH_2PO_2 , KH_2PO_2 . And ammonium hydroxide and hydrochloric acid often used to regulate the pH leading to the tunable proportion of B or P in the as-prepared amorphous alloy.

Figure 1.18 Obtaining amorphous materials by electroless plating. (a) Fabrication of a-MoS₂ nanosheets grown on Cu@Ni-P dendritic structure. And (b) TEM images of a Cu@Ni-P@a-MoS₂. Reproduced with permission.¹⁸⁰ © 2017 Elsevier B.V. All rights reserved.

Thermal and photochemical decomposition. In the above preparation, another method of thermal decomposition was further introduced to obtain one more layer of amorphous MoS₂ by thermal decomposition of $(\text{NH}_4)_2\text{MoS}_4$ at 373.15 K and rapid annealing. Similar approaches were often used to obtain amorphous materials with the precursor that could be decomposed to release a lot of gas. For instance, amorphous Si_3N_4 could be synthesized by thermal decomposition of $\text{Si}(\text{NH})_2$.¹⁸⁷ The $\text{Si}(\text{NH})_2$ was prepared by reaction of SiCl_4 with NH_3 in the liquid phase. And the conditions required for thermal decomposition were very strict in which the temperature was required to be 1100 °C, and the ammonia stream was required to protect the decomposed reaction. $\text{M}(\text{CO})_y$ (M could be Fe, Co, Ni) were another kind of precursors which could release a lot of gas under high temperature. Jacques van

Wouterghem reported that the amorphous Fe metal could be obtained by thermal decomposition of $\text{Fe}(\text{CO})_5$.¹⁸⁸ By heating the mixture containing n oleoyl sarcosine, iron pentacarbonyl and Decalin at 390 K for 5-6 hours, then rising to 460 K, the $\text{Fe}(\text{CO})_5$ decomposed gradually with the formation of amorphous Fe and release of CO gas. Besides, based on photodecomposition of organometallic precursors, Rodney D. L. Smith achieved a series of amorphous metal oxide materials for OER.¹⁷⁶ By spin-coting the precursor solution consisting of (Ni, Fe, Co)-2-ethyl hexanoate and hexanes onto FTO, and then irradiated under UV light, the amorphous NiO_x , FeO_x , CoO_x were obtained.

Room temperature reduction by sodium or potassium borohydride. Besides, the reduction of metal ions by sodium or potassium borohydride at room temperature is the conventional approach achieving amorphous alloy, and usually the introduction of substrate accounting for a more stable amorphous structure. As shown in Figure 1.19a and b, Co^{2+} and Fe^{3+} ions were reduced onto MWCNTs by potassium borohydride. In details, the feed order, the precursor salt, pH and adding rate showed a significant effect on the surface area and ratio of B. Further study by Yonggen He¹⁸⁹ indicated that addition of salt solution into sodium borohydride solution rather than adding sodium borohydride solution into salt solution led to a 3 times increased surface area of the obtained amorphous NiB alloy. By comparing the precursors of $\text{Ni}(\text{NO}_3)_2$, NiSO_4 , NiCl_2 , $\text{Ni}(\text{CH}_3\text{COO})_2$, a 10% increased surface area was observed in the order meanwhile increased pH values for these precursor solutions. It should be noted that the reduction of $\text{Ni}(\text{NO}_3)_2$ can't be achieved due to the strong oxidizing

nitric acid forming during the reaction. Besides, the study of adding speed of NiCl_2 demonstrated the decrease in both B ratio and surface area of as-prepared samples with increased adding rate, which was interpreted by the lower pH of the solution at higher adding speed. Due to the electron donation from boron to metal offering a tunable electronic state of the metal centers, this study presented a method of regulating the electronic structure of the obtained amorphous materials for further applications in the electrochemical reaction.

Figure 1.19 Room temperature reduction by sodium or potassium borohydride. (a) The preparation process of PANI-FeCo/MWCNT nanohybrids. And (b) TEM image of PANI-FeCo/MWCNT nanohybrids. Reproduced with permission.¹⁸² © 2018 Elsevier B.V. All rights reserved.

Surface amorphization of crystalline solid. As shown in chapter 1.3, surface amorphization was inevitable during oxygen evolution. The other method of obtaining heterogeneous amorphous catalysts was the surface corrosion amorphization of crystalline catalyst. The schematic diagram was shown in Figure 1.20, at first, cobalt boride surface was doped by fluorine acting as an amorphization agent, then the F-doped cobalt boride was heated in air to decompose leaving cracks on the surface and

finally brought about a high density of the crystalline-amorphous interface which was regarded as catalytic sites. And many experimental examples had been discussed above, the amorphous surface was obtained by ion etching and oxygen vacancies self-reconstruction.

Figure 1.20 Surface amorphization of crystalline solid. (a), (b), (d) Schematic of the c–a (crystalline-amorphous) interface via fluorine surface doping in cobalt boride. And (c) HRTEM image of the crystalline–amorphous phase boundary. Reproduced from Ref.¹⁸⁵ with permission from The Royal Society of Chemistry.

Electrodeposition. Additionally, the electrodeposition was also developed to prepare the amorphous catalyst beyond electroless methods as shown in Figure 1.21a and b. Amorphous Co-S-P was obtained by electrodeposition in the electrolyte containing Co^{2+} , NaH_2PO_2 and $\text{CH}_4\text{N}_2\text{S}$. It should be noted that an amorphous structure can't be achieved with a single reductant due to the high crystalline Co_2P and CoS by electrodeposition. This electrodeposition method, in fact, was similar to

the electroless plating but required an externally applied potential, which could be extended to amorphous oxides and hydroxides materials.¹⁹⁰⁻¹⁹² For instance, a work reported by Qianqian Zhou¹⁹³ presented the preparation of amorphous NiFe hydroxide/CuO nanorods on carbon fiber (CF) by an electrochemical deposition method. In a typical process, a three electrodes system was applied with the as-prepared CuO/CF, a platinum foil, Ag/AgCl electrode as working electrode, counter electrode, reference electrode. The electrodeposition experiment was conducted at -1.2 V vs Ag/AgCl electrode in electrolyte consisted of nickel nitrate and iron nitrate with a ratio of Ni/Fe equal to 4. Amorphous transition oxides include cobalt, manganese, iron, nickel, silicon oxides were also reported to be achieved by the electrochemical deposition approach.

Figure 1.21 Obtaining amorphous materials by electrodeposition. (a) A facile electrodeposition method of fabricating amorphous cobalt phosphosulfate electrocatalysts on nickel foams. And (b) TEM images and SAED patterns of Co-P, Co-S, Co-P-S. Reproduced with permission.¹⁸⁴ © 2019 Elsevier B.V. All rights reserved.

1.4.3 Characterization of the structural property

In order to gain a deep understanding of the difference between amorphous and crystalline structure for oxygen evolution reaction, it is very significant to have a specific investigation on the unique amorphous structure comparing to the crystal. However, there were few extensive studies on the amorphous physical structure. Generally, as shown in Figure 1.22a, an amorphous solid displayed the disordered packing of atoms, thus no periodic unit could be observed in such kind of structure. The conventional method of X-ray diffraction used for characterizing crystalline materials could provide specific information on the periodic unit cell, however, it presented little information for short-range ordering amorphous structure. Figure 1.22e showed the XRD patterns of amorphous CoBNH and its crystallization at 523 K, 623 K, 723 K, 823 K. It suggests that the amorphous at 298 K and 523 K showed only a broad peak at the degree of around 45° while the patterns at 723 K and 823 K present a group of sharp peaks which could be identified as different crystals. The feature of single broad peak¹⁹⁴ could be due to the long-range disordering in the amorphous solid and the position of the peak was not an identical value, which usually related to the main peak for the crystalline phase transformed from the

amorphous. For example, 30° and 55° were discovered at amorphous Sn oxides,¹⁹⁵ 45° was often observed at amorphous alloy.¹⁹⁶ Besides, the selected area electron diffraction was a more accurate approach to figure out the crystalline structure due to the diffraction in a small area. However, for a typical amorphous material, only a diffractive halo could be acquired which is corresponding to the broad peak in the XRD pattern. Figure 1.22c was an example of amorphous Mg_2Si films reported by Seung-Wan Song, the diffractive halo indicating the highly disordering structure. And for some amorphous, a diffusing ring could be observed. As shown in Figure 1.22d, the SAED pattern of amorphous $\text{Zr}_{55}\text{Cu}_{30}\text{Al}_{10}\text{Ni}_5$ presented a single diffusing ring while a fully amorphous feature was displayed in HTERM images, although it is not very clear today, this diffusing ring could be due to the short-range ordering in the amorphous structure corresponding to the broad peak in XRD patterns. Additionally, the normal TEM showed little information for the amorphous structure, and HRTEM or STEM-HAADF was required to have the extremely high resolution of the images at a scale less than 5 nm, which could offer a direct view on the long-range disordering but short-range ordering structure. A typical HRTEM for the melt-spun ribbon of the $\text{Ti}_{25}\text{Zr}_{17}\text{Ni}_{29}\text{Cu}_{29}$ alloy was shown in Figure 1.22b, where no obvious regular lattice was observed, especially, indicating a high degree of amorphous. On the other hand, due to the certain range of ordering in some amorphous solid, lattice could be displayed on a scale less than 1 nm packaged by more than ten atoms. This kind of image was discovered by L. Q. Xing for $\text{Zr}_{62-x}\text{Ti}_x\text{Cu}_{20}\text{Ni}_8\text{Al}_{10}$, where the disordered image contained regions with parallel fringes offering a spacing of 0.25

nm.¹⁹⁷ However, to obtain more detailed information on the short ordering range and the coordination environment, the extended X-ray absorption fine structure (EXAFS) provided an effective technique.¹⁹⁸ Due to the binding energy of an electron in an atom matches the incident X-ray energy, X-ray energy is absorbed in a certain energy range leading to an adsorption edge spectrum. Besides, EXAFS can be modeled with the EXAFS equation:

$$\chi(k) = \sum_j \frac{N_j S_0^2}{k R_j^2} F_j(k) e^{-\frac{2R_j}{\lambda_j(k)}} e^{-2k^2 \sigma_j^2} \sin[2kR_j + \Phi_j(k)] \quad (1.16)$$

$$k = \frac{2\pi}{\lambda} = \sqrt{\frac{2m_e(E - E_0)}{\hbar^2}} \quad (1.17)$$

Where k is the photo-electron wavenumber, $F(k)$ is effective scattering amplitude, $\Phi(k)$ is effective scattering phase shift, $\lambda(k)$ is free path, R is path length, N is the degeneracy of path, S^2 is passive electron reduction factor, σ^2 is squared displacement, E is energy shift. The quantitative information of neighboring atoms (N) and bonding distance (R) within a few ligating shells of the central absorber atom could be obtained from the FFT EXAFS. Therefore, the EXAFS offered a useful way to determine the local structure of the short-range ordering structure for amorphous materials. A systematic comparison of amorphous NiB alloy and the annealing crystalline was studied by Shiqiang Wei, as shown in Figure 1.22f, in which the radial distribution functions were Fourier transformed from the $k^3\chi(k)$. There was only a single peak at around 2 Å of the as-prepared amorphous NiB alloy and the sample annealed at 473 K indicating the fully amorphous feature. This weak peak was

accounting for the short ordering range in the long disordering system and was reported by many other works.¹⁹⁹⁻²⁰¹ With further increased annealing temperature, the amorphous NiB alloy transformed into crystalline samples, thus accompanied by the two peaks arising at around 4 Å and 5 Å which was consistent with the signal from Ni foil. Other EXAFS in amorphous transition metal oxides could present a disappearing metal-oxide bond for the certain metal centers in the amorphous ligand shell,¹⁹⁹ indicating the unsaturated coordination. Furthermore, to observe the dynamic state of amorphous electrocatalysts, in situ EXAFS could be a more effective method. Marcel Risch discovered the Co-Co distances increasing from 0.37 nm to 0.47 nm in amorphous cobalt oxides with the increase of anodic potential due to the oxidation of Co.²⁰² Generally, it was recommended that a complete work should combine these techniques to gainfully understanding for the amorphous structure due to the few information obtained from the conventional XRD.

Figure 1.22 Characterization of the structural property of amorphous materials. (a) Atomic model of amorphous structure. (b) HRTEM image of melt-spun ribbon of the $\text{Ti}_{25}\text{Zr}_{17}\text{Ni}_{29}\text{Cu}_{29}$ alloy. Reproduced with permission.²⁰³ Copyright © 2008 Published by Elsevier Ltd. (c) Selected area electron diffraction (SAED) patterns of the amorphous Mg_2Si films. Reproduced with permission.²⁰⁴ Published by Elsevier B.V. (d) Selected area electron diffraction (SAED) patterns of the amorphous $\text{Zr}_{55}\text{Cu}_{30}\text{Al}_{10}\text{Ni}_5$. Reproduced from Ref.²⁰⁵ with permission from The Royal Society of Chemistry. (e) XRD patterns of the Co-B-N-H nanowires treated at different temperatures. Reproduced from Ref.²⁰⁶ with permission from The Royal Society of Chemistry. (f) RDF's of ultrafine amorphous NiB alloy annealed at different temperatures. Reproduced from Ref.²⁰⁷ with permission from ©2001 American Physical Society.

1.5 Challenge of Electrocatalysts for OER and Research Motivation

To facilitate the sluggish four-electron transfer kinetics of oxygen evolution reaction (OER), various catalysts have been developed as effective electrocatalysts. As discussed above, noble metal-based materials: ruthenium oxide and iridium oxide are discovered as the efficient OER catalysts with the highest activity in both acidic and alkaline media, however, the application in a large scale is impeded due to the high expense and scarcity of catalysts. In addition, numerous efforts have been put into oxides, hydroxides, and oxyhydroxides containing Ni, Fe, Co, Mn et al. exhibiting remarkably high OER performances. However, due to the worse performance than RuO_2 and IrO_2 on conventional nonprecious metal-based

electrocatalysts. Innumerable grand designs have been established to improve the activity of transition metal-based catalysts.

(1) **Improving the intrinsic activity of the active site.** It has been proved in both theory and experiments, the OER activity correlated with the binding strength of the intermediates include OH^* , O^* , and OOH^* on the catalytic surfaces. The main descriptor has been constructed with the difference of standard adsorption free energy between OH^* and O^* , showing a good consistency with the trends of observed activity for reported materials. Therefore, the method of introduction of other metal elements so-called doping results modifications of the adsorption strength of intermediates, which means a multimetal based electrocatalyst usually show a much-enhanced performance than the single one. However, the conventional crystalline materials usually show limit kind of multimetal based oxides, hydroxides, et al due to the strict crystalline lattice, where an improper ratio of metal centers usually causes a phase to degrade within the solid.

(2) **Increasing the number of active sites.** It is obvious that the number of active sites for heterogeneous catalyst determines the mass activity of the catalysts. The more active site, the higher the mass activity. Therefore, the common strategies of surface engineering and nanoengineering, in fact, provide an effective approach to increasing the number of active sites at the unit area or mass. However, excessive defects which act as active sites usually lead to an unstable structure sometimes transform into amorphous where the mechanism on amorphous still remains unclear.

(3) **Enhancing the conductivity of the OER catalysts.** It is known that the low conductivity of oxides, hydroxides and oxyhydroxides for both amorphous and crystalline structures offer an external consumption of overpotential for the catalytic reaction. On the other hand, the design principle of metal nitrides, phosphides, et al. is a useful route to enhance the conductivity of metal oxides and hydroxides. Generally, compared with the metal nitrides, phosphides, the alloy is expected to present a better conductivity.

To design the ideal catalyst solving these problems, amorphous alloy, with the unique structure of long-range disordering but short-range ordering structure, naturally possesses the three merits as effective OER catalysts. Therefore, we report that amorphous alloys could be new and promising OER catalysts with outstanding performance, based on three important features of amorphous alloy.²⁰⁸⁻²¹¹

(1) It provides a potential method of continuously adjusting the composition of the amorphous alloy, offering a tunable electronic property to achieve the best energetics of intermediates toward higher catalytic performance.

(2) It provides a high density of active catalytic sites on amorphous alloys due to the abundant coordinative unsaturated sites (CUSs) which is similar to defects including step sites, kink sites, point defects, etc., for crystalline planes. It has been universally proved that these coordinative unsaturated sites play a critical role in bonding and activating the reactants for heterogeneous catalysts, accounting for excellent catalytic performance.²¹²⁻²¹⁴

(3) As a special kind of alloy, the amorphous alloy shows good conductivity comparable to the metal which decreases the external consumption of potential in the process of oxygen evolution.

(4) Besides, it is beneficial to develop the surface with identical active sites toward a purposed selected catalytic activity for the reaction with multi byproducts, while there are always several kinds of sites on different crystalline planes resulting in a lot of unwanted products.

In spite of the high level of conductivity, a huge amount of active sites and tunable chemical components, amorphous alloy received limited concerns despite their attested unity as OER catalysts while there are various reported works concentrate on crystal materials. As discussed in chapter 1.4. One problem depressing the further developments of amorphous alloy as electrocatalyst for OER is the limited understanding of the mechanism on the origin of the excellent performance of amorphous outperforming than crystalline. Another reason is the difficulty in obtaining a stable homogeneous structure with a widely tunable composition under applied potential.

In this thesis, we are going to figure out the detailed mechanism of amorphous alloy outperforming better OER performance than the crystalline counterpart rather than the general conclusion of a high amount of active catalytic sites. Then based on the understanding of the mechanism on amorphous alloy for OER, we finely adjust the binding strength of intermediates on the catalytic surface toward the best OER

activity in the world. Finally, designing the electrolyzer for long-term stable water splitting.

1.6 Overall Objectives

(1) To develop an amorphous alloy exhibiting high OER catalytic activity with well define homogeneous and isotropic characters of long-range disordered and short-range ordered structure. By comparing with the crystalline catalyst, our work aims to probe the origin of enhanced activity of amorphous catalysts using the method of in situ electrochemical impedance spectroscopy, in situ X-ray absorption spectroscopy (XAS), in situ Mass spectroscopy, ex situ X-ray photoelectron spectroscopy (XPS), High-resolution transition electron microspectroscopy (HRTEM).

(2) To design an amorphous alloy with optimal binding energy to the OER intermediates by tuning the composition of the alloy. And identify how the added metals affect the catalytic activity to provide the basis for an empirical model enabling the rational design of OER catalyst using experimental methods of Valence band study, High-angle annular dark-field scan transition electron microspectroscopy (HADDF-STEM, X-ray photoelectron spectroscopy (XAS) and theoretical method of the microkinetic model.

(3) To design supported amorphous alloy catalysts and proper electrolyzer for overall water splitting, solving the problem of stability.

Chapter 2 Amorphous vs Crystalline in Water Oxidation Catalysis

2.1 Introduction

Catalytic water splitting to molecular hydrogen and oxygen driven by renewable electricity is considered as one of the most promising solutions for the sustainable energy conversion,^{14,215-218} but its efficiency is greatly restricted due to the high overpotential required for the anodic water oxidation half reaction.²¹⁹ To facilitate the sluggish four-electron transfer kinetics in the oxygen evolution reaction (OER), various design strategies including improving the intrinsic activity of active sites^{220,221} and increasing the number of active sites were proposed.²²²⁻²²⁴ Recently, amorphous materials have attracted increasing attention for electrocatalysis,^{171-173,225-227} particularly in water oxidation,^{174-177,226,228-230} which exhibit better catalytic activities in terms of overpotential as compared to their crystalline counterparts. It has been claimed that an amorphous structure could offer more active sites for OER. Dau et. al., attributed the high OER activity of electrodeposited amorphous CoCat film to the bulk oxide.^{231,232} But, recent studies on amorphous cobalt hydroxide by Liu¹⁷⁰ and Menezes¹⁶⁷ ascribed the abundant active sites to the high density of oxygen vacancies. So the exact reasoning why amorphous catalysts outperform their crystalline counterparts remains controversial. Additionally, the long term operating stability of

amorphous catalysts at temperatures ($\geq 60\text{ }^{\circ}\text{C}$) and current densities ($\geq 500\text{ mA/cm}^2$) needed for practical water electrolysis is still questionable.

Figure 2.1 The scheme illustrating the main opinion of chapter 2.

To decipher these obstacles, in this work, we present a room temperature solution technique to prepare an amorphous nickel-iron alloy catalyst for water oxidation. The amorphous nickel-iron alloy catalyst can be converted to crystal via thermal annealing in inert atmosphere without changing composition. On the basis of cyclic voltammetry, electrochemical impedance spectroscopy, isotope labeling and in situ X-ray absorption spectroscopy studies on both amorphous and crystalline nickel-iron alloy catalysts, it was demonstrated that the amorphous nickel-iron alloy catalyst could be electrochemically activated to expose active sites in the bulk by applying a positive anodic potential resulting from the short-range order of the amorphous structure, which greatly increased the number of active sites and thus significantly

improved the water oxidation activity (Figure 2.1). The amorphous nickel-iron alloy catalyst with Ni to Fe atomic ratio of 3:1 could reach a water oxidization current density of 10 mA/cm² at an overpotential of 265 mV (*iR* corrected) on a glassy carbon electrode, which is 100 mV lower as compared to the crystalline counterpart. By further optimizing the loading amount of amorphous catalysts, the lowest overpotential at 10 mA/cm² could be reached at 242 mV. Additionally, by coating the as-prepared amorphous nickel-iron alloy catalyst onto nickel foam, long term OER stability at 80 °C and 500 mA/cm² could be achieved, rendering the amorphous nickel-iron alloy catalyst practically attractive for high-performance water electrolysis.

2.2 Materials and Methods

2.2.1 Chemicals preparation and characterization

Chemicals. Nickel (II) acetate tetrahydrate (98%), iron (II) acetate (99.995%), potassium hydroxide (semiconductor grade, 99.99% trace metals basis), and sodium borohydride (granular 99.99% trace metals basis), sodium (cubes, contains mineral oil, 99.9% trace metals basis), water-¹⁸O (97 atom % ¹⁸O). All chemicals were purchased from Sigma-Aldrich and used as received without further purification.

Materials Preparation. For the preparation of amorphous nickel-iron alloy catalyst, 8.52 mmol of Ni(CH₃COO)₂·4H₂O and Fe(CH₃COO)₂ with varying molar ratios of Ni to Fe were added into 50 mL of deionized (DI) water in a conical flask under magnetic stirring, followed by slowly adding 20 mL of 1.28 M NaBH₄ aqueous

solution 10 minutes later. Instantaneous formation of black precipitates was observed. After stirring for 10 minutes, the black precipitate was collected and washed with deionized (DI) water and ethanol several times, and then stored in acetone. To prepare the crystalline nickel-iron alloy catalyst, the as-prepared amorphous nickel-iron alloy catalyst was annealed in N₂ at 600 °C for 2 hours. The amorphous nickel-iron alloy catalyst could be directly grown on three-dimensional (3D) nickel foam by sequentially dropping the transition metal salt and NaBH₄ solution onto nickel foam.

Materials Characterization. The as-prepared catalysts were examined by powder X-ray diffraction (XRD) on a D8 Advance diffractometer with Cu K α radiation (λ = 1.5418 Å). The particle size, composition and morphology were studied by field emission scanning electron microscopy (FESEM, JSM-6701) with energy-dispersive X-ray spectroscopy (EDX) and transmission electron microscopy (TEM, JOEL-2010) with selected area electron diffraction (SAED), high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM, JEOL JEM-ARM200F) with energy-dispersive X-ray spectroscopy (EDX). Detailed chemical compositions were analyzed by X-ray photoelectron spectroscopy (XPS) on an ESCALAB 250 photoelectron spectrometer (Thermo Fisher Scientific) using a monochromatic Al K α X-ray beam (1486.6 eV). All binding energies were referenced to the C 1s peak (284.6 eV). The dissolution of transition metals during the stability test was quantified by inductively coupled plasma optical emission spectrometry (ICP-OES, Optima 2000). Isotope (¹⁸O) labeling studies were conducted on the Hiden QGA (quantitative gas analysis) system.

2.2.2 Electrochemical measurements and in situ experiments.

Electrochemical measurements. Electrochemical measurements were performed at room temperature on a rotating disk glassy carbon electrode (PINE, 5 mm diameter, 0.196 cm²). Pt coil (area: 2 cm²) and Hg/Hg₂Cl₂ (PINE, saturated with KCl) were used as counter and reference electrodes, respectively. The potential was referenced to the reversible hydrogen electrode (RHE) through:

$$E(RHE) = E(Hg/Hg_2Cl_2) + 0.241 + 0.059 \times pH \quad (2.1)$$

The working electrode on glassy carbon was prepared as follows: first, 3 mg of catalyst powder was dispersed in a mixed solution of deionized water (500 µL) and ethanol (500 µL), and then ultrasonicated for 1 hour. Subsequently, 5 µL of the catalyst ink suspension was pipetted onto a pre-cleaned glassy carbon disk electrode with a catalyst loading amount of 75 µg/cm². Finally, the glassy carbon electrode was dried at room temperature in air for at least 1 hour.

Before acquiring electrochemical data, the glassy carbon working electrodes were subjected to continuous potential cycling in the potential window from 1.0 to 1.5 V (vs RHE) until reproducible voltammograms were obtained at room temperature, 1600 rpm, and a sweep rate of 100 mV/s. The solution resistance R_Q was determined from the resulting Nyquist plot and used for the Ohmic drop correction according to the relation $E_c = E_m - iR_Q$ (where E_c is the corrected potential and E_m is the measured potential, respectively). OER activity was recorded by linear sweep voltammetry and

cyclic voltammetry at a scan rate of 10 mVs^{-1} in 1 M ultrapure KOH (semiconductor grade, 99.99% trace metals basis) solution at 1600 rpm.

Calibration of the reference electrode. The standard potential of reference electrode vs. RHE was calibrated in a two-electrode system, where the electrolyte is hydrogen saturated 0.5 M H_2SO_4 . One electrode is Hg/Hg₂Cl₂ (PINE, saturated with KCl) and the other electrode is Pt foil ($1 \times 1 \text{ cm}^2$) with bubbling H_2 . The standard value of the reference electrode was obtained as the stable absolute value in the open circuit potential measured by a CHI 760E electrochemical workstation.

Electrochemical impedance spectroscopy studies. Electrochemical impedance spectroscopy (EIS) measurements were conducted on a Solartron 1287A potentiostat coupled with a 1260 FRA (Frequency Response Analysis). EIS spectra were collected by applying different DC potentials covering the frequency range from 100 K to 0.1 Hz. The sinusoidal amplitude of 10 mV was applied to ensure the linear response of the electrode. The EIS data were analyzed and fitted with an equivalent circuit using ZView software.

Isotope (^{18}O) labeling studies. Amorphous or crystalline nickel-iron alloy catalyst was electrochemically polarized under OER condition in 1 M Na^{18}OH (sodium dissolved in H_2^{18}O) at 40 mA/cm^2 for 30 min inside a three-electrode electrochemical cell. After the reaction, the catalyst was washed with deionized water (H_2^{16}O), collected and dried in air at $80 \text{ }^\circ\text{C}$ for 18 h. Then 1 mg of the catalyst was put into a quartz tube that is connected to a mass spectrometry for real-time detection of

released species from the catalyst. Before data acquisition, the catalyst was blown with helium at room temperature for 12 h until the signal on mass spectrometry showed a flat and stable line. Afterward, the quartz tube was heated to 800 °C at a heating rate of 100 °C/min in helium and real-time information of released species was recorded.

In situ XAS measurement. In situ XAS measurements were collected through synchrotron radiation light source at the BL12B2 beamline of the National Synchrotron Radiation Research Center (NSRRC) in SPring 8 (Japan) at room temperature. Fluorescence spectra were recorded using a seven-element Ge solid state detector. Extended X-ray absorption fine structure (EXAFS) spectra were fitted using the FEFF 6.0 code (Athena). To conduct the in situ experiments, a homemade electrochemical cell was designed and we used 1 M KOH, saturated calomel electrode and Pt as the electrolyte, reference and counter electrode, respectively. Carbon paper was used as the substrate to load catalyst. The data were collected at following conditions, under applied potential of 1.3 V vs RHE and 1.5 V vs RHE.

Determination of the electrochemically active surface area. The electrochemically active surface area (ECSA) was measured by a double layer capacitance method. Typically, a double-layer charging potential region was first determined from the static CV scan. The charging current i_c was measured from CV curves obtained at different scan rates, as shown in Figure 2.3. The relation between i_c , scan rate (ν) and the double layer capacitance (C_{dl}) is given by $i_c = \nu C_{dl}$. The ECSA

can thus be estimated from double-layer capacitance according to $\text{ECSA} = \frac{C_{dl}}{C_s}$, where C_s is the ideal specific capacitance of a smooth planar surface made of the same material.

2.3 Results and Discussion

2.3.1 Structure and morphology

Amorphous nickel-iron alloy catalysts (Figure 2.2) were synthesized by reacting aqueous NaBH_4 solution with nickel and iron acetate at room temperature and ambient pressure. The molar ratio of nickel to iron in nickel-iron alloy catalysts could be easily tuned by changing the amount of nickel and iron salt. Figure 2.2b displays the X-ray diffraction (XRD) pattern of a typical as-prepared nickel-iron alloy catalyst, which shows only a very broad diffraction peak centered at around 45° , arising from the unique short-range atomic ordering but long-range disordered structure.^{233,234} The morphology was examined by transmission electron microscopy (TEM) and scanning electron microscopy (SEM). As shown in Figure 2.2c, d and e, both TEM and SEM images show that the as-prepared nickel-iron alloy catalyst with Ni/Fe molar ratio of 3:1 comprises of interconnected nanoparticles with a mean size of 50 nm. The amorphous feature of the as-prepared nickel-iron alloy catalyst is further verified by selected area electron diffraction (SAED) pattern (inset in Figure 2.2d), which displays diffusive rings. The bright inner ring in the SAED pattern suggests the presence of short-range atomic order,²³⁵⁻²³⁷ which matches well with the broad diffraction peak in the XRD pattern. Furthermore, the high-angle annular dark field

scanning transmission electron microscope (HAADF-STEM) (Figure 2.2e) shows the short-range ordered and long-range disordered structure of the nickel-iron alloy catalyst at the atomic level. Annealing the as-prepared nickel-iron alloy catalyst at 600 °C in nitrogen transformed the amorphous nanoparticles into phase-pure crystal (Figure 2.2b), which slightly increased the particle size to 100 nm (Figure 2.2f and g). Both Ni and Fe elements are uniformly distributed across the entire amorphous and crystalline nickel-iron alloy catalysts as shown in the energy-dispersive X-ray spectroscopy (EDX) mappings (Figure 2.2i, j), which give Ni to Fe atomic ratio of around 3 (detailed composition in Table 2.1), agreeing well with the amount of nickel and iron salts used in the synthesis.

Figure 2.2 Structural and morphological characterization of amorphous and crystalline nickel-iron alloy catalysts. (a) atomic model of crystalline and amorphous structure. (b) XRD patterns of the as-prepared nickel-iron alloy catalyst (Ni/Fe = 3:1) with and without undergoing thermal annealing at 600 °C in nitrogen. (c, d, e) SEM, TEM and HAADF-STEM images of the as-prepared amorphous nickel-iron alloy catalyst

(Ni/Fe = 3:1). (f, g, h) SEM, TEM and HAADF-STEM images of annealed nickel-iron alloy catalyst (Ni/Fe = 3:1) at 600 °C in nitrogen. (i, j) elemental mapping images of both catalysts. Insets in d and g show the corresponding selected area electron diffraction (SAED) pattern.

Table 2.1 Compositions obtained by ICP-OES measurements.

	Ni	Fe	B	O
a-NiFeB	0.714	0.232	0.033	0.021
c-NiFeB	0.713	0.235	0.038	0.014

2.3.2 Valence states

The surface valence states of amorphous and crystalline nickel-iron alloy catalysts were examined by X-ray photoelectron spectroscopy (XPS). As displayed in Figure 2.3, the Ni 2p spectrum shows the $2p_{3/2}$ and $2p_{1/2}$ peak at 852.7 eV and 870.2 eV for both amorphous and crystalline samples, which are typical for nickel alloyed with boron.^{238,239} The Ni $2p_{3/2}$ and Ni $2p_{1/2}$ peaks at 855.6 and 873.0 eV are assigned to Ni^{2+} , indicative of surface oxidation.²⁴⁰ The degree of surface oxidation is higher for amorphous nickel-iron alloy catalyst as compared to the crystalline counterpart. The Fe 2p spectrum (Figure 2.3b) displays two peaks of Fe $2p_{3/2}$ at 710.4 eV and 713.9 eV, respectively, which are assigned to Fe^{2+} and Fe^{3+} , indicating that Fe is mainly present in the oxidized states on surface.²⁴¹ B 1s spectrum as shown in Figure 2.3c can be deconvoluted into three distinctive species at 188.1, 191.6, and 192.5 eV, respectively. The peak at 188.1 eV is due to the interaction of boron with nickel/iron, whereas the

other two peaks are from BO_3^{3-} and B_2O_3 .²⁴² Notably, there is a clear positive shift of the boron peak at 188.1 eV, which should result from electron transfer from boron to transition metal.^{238,239} The O 1s spectrum (Figure 2.3d) is deconvoluted into two peaks at 531.2 and 532.4 eV, corresponding to B-O-M and B-O bond in B_2O_3 .²⁴³

Figure 2.3 Surface valence states. High-resolution XPS spectra of (a) Ni 2p, (b) Fe 2p_{3/2}, (c) B 1s, and (d) O 1s for amorphous (top) and crystalline (bottom) nickel-iron alloy catalysts with Ni/Fe of 3:1.

By removing the surface layers through argon plasma, the bulk composition and valence states of the catalysts could be further probed by XPS. Based on the fitting results, the relative elemental ratio can be calculated by:

$$\frac{n_i}{n_j} = \frac{I_i}{I_j} \times \frac{\sigma_j}{\sigma_i} \times \frac{E_{k_j}^{0.5}}{E_{k_i}^{0.5}} \quad (2.2)$$

$$E_k = h\nu - E_b \quad (2.3)$$

n: number of atoms, I: intensity (integral peak area), E_k : kinetic energy, E_b : binding energy, $h\nu$: X-ray photonic energy (1486.6 eV), σ : photoionization cross-section. Here we used Fe 2p_{3/2} with $\sigma = 10.82$ for analysis. As shown in Figure 2.4 and Table 2.2, we could conclude that the bulk chemical states of amorphous and crystalline alloy nanoparticles are similar. Although the use of Al source resulted in an overlap of Fe 2p and Ni LMM Auger peaks, the fitted elemental ratio for Ni/Fe is close to that used in the synthesis. Additionally, the high-resolution Fe 3s spectra are displayed in Figure 2.5, where amorphous and crystalline nanoparticles show the same features.

Figure 2.4 High-resolution XPS spectra of (a) Ni 2p, (b) Fe 2p, (c) B 1s, and (d) O 1s for amorphous (top) and crystalline (bottom) nickel-iron alloy catalysts with Ni/Fe = 3:1. The spectra were collected after Ar plasma etching for 300 s.

Figure 2.5 Comparison of the XPS spectra for Fe 3s of amorphous (top) and crystalline (bottom) nickel-iron alloy catalysts with Ni/Fe = 3:1.

Table 2.2 The detailed XPS fitting results of Figure 2.4.

Catalyst	Peak	Binding energy (eV)	Area	FWHM	σ	Elemental ratio
Amorphous NiFe catalyst	Ni 2p	852.7	61492.55	1.084	13.92	0.373
		853.7	29639.22	1.678		
		858.2	78053.3	7.416		
		869.8	27847.86	1.568		
		871.2	14959.2	1.991		
		874.4	22514.5	4.482		
	Fe 2p _{3/2}	707.1	20869.6	3	10.82	0.127
		712.1	39912.938	5.269		
		703.7	4445.057	3.356		
	B 1s	188.1	1025.991	0.952	0.486	0.173
		192.6	4435.242	2.268		
	O 1s	532.6	32321.33	2.124	2.93	0.327
		531.3	21268.78	2.211		
Crystalline NiFe catalyst	Ni 2p	852.7	52737.36	1.224	13.92	0.357
		853.7	26662.29	3.308		
		858.2	38480.21	5.335		
		869.8	22607.83	1.734		
		871.2	10286.58	2.524		
		874.4	24370.36	5.193		
	Fe 2p _{3/2}	707.1	16646.76	2.703	10.82	0.121
		712.2	29843.53	4.854		

		703.7	4968.577	3.801		
	B 1s	188.1	268.383	1.357	0.486	0.196
		192.6	4574.684	2.761		
	O 1s	532.6	29379.37	2.167	2.93	0.326
		531.3	12180.35	2.581		

2.3.3 Electrochemical performance and stability.

The electrochemical performance was studied on rotating disk electrode. First of all, we optimized the composition of nickel-iron alloy catalysts (Figure 2.6), of which the catalyst with Ni/Fe atomic ratio of 3:1 gave the best OER activity. Therefore, we used the nickel-iron alloy catalyst with Ni/Fe = 3:1 in all electrochemical measurements. Figure 2.7a compares the OER polarization curves of amorphous and crystalline nickel-iron alloy catalysts. Apparently, the amorphous nickel-iron alloy catalyst displays a much better catalytic activity for water oxidation, reaching a current density of 10 mA/cm² at an overpotential of only 265 mV, 100 mV less than that of the crystalline counterpart. Additionally, by optimizing the loading amount of amorphous catalysts, the lowest overpotential at 10 mA/cm² could be reached at 242 mV. Besides activity, the stability of the catalyst is equally important for practical applications in water electrolysis. We first examined the stability of the amorphous nickel-iron alloy catalyst at a constant anodic current density of 40 mA/cm². From Figure 2.7b, it is clear to see that the amorphous catalyst is very stable and keeps the amorphous state during OER. After 200 h of continuous reaction, the overpotential only increases by 1.6%. Furthermore, by loading the catalysts on three-dimensional

(3D) porous nickel foam support, the nickel foam electrode could reach current densities greater than 1 A/cm^2 at overpotentials slightly larger than 290 mV, which is more than sufficient for water electrolyzers.

Figure 2.6 Linear sweep voltammetry (LSV) curves to determine the optimized composition of the amorphous nickel-iron alloy catalyst.

Figure 2.7 Electrochemical performance and stability. (a) OER polarization curves (with 100% iR correction) of amorphous and crystalline nickel-iron alloy catalyst with Ni/Fe of 3:1. The inset shows the overpotential of amorphous nickel-iron alloy catalysts with varying loading amounts at 10 mA/cm². (b) Chronopotentiometric curve of amorphous nickel-iron alloy catalyst (Ni/Fe = 3:1) at a constant current density of 40 mA/cm² and room temperature (without iR correction). The inset shows the XRD pattern before and after stability test. (c) Chronopotentiometric curves of nickel foam, amorphous and crystalline nickel-iron alloy catalyst (Ni/Fe = 3:1) loaded nickel foam at a constant current density of 500 mA/cm² and 80 °C. The thick lines resulted from the physical adsorption of evolved oxygen bubbles. (d) The corresponding CV curves (without iR correction) collected before and after stability tests at 80 °C.

To test the practical application potential, the catalyst loaded nickel foam electrode was kept at 80 °C and 500 mA/cm² for 20 h (Figure 2.7c). Both amorphous and crystalline catalyst loaded nickel foam electrode display stable performance, of which the amorphous catalyst loaded electrode exhibits much smaller overpotential. The CV curves of the amorphous catalyst loaded electrode were collected before and after stability tests, which overlap with each other (Figure 3d). Additionally, we further measured the concentrations of nickel, iron and boron ions in electrolyte after stability test using inductively coupled plasma optical emission spectrometry (ICP-OES), the concentrations of nickel, iron and boron were well kept below the detecting limit (< 0.1 ppm) of ICP-OES, demonstrating the good durability of amorphous nickel-iron alloy catalyst for water oxidation.

2.3.4 Anodic activation of amorphous catalysts

To probe the origin of greatly enhanced water oxidation activity on the amorphous catalyst, we first compared the electrochemically active surface area (ECSA, obtained by measuring the double layer capacitance in the non-faradaic potential region as shown in Figure 2.8, Figure 2.9, details are discussed in chapter 2.2.2). Both of amorphous and crystalline catalysts show comparable ECSA before and after OER. Furthermore, Tafel plots also give similar Tafel slope of 24 and 25 mV/dec for amorphous and crystalline samples (Figure 2.9c), indicating that the water oxidation reaction is rate limited at the same elementary reaction step for both catalysts.^{244,245} However, the amorphous and crystalline catalysts show distinct redox peaks in the cyclic voltammetry (CV) curves (Figure 2.9b), in which, the redox peaks of the amorphous catalyst are much stronger. The position of the anodic redox peak reflects the binding strength of the OH intermediate in OER,²⁴⁶⁻²⁴⁸ herein, the similar anodic redox peak position of amorphous and crystalline catalysts suggests that the binding strength of OH with catalyst does not change when the amorphous catalyst is transformed to crystal, so does the activity of the active site.

Figure 2.8 The corresponding double layer capacitance recorded after the activation process.

Figure 2.9 Amorphous vs crystalline. (a) Double layer capacitance acquired at the potential from 1.01 to 1.05 V vs RHE to determine the ECSA. (b) CV curves obtained

at a scan rate of 10 mV/s. (c) Tafel plots for amorphous (cyan) and crystalline (pink) nickel-iron alloy catalysts with Ni/Fe of 3:1. (d) Relative adsorption amount of OH. (e) Nyquist plots acquired at 1.26 and 1.44 V vs RHE. Note: the complete version of this figure is shown in Figure 2.10. (f) Dispersion parameter α of CPE for C_{ads} as a function of potential. (g) Equivalent circuit of OER. (h) From top to bottom, mass spectra of $H_2^{18}O$ for (1) amorphous nickel-iron alloy catalyst immersed in 1 M $Na^{18}OH$, (2) amorphous nickel-iron alloy catalyst undergoing OER in 1 M $Na^{18}OH$, and (3) crystalline nickel-iron alloy catalyst undergoing OER in 1 M $Na^{18}OH$, respectively.

To gain an in-depth understanding of the anodic peak, electrochemical impedance spectroscopy (EIS) spectra were collected as displayed in Figure 2.9e and Figure 2.10. Figure 2.9g shows the electrical equivalent circuit that we used to simulate the process of OER,²⁴⁹ where R_Q represents the uncompensated electrolyte resistance, C_{dl} models the double layer capacitance, R_p and R_s are related to the kinetics of the interfacial charge transfer, and C_{ads} models (Table 2.3) the relaxation of charge associated with the adsorbed intermediates. The surface intermediate coverage can be estimated by:

$$\theta(E) = \frac{1}{\sigma} \int_{E_o}^E C_{ads}(E) dE \quad (2.4)$$

where σ is the charge density for monolayer coverage, E_o refers to the potential under which no obvious adsorption occurs, and E is the potential that gives rise to $\theta(E)$.²⁵⁰ Figure 2.9d compares the OH adsorption on amorphous and crystalline nickel-iron alloy catalysts at various anodic potentials. It is clear to see that in the redox potential region (below 1.4 V vs RHE) prior to OER, the amorphous catalyst is able to adsorb significantly higher amount of OH, suggesting more active sites.

Figure 2.10 The time dependent Nyquist and Bode plots. The time dependent Nyquist and Bode plots for amorphous (a, c) and crystalline (b, d) nickel-iron alloy catalyst (Ni/Fe = 3:1). Note: Bode plot shows the relation between phase angle and frequency in the Nyquist plot; the change of phase angle represents the conversion from double layer capacitor to adsorption capacitor.

Table 2.3 Fitting results of C_{ads} .

Potential (V vs RHE)	C_{ads} of amorphous	C_{ads} of crystalline
1.48	0.00148	7.7725×10^{-6}
1.46	0.00154	1.1746×10^{-5}
1.44	0.00156	2.5879×10^{-5}
1.42	0.00166	2.0497×10^{-5}
1.40	0.00299	1.5048×10^{-5}
1.38	0.00102	1.1323×10^{-5}
1.36	4.9896×10^{-5}	1.0669×10^{-5}
1.34	3.539×10^{-5}	1.0954×10^{-5}
1.32	3.1526×10^{-5}	1.0663×10^{-5}
1.30	2.9486×10^{-5}	1.029×10^{-5}

1.28	2.8097×10^{-5}	9.8999×10^{-6}
1.26	2.7196×10^{-5}	9.4873×10^{-6}

To further analysis the number of active sites. On the one hand, we could obtain the number of active sites experimentally by estimating the adsorption of OH* on the catalyst. The amount of transferred charges was determined by the reduction peak as shown in Figure 2.11.

For amorphous catalyst:

$$\begin{aligned}
 \text{Amount of transferred charges} &= \frac{\text{area of reduction peak}}{\text{scan rate} \times F} \\
 &= \frac{1.06 \times 10^{-1} \text{mA} \cdot \text{V} \cdot \text{cm}^{-2} \times 0.196 \text{cm}^2}{10 \text{mV} \cdot \text{s}^{-1} \times 96485 \text{C} \cdot \text{mol}^{-1}} \\
 &= 2.16 \times 10^{-8} \text{mol}
 \end{aligned} \tag{2.5}$$

For crystalline catalyst:

$$\begin{aligned}
 \text{Amount of transferred charges} &= \frac{\text{area of reduction peak}}{\text{scan rate} \times F} \\
 &= \frac{8.13 \times 10^{-4} \text{mA} \cdot \text{V} \cdot \text{cm}^{-2} \times 0.196 \text{cm}^2}{10 \text{mV} \cdot \text{s}^{-1} \times 96485 \text{C} \cdot \text{mol}^{-1}} \\
 &= 1.65 \times 10^{-10} \text{mol}
 \end{aligned} \tag{2.6}$$

Considering that OH* directly binds on the surface of the catalyst, the total active sites could be estimated as $2.16 \times 10^{-8} \text{mol}$ and $1.65 \times 10^{-10} \text{mol}$ for amorphous and crystalline catalysts, respectively.

Figure 2.11 The number of charges associated with OH adsorption was determined by integrating the reduction peak. CV curves of amorphous (a) and crystalline (b) nickel-iron alloy catalyst (Ni/Fe = 3:1) obtained at a scan rate of 10 mV/s.

On the other hand, we could obtain the theoretical number of active sites by considering Ni as the active species for OER. Only the Ni species at the outer surface of catalyst nanoparticles were assumed active.

(1). The electrochemically active surface area (ECSA) was estimated from the double-layer capacitance method according to $ECSA = \frac{C_{dl}}{C_s}$, where C_s is the ideal specific capacitance of a smooth planar surface made of the same material.

For amorphous catalyst:

$$ECSA = \frac{C_{dl}}{C_s} = \frac{0.075 \times 0.196 \text{ mF}}{0.060 \frac{\text{mF}}{\text{cm}^2}} = 0.25 \text{ cm}^2 \quad (2.7)$$

For crystalline catalyst:

$$ECSA = \frac{C_{dl}}{C_s} = \frac{0.065 \times 0.196 \text{ mF}}{0.060 \frac{\text{mF}}{\text{cm}^2}} = 0.21 \text{ cm}^2 \quad (2.8)$$

Figure 2.12 Determination of electrochemically active surface area (ECSA). CV curves of amorphous (a) and crystalline (b) nickel-iron alloy catalyst (Ni/Fe = 3:1) acquired in the potential range from 1.00 to 1.05 V vs RHE. (c, d) The corresponding double layer capacitance.

(2). Assuming that all nickel atoms are hexagonally close-packed on the surface (Figure 2.13),

$$\begin{aligned}
 \text{density of atom} &= \frac{\frac{\text{the number of atom}}{N_A}}{\text{area of the triangle}} \\
 &= \frac{\frac{\frac{1}{6} \times 3}{(6.022 \times 10^{23}) \text{ mol}}}{\sqrt{3} \times (125 \times 10^{-12})^2 \text{ m}^2} \\
 &= 3.07 \times 10^{-5} \text{ mol} \cdot \text{m}^{-2}
 \end{aligned} \tag{2.9}$$

For amorphous catalyst (0.75 is the percentage of Ni in the catalyst):

$$\text{Number of active sites} = \text{density of atom} \times \text{ECSA}$$

$$= 3.07 \times 10^{-5} \text{ mol} \cdot \text{m}^{-2} \times 0.25 \text{ cm}^2 \times 0.75 = 5.76 \times 10^{-10} \text{ mol} \quad (2.10)$$

which is much less as compared to that obtained in the experiment.

For crystalline catalyst:

$$\text{Number of active sites} = \text{density of atom} \times \text{ECSA}$$

$$= 3.07 \times 10^{-5} \text{ mol} \cdot \text{m}^{-2} \times 0.21 \text{ cm}^2 \times 0.75 = 4.84 \times 10^{-10} \text{ mol} \quad (2.11)$$

The value is comparable to the experimental result of $1.65 \times 10^{-10} \text{ mol}$.

Figure 2.13 Model of a close packing surface.

By comparing the theoretical results with experiments, it is deduced that for crystalline catalysts, the active sites are located on the external surface of the catalyst nanoparticles. However, for an amorphous catalyst, the external surface could not provide enough active sites to match that obtained in the experiment. It is thus we proposed that with applying anodic potential, the amorphous catalyst will be electrochemically activated to expose active sites in the bulk (Figure 2.14), which shall increase the number of active sites and thus enhance the water oxidation activity.

To consider the bulk contribution (amorphous material is long-range disordered, but short-range ordered), we took the smallest unit of a short-range ordered structure as the catalytic unit as shown in Figure 2.14, the theoretical number of active sites for amorphous catalyst was thus re-calculated. The size of the smallest unit of short-range ordered structure in the amorphous catalyst was obtained by both the Scherrer's equation and HAADF-STEM.^{251,252} The Scherrer's equation:

$$D = \frac{K\gamma}{\beta \cos(\theta)} \quad (2.12)$$

for the amorphous alloy nanoparticle, $K = 0.89$ is the shape factor, $\beta = 10\pi/180$ is the line broadening at half the maximum intensity (FWHM), $\theta = \pi/4$ is the Bragg angle, $\gamma = 0.154056$ nm is the X-ray wavelength. Thus, the obtained D is ~ 1 nm, which is consistent with that obtained from HAADF-STEM (Figure 2.2e).

Figure 2.14 Schematic illustration showing the electrochemical activation of the amorphous catalyst to expose the active sites in the bulk of the catalyst nanoparticles.

Therefore, based on the geometric factor (the size of the catalytic unit changes from the particle size of ~100 nm to the smallest unit size of the short-range ordered structure of ~1 nm),

$$\text{Specific surface area} = \frac{\text{area}}{\text{weight}} = \frac{4\pi r^2}{\rho \frac{4}{3}\pi r^3} = \frac{3}{\rho r} \quad (2.13)$$

$$\begin{aligned} \text{Number of active sites} &= \text{density of atom} \times \text{activated surface area} \\ &= 3.07 \times 10^{-5} \text{ mol} \cdot \text{m}^{-2} \times 0.25 \text{ cm}^2 \times \left(\frac{100 \text{ nm}}{1 \text{ nm}} \right) \times 0.75 \\ &= 5.76 \times 10^{-8} \text{ mol} \end{aligned} \quad (2.14)$$

which is comparable to the value obtained experimentally ($2.16 \times 10^{-8} \text{ mol}$).

To further account for the catalytic contribution from the bulk in an amorphous catalyst, we conducted a detailed analysis of the adsorption feature based on EIS. As shown in the Nyquist plot (Figure 2.9e), the semicircles for amorphous catalysts are depressed, indicative of frequency dispersion in the capacitive responses. To simulate the frequency dispersion, constant phase elements (CPEs) were used in the equivalent circuit model in place of pure capacitors, where $Z_{CPE} = A(j\omega)^{-\alpha}$, A is the CPE coefficient and α is the dispersion parameter ($\alpha = 0$ for an ideal resistor and $\alpha = 1$ for a pure capacitor).²⁵³ Figure 2.9f compares the change of intermediate-adsorption related dispersion parameter α with applied potential for both amorphous and crystalline nickel-iron alloy catalysts. It is clear to see that at applied anodic potentials below redox potential, the amorphous catalyst has a small value of α , suggesting

limited OH^- diffusion inside the catalyst nanoparticles.²⁵⁴ Further increase in applied anodic potential causes a sudden increase of α . The turning point of α is located at the same potential as the appearance of OH adsorption (Figure 2.9f), indicative of interface change,^{253,255-257} which demonstrates the activation of active sites within the amorphous bulk catalyst nanoparticles. On the contrary, for a crystal catalyst, the dispersion parameter α is almost independent on the applied anodic potential. Additionally, as shown in Figure 2.15a the redox peaks remain stable after the 1st CV scan, suggesting instantaneous activation of the amorphous catalyst to expose the active sites in the bulk of the particles. And the nearly 100% Faradaic efficiency suggests a high current density of OER with little influence from double layer capacitance and dissolution of catalyst.

Figure 2.15 (a) Cyclic voltammetry (CV) curves of amorphous nickel-iron alloy catalyst collected at a scan rate of 50 mV/s. (b) Faradaic efficiency measured at a constant applied current of 20 mA.

To further verify our hypothesis that the bulk part of the amorphous catalyst contributed the active sites, we performed isotope (^{18}O) labeling experiments to examine OH adsorption during OER. Figure 2.9h compares the released H_2^{18}O from

amorphous and crystalline catalysts. It is observed that the signal of H_2^{18}O can only be detected on amorphous or crystalline catalysts that undergoes OER in 1 M Na^{18}OH electrolyte. Moreover, at the same testing condition, the intensity of the H_2^{18}O signal from the amorphous catalyst is 2 orders of magnitude larger than that from the crystalline counterpart. Considering amorphous and crystalline catalysts with nearly the same specific surface area, these results clearly indicate electrochemical activation of the amorphous catalyst to expose active sites in the bulk.

Figure 2.16 In situ XAS. (a) In situ XANES spectra of Ni K-edge. (b) In situ EXAFS spectra of Ni.

Further evidence is provided by the atomic structure information obtained from in situ XAS spectra as shown in Figure 2.16. The XANES spectra demonstrate that the increase in the valence state of Ni is due to OER at high overpotential (Figure 2.16a). The EXAFS spectra reveal that the amorphous nickel-iron alloy shows broad peaks at 2.0 Å with a width of 1.6 Å, corresponding to Ni-Ni/Fe bond. Under applied potential, the positive shift of the EXAFS peak indicates an increase of Ni-Ni/Fe bond length,

which demonstrates that the elements are stretched and forced to move away from each other under anodic potential, the higher peak also suggests increased coordination numbers, indicative of adsorption of OH intermediates (Figure 2.16b).

Figure 2.17 A digital photograph of the amorphous nickel-iron alloy catalyst from one-pot synthesis (the yield of synthesis is close to 100%).

2.4 Conclusion

In summary, we have successfully developed a room temperature solution method to prepare amorphous nickel-iron alloys in a large scale (Figure 2.17) for water oxidation. The as-prepared amorphous alloy catalyst exhibits both high catalytic

activity, reaching 10 mA/cm² OER current density at an overpotential of 242 mV, and outstanding durability, having a stable performance at 80 °C and 500 mA/cm² for 20 h. Based on cyclic voltammetry, electrochemical impedance spectroscopy, isotope labeling and in situ X-ray absorption spectroscopy (XAS) studies, it is found that the amorphous nickel-iron alloy catalyst can be electrochemically activated to expose active sites in the bulk by applying anodic potential because of the short-range ordering of the amorphous structure, which greatly increases the number of active sites and thus significantly improves the water oxidation activity.

Chapter 3 Amorphous Multimetal Alloy

Oxygen Evolving Catalysts

3.1 Introduction

Water splitting driven by renewable electricity offers a green and sustainable strategy for hydrogen fuel production.^{14,147,183,258,259} However, the oxygen evolution reaction (OER) requires a substantial overpotential to reach the desired current densities typically greater than 500 mA/cm² in water electrolysis cells even with the aid of the most efficient OER electrocatalyst owing to the sluggish four-electron water oxidation kinetics.^{15,260} Over the past decades, researchers have made extensive efforts in exploring earth-abundant first-row transition metal oxides, (oxy)hydroxides^{174,176} and amorphous metal borides²⁶¹⁻²⁶⁴ for OER, among which NiFe layered double hydroxides (LDHs) have been most attractive with fastest OER kinetics, but the low electrical conductivity and poor chemical stability severely restrict their practical applications in water electrolyzers.^{97,154}

Figure 3.1 The scheme illustrating the main opinion of chapter 2.

An ideal OER catalyst should have optimal adsorption energies for oxygenated intermediates while at the same time must be electrically conductive to transport charges quickly.^{95,220} Taking into consideration these two criteria, we expect amorphous first-row transition metal alloys to be promising as highly efficient OER catalysts. Firstly, the amorphous structure is able to provide a large abundance of catalytically active sites. Secondly, the composition of metal alloys can be easily changed to modulate their 3d electronic structure and thus tune the adsorption energies for oxygenated intermediates. Finally, metal alloys possess characteristics of metal with high electrical conductivity.^{208,265,266} All of these features should positively benefit the OER catalysis. In this work, we developed a facile room temperature synthesis to prepare homogeneously dispersed, amorphous 3d transition-metal boron alloys. We used high-valence metals (e.g., molybdenum) to tune the electronic structure, yielding near optimal adsorption energies for oxygenated intermediates. Last but not least, we demonstrated an alkaline water electrolysis cell with an amorphous NiFeMoB alloy anode and a crystalline NiB alloy cathode that could stably deliver a water splitting current density of 500 mA/cm² with input voltage 1.57 V (in 6 M KOH at 80 °C without solution resistance correction).

3.2 Materials and Methods

3.2.1 Chemicals preparation and characterization

Chemicals: Nickel (II) acetate tetrahydrate (98%), iron (II) acetate (99.995%), manganese (II) acetate (99%), sodium molybdate dihydrate (99%), potassium

hydroxide (semiconductor grade, 99.99% trace metals basis), and sodium borohydride (granular 99.99% trace metals basis), iridium(IV) oxide (IrO_2 , 99.9% trace metals basis, product code: 206237-5G). All chemicals were purchased from Sigma-Aldrich and used as received without further purification.

Synthesis of amorphous alloy catalysts. To prepare amorphous nickel-iron alloy catalyst, 8.52 mmol of $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ and $\text{Fe}(\text{CH}_3\text{COO})_2$ with a molar ratio of 3 : 1 were added into 50 mL of deionized (DI) water in a conical flask under magnetic stirring, followed by quickly adding 20 mL of 1.28 M NaBH_4 aqueous solution 10 minutes later. Instantaneous formation of black precipitates was observed. After stirring for 10 minutes, the black precipitate was collected and washed with deionized (DI) water and ethanol several times, and then stored in acetone. To prepare Mn and Mo incorporated nickel-iron alloy catalysts, manganese (II) acetate with a molar ratio of $\text{Mn}/(\text{Ni} + \text{Fe}) = 0.1$ and sodium molybdate dihydrate with a molar ratio of $\text{Mo}/(\text{Ni} + \text{Fe}) = 0.05$ were added into the nickel acetate and iron acetate solution. Additionally, amorphous nickel-iron alloy catalysts could be directly grown on three-dimensional (3D) nickel foam by sequentially dropping transition metal salt solution and NaBH_4 solution onto nickel foam.

Synthesis of crystalline nickel boron catalysts. To prepare the crystalline nickel boron catalyst, 8.52 mmol of $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ was added into 50 mL of deionized (DI) water in a conical flask under magnetic stirring, followed by quickly adding 20 mL of 1.28 M NaBH_4 aqueous solution 10 minutes later. Instantaneous formation of black precipitates was observed. After stirring for 10 minutes, the black precipitate

was collected and washed with deionized (DI) water and ethanol several times, and dried in air at room temperature, followed by annealing at 500 °C for 2 hours under nitrogen atmosphere to obtain crystalline nickel boron.

Materials characterization: The structure of the as-prepared catalysts was examined by powder X-ray diffraction (XRD) on a D8 Advance diffractometer with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$). The composition and morphology were studied by field emission scanning electron microscopy (FESEM, JSM-6701), transmission electron microscopy (TEM, JOEL-2010) with selected area electron diffraction (SAED), and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM, JEOL JEM-ARM200F) with energy-dispersive X-ray spectroscopy (EDX). Detailed chemical compositions were analyzed by X-ray photoelectron spectroscopy (XPS) on an ESCALAB 250 photoelectron spectrometer (Thermo Fisher Scientific) using a monochromatic Al K α X-ray beam (1486.6 eV). All binding energies were referenced to the C 1s peak (284.6 eV).

3.2.2 Electrochemical measurements

Electrochemical measurements were performed on a CHI 760E electrochemical workstation at room temperature on a rotating disk glassy carbon (GC) electrode (PINE, 5 mm diameter, 0.196 cm²). Pt coil (area: 2 cm²) and Hg/Hg₂Cl₂ (PINE, saturated with KCl) were used as counter and reference electrodes, respectively. The potential was referenced to the reversible hydrogen electrode (RHE) through:

$$E(RHE) = E(Hg/Hg_2Cl_2) + 0.241 + 0.059 \times pH \quad (3.1)$$

The working electrode on GC was prepared as follows: first, 3 mg of catalyst was dispersed in a mixed solution of deionized water (500 μL) and ethanol (500 μL), and then ultrasonicated for 1 hour. Subsequently, 5 μL of the catalyst ink suspension was pipetted onto a pre-cleaned GC electrode with a catalyst loading amount of 75 $\mu\text{g}/\text{cm}^2$. Finally, the GC electrode was dried at room temperature in air for at least 1 hour.

Before acquiring electrochemical data, the standard potential of reference electrode vs. RHE was calibrated in a two-electrode system, where the electrolyte is hydrogen saturated 0.5 M H_2SO_4 . One electrode is $\text{Hg}/\text{Hg}_2\text{Cl}_2$ (PINE, saturated with KCl) and the other electrode is Pt foil ($1 \times 1 \text{ cm}^2$) with bubbling H_2 . The standard value of the reference electrode was obtained as the stable absolute value in the open circuit potential measured by a CHI 760E electrochemical workstation. The GC working electrodes were subjected to continuous potential cycling in the potential window from 1.0 to 1.5 V (vs. RHE) until reproducible voltammograms were obtained at room temperature, 1600 rpm, and a sweep rate of 100 mV/s. The solution resistance R_s was determined by electrochemical impedance spectroscopy (EIS) and used for the Ohmic drop correction according to the relation $E_c = E_m - iR_s$ (where E_c is the corrected potential and E_m is the measured potential, respectively). OER activity was recorded by linear sweep voltammetry and cyclic voltammetry at a scan rate of 5 mV s^{-1} in 1 M ultrapure KOH (semiconductor grade, 99.99% trace metals basis) at 1600 rpm. Methanol oxidation test was acquired by cyclic voltammetry at a scan rate of 20 mV s^{-1} in a mixture solution of 1 M ultrapure KOH (semiconductor grade, 99.99% trace metals basis) and 1M methanol (HPLC grade, assay $\geq 99.9\%$) at 1600 rpm.

X-ray absorption spectroscopy (XAS) measurements. X-ray absorption spectroscopy (XAS) measurements were conducted using the synchrotron radiation light source of Si 111 double crystal monochromator at 12B2 Taiwan beamline of the National Synchrotron Radiation Research Center (NSRRC) in Spring 8 (Japan) at room temperature. The electron storage ring was operated at 8.0 GeV with a constant current of ~ 100 mA. The photon energy was calibrated with the first inflection point of the Fe K-edge and Ni K-edge in Fe and Ni metal foil, respectively. XAS data were collected in total electron yield mode. Extended X-ray absorption fine structure (EXAFS) spectra were fitted using the FEFF 6.0 code (Athena).

MOR test. Methanol oxidation test was conducted by three-electrode system in a mixture solution of 1 M ultrapure KOH (semiconductor grade, 99.99% trace metals basis) and 1M methanol (HPLC grade, assay $\geq 99.9\%$). Here, Pt coil (area: 2 cm²) and Hg/Hg₂Cl₂(PINE, saturated with KCl) were used as counter and reference electrodes, respectively. The data was acquired by cyclic voltammetry at a scan rate of 20 mV s⁻¹ at 1600 rpm.

Determination of the electrochemically active surface area. The electrochemically active surface area (ECSA) was measured by a double layer capacitance method. Typically, a double-layer charging potential region was first determined from a static CV scan. The charging current i_c was measured from CV curves obtained at different scan rates. The relation between i_c , scan rate (ν) and the double layer capacitance (C_{dl}) is given by $i_c = \nu C_{dl}$. The ECSA can thus be estimated from double-layer capacitance according to $ECSA = C_{dl}/C_s$, where C_s is the ideal

specific capacitance of a smooth planar surface made of the same material.

3.3 Results and Discussion

3.3.1 Structure and morphology

Figure 3.2 Structural and morphological characterization. (a), (b), (c), (d), SEM, TEM, HAADF-STEM images, and EDX elemental mapping images of amorphous Mn incorporated nickel iron alloy. (e), (f), (g), (h), SEM, TEM, HAADF-STEM image, and EDX elemental mapping images of amorphous nickel iron alloy. Inset in (b) and (f) show the corresponding selected area electron diffraction (SAED) patterns. (i), (j), (k), (l), SEM, TEM, EDX elemental mapping, and HAADF-STEM images of amorphous Mo incorporated nickel iron alloy. Insets in (b), (f), (j) show the corresponding selected area electron diffraction (SAED) patterns.

Ni and Fe have been shown very active and synergistic in OER catalysis, therefore, we choose Ni and Fe as the metal elements to constitute 3d transition-metal boron alloys. Amorphous NiFe boron (NiFeB) alloys were synthesized at room temperature and ambient pressure by reacting NaBH_4 aqueous solution with nickel and iron salt. High/low-valence transition metals such as Mo/Mn could be incorporated into NiFeB

alloys to modulate their 3d electronic structure via adding respective metal salt during synthesis. Figure 3.2 shows scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images of the as-prepared NiFeB, NiFeMoB and NiFeMnB alloys, which comprise of interconnected nanoparticles with a similar mean size of around 50 nm. Atomic resolution high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), together with selected area electron diffraction (SAED) and X-ray diffraction analyses reveals the absence of long-range ordered crystalline phase.^{234,237} The transition metal and boron elements are uniformly distributed across the entire samples as shown in the energy-dispersive X-ray spectroscopy (EDX) mappings performed in HAADF-STEM. And the detailed compositions are determined by both ICP-MS and TGA, which give Ni to Fe atomic ratio of around 3 (Figure 3.3, Table 2.1), agreeing well with the amount of nickel and iron salts used in the synthesis. And there is a very small amount of B and O in all catalysts.

Figure 3.3 Thermogravimetric analysis of the three samples under nitrogen atmosphere.

Table 3.1 Compositions obtained by ICP and TGA results.

	Ni	Fe	Mn	Mo	B	O	H₂O
NiFeMnB	0.682	0.233	0.031	0	0.043	0.011	0.114
NiFeB	0.718	0.235	0	0	0.037	0.010	0.102
NiFeMoB	0.693	0.227	0	0.028	0.032	0.020	0.201

We further employed X-ray absorption fine structure spectroscopy (XAFS) to resolve the local structure information of NiFeB, NiFeMoB and NiFeMnB alloys. The bond length was extracted from extended XAFS spectra as shown in Figure 3.4 and is displayed in Table 3.2. The EXAFS spectra in Figure 3.4a revealed that the amorphous alloys showed broad peaks at 2.0 Å with a width of 1.6 Å, corresponding to Ni-Ni bond compared with the peak of Ni foil. And the peak at 2.2 Å in Figure 3.4b was attributed to Fe-Fe bond compared with Fe foil. Although there were small peaks at 1.5 Å in Figure 3.4a and 1.6 Å in Figure 3.4b, corresponding to the Ni-O and Fe-O bonds, it was due to the surface oxidation on the amorphous alloys. We could still conclude that all three samples show strong metal-metal interactions, suggesting their metallic alloy structures.

Figure 3.4 Ni K-edge (a) and Fe K-edge (b) EXAFS spectra.

Table 3.2 EXAFS fitting parameters.

Sample	Bond type	Bond length	CN	Sigma ²
NiFeB	Ni-Ni	2.4	2.0	0.056
NiFeB	Fe-Fe	2.41	5.6	0.141
NiFeB	Fe-Fe	2.81	8.7	0.179
NiFeMnB	Ni-Ni	2.41	2.4	0.065
NiFeMnB	Fe-Fe	2.35	5.9	0.192
NiFeMnB	Fe-Fe	2.64	7.5	0.183
NiFeMoB	Ni-Ni	2.41	1.4	0.044
NiFeMoB	Fe-Fe	2.49	5.6	0.147
NiFeMoB	Fe-Fe	2.78	7.5	0.139

3.3.2 Valence states

The surface valence states of amorphous alloys were examined by X-ray photoelectron spectroscopy (XPS). As displayed in Figure 3.5a, the Ni 2p spectra show the 2p_{3/2} and 2p_{1/2} peaks at 852.7 and 870.2 eV, respectively for all samples,

typical for nickel alloyed with boron. The Ni 2p_{3/2} and Ni 2p_{1/2} peaks at 855.6 and 873.0 eV can be assigned to Ni²⁺, indicative of surface oxidation.²⁶⁷ The Fe 2p spectra (Figure 3.5b) show two peaks of Fe 2p_{3/2} at 710.4 and 713.9 eV, respectively, which are assigned to Fe²⁺ and Fe³⁺, indicating that Fe is oxidized on the alloy surface,²⁴¹ while Ni and Fe in bulk are mainly present in metallic states as shown in the Ni 2p and Fe 2p XPS spectra recorded after surface Ar plasma etching (Figure 3.6). B 1s spectra as shown in Figure 3.5c can be deconvoluted into two species at 188.1 and 192.5 eV, respectively. The peak at 188.1 eV is due to the interaction of boron with nickel/iron, whereas the other peak comes from B₂O₃.^{242,267} Figure 3.5f shows the Mn 3s XPS spectrum of NiFeMnB, which displays two peaks with $\Delta E = 6.0$ eV, indicating that Mn is present as low-valent Mn²⁺,^{241,268} while the peak at 233.1 eV in the Mo 3d XPS spectrum of NiFeMoB (Figure 3.5g) suggests that Mo is present as high-valent Mo⁶⁺.²⁶⁹ The O 1s spectrum (Figure 3.5e) can be deconvoluted into two peaks at 531.2 and 532.4 eV, corresponding to lattice oxygen and adsorbed oxygen, respectively.^{270,271} The ratio of lattice oxygen to adsorbed oxygen decreases/increases by incorporating a trace amount of Mn/Mo into NiFeB, indicating enhanced/reduced bindings to oxygenated species. To understand these phenomena, we examined the valence band of NiFeB, NiFeMoB and NiFeMnB alloys by XPS as shown in Figure 3.5d. The valence band for NiFeB, NiFeMoB and NiFeMnB samples are all located across the Fermi surface, confirming the alloy state of the catalysts. The electron density near the Fermi level (E_F) is found to decrease in the order of NiFeMnB > NiFeB > NiFeMoB, which could be interpreted by redistribution of electrons in the d

states of Ni and Fe with incorporated Mn (Mo), thus changing their interactions with oxygenated species.^{272,273} As schematically illustrated in Figure 3.5h, the incorporation of low-valent Mn^{2+} (high-valent Mo^{6+}) into NiFeB results in an increase (decrease) in electron density near E_F owing to the low (high) electron affinity of Mn^{2+} (Mo^{6+}),^{274,275} which in turn enhances (weakens) the adsorption of oxygenated species.

Figure 3.5 Surface valence states. High-resolution XPS spectra of (a), Ni 2p, (b), Fe 2p, (c), B 1s, and (e), O 1s for amorphous Mn incorporated nickel iron alloy (top), nickel iron alloy (middle), and Mo incorporated nickel iron alloy (bottom), respectively. (f), Mn 3s, (g), Mo 3d, for Mn incorporated nickel iron alloy and Mo incorporated nickel iron alloy, respectively. (d), (h), Valence bands and schematics of the density of states.

Figure 3.6 Bulk electronic states. (a), (b), (c), (d), High-resolution XPS spectra of Ni 2p, Fe 2p, B 1s, O 1s for amorphous NiFeMnB (bottom), NiFeB (medium), and NiFeMoB (top) alloy catalysts after Ar plasma etching for 300 s. (e), Mo 3d, and (f), Mn 3s XPS spectra. **Note:** The metallic elements confirm the alloy phase of the three catalysts.

3.3.3 Electrocatalytic performance

The electrocatalytic performance of the as-prepared amorphous alloys was studied on glassy carbon (GC) rotating disk electrode (RDE). Figure 3.7a compares the OER polarization curves, among which, NiFeMoB exhibits the lowest OER onset potential at 1.42 V vs. RHE with a catalyst loading of 0.075 mg/cm² and requires an overpotential of only 260 mV to reach 10 mA/cm². This overpotential is 50 and 90 mV smaller than that of NiFeB and NiFeMnB, and 230 mV smaller than that of the commercial IrO₂. Optimizing catalyst loading on RDE further reduces the overpotential at 10 mA/cm² to as low as 220 mV (Figure 3.7b). By loading the best

OER catalyst of NiFeMoB on three-dimensional (3D) porous nickel foam support (thickness: 0.08 cm), the NiFeMoB-nickel foam electrode is able to deliver current densities greater than 500 mA/cm^2 at overpotentials slightly larger than 330 mV without correcting solution resistance (220 mV with 95% solution resistance correction) in 1 M KOH at room temperature, which is the best OER catalyst ever reported (Table 3.3, Table 3.4).

Figure 3.7 Electrochemical performance. (a), OER polarization curves (with 95% iR correction) of amorphous alloy catalysts and IrO_2 . The loading amount is 0.075 mg/cm^2 . (b), Overpotential (with 95% iR correction) of amorphous NiFeMoB with different catalyst loading amounts. (c), Chronopotentiometric curve of amorphous NiFeMoB Ni foam electrode at a constant current density of 500 mA/cm^2 and room temperature. (d), Chronopotentiometric curve of overall water splitting at a constant current density of 500 mA/cm^2 and room temperature with amorphous NiFeMoB Ni foam as anode and crystalline NiB Ni foam as the cathode. Inset in (c) shows the potential step (P_{step}) measured polarization curves and CV curves (at 5 mV/s) recorded on amorphous NiFeMoB Ni foam electrode (details are shown in Figure 3.8). Inset in (d) shows the CV curves (at 5 mV/s) collected before and after stability test together with a digital photograph of the alkaline electrolyzer. The slight increase in cell

voltage along with operation time is caused by the slow deactivation of the crystalline NiB hydrogen-evolving cathode (Figure 3.20).

Figure 3.8 The potential step (P_{step}) method and acquired polarization curve (inset) for the amorphous NiFeMoB Ni foam electrode. This method uses steady-state current density at each potential (0.05 V interval).

Table 3.3 OER catalytic performance comparison of various OER catalysts on three-dimensional electrodes.

Catalyst	Potential (V vs RHE)	Electrolyte	Electrode	Reference
NiFeMoB	1.43 @ 100 mA/cm ²	1 M KOH	Ni foam	This work
NiFeMoB	1.45 @ 500 mA/cm ²	1 M KOH	Ni foam	This work
e-ICLDH@GDY/NF	1.51 @ 500 mA/cm ²	1 M KOH	Ni foam	Ref. ²⁷⁶
Ni ₃ Fe _{1-x} V _x NS	1.52 @ 500 mA/cm ²	1 M KOH	Carbon paper	Ref. ²⁷⁷
O ₂ -Cat-1	1.53 @ 500 mA/cm ²	1 M KOH	Fe foam	Ref. ²⁷⁸

G-FeCoW	1.49@100 mA/cm ²	1 M KOH	Ni foam Au plated	Ref. ¹⁴⁷
W _{0.5} Co _{0.4} Fe _{0.1} /NF	1.54@100 mA/cm ²	1 M KOH	Ni foam	Ref. ²⁷⁹
^s Au/NiFe LDH	1.52@200 mA/cm ²	1 M KOH	Ti mesh	Ref. ²⁸⁰
CoN-1 min/NF	1.56@100 mA/cm ²	1 M KOH	Ni foam	Ref. ²⁸¹
Fe-Ni-P	1.5@500 mA/cm ²	1 M KOH	Ni foam	Ref. ²⁸²
CoFeNiO _x	1.5@100 mA/cm ²	1 M KOH	Ni foam	Ref. ²⁸³

Table 3.4 OER performance comparison on glassy carbon electrode in 1 M KOH.

Catalyst	η @10 mA/cm ²	Tafel Slope (mV/dec)	Electrode	Reference
NiFeMoB	220 mV	24	Glassy carbon	This work
G-FeCoW	217(-/+2) mV	37	Glassy carbon	Ref. ¹⁴⁷
CoFe LDHs	232 mV	36	Glassy carbon	Ref. ²⁸⁴
NiFe LDHs-V _{Ni}	229 mV	62.9	Glassy carbon	Ref. ²⁸⁵
NiFe-NS	302 mV	40	Glassy carbon	Ref. ²⁸⁶
AH-Co	280 mV	40	Glassy carbon	Ref. ⁷¹
Amorphous Fe-Co-2.3Ni-B	274 mV	37	Glassy carbon	Ref. ²²⁵
P-Co ₉ S ₈	280 mV	87.5	Glassy carbon	Ref. ²⁸⁷
Ni _{2/3} Fe _{1/3} -rGO ^a	210 mV	40	Glassy carbon	Ref. ²⁸⁸

NiFe LDH- NS@DG10 ^b	210 mV	52	Glassy carbon	<i>Ref.</i> ²⁸⁹
NiFe LDH/CNT	240 mV	31	Glassy carbon	<i>Ref.</i> ²⁹⁰

^aThe overpotential of 210 mV at 10 mA/cm² is not strict, which quickly increases to 240 mV by holding the current density at 10 mA/cm², indicating non-Faradic current contribution. ^bThe overpotential of 210 mV at 10 mA/cm² was incorrectly determined, which was determined from the LSV curve with redox contribution. The appropriate way should be at a steady-state by removing the redox contribution.

Besides activity, the stability of the catalyst is equally important for practical applications in water electrolysis. We examined the stability of NiFeMoB at a constant anodic current density of 500 mA/cm² at room temperature as shown in Figure 3.7c, it is clear to see that the NiFeMoB electrode is very stable in water oxidation catalysis. After 40 h of continuous reaction, there is no obvious increase in overpotential. XPS study after stability test shows that only a few surface layers of NiFeMoB are oxidized and the bulk of catalyst keeps the alloy state (Figure 3.9). We further measured the concentrations of dissolved Ni, Fe, Mo and B in the electrolyte and on the counter electrode by inductively coupled plasma mass spectrometry (ICP-MS) after the reaction. The concentrations are well below the detecting limit (0.1 ppb). Additionally, we also measured the Faradaic efficiency of OER as shown in Figure 3.10, which is around 100%. All of these results demonstrate an excellent stability of NiFeMoB in OER.

Figure 3.9 Valence states after OER. (a), (b), (c), (d), High-resolution XPS spectra of Ni 2p, Fe 2p, O 1s, and B 1s for amorphous NiFeB alloy catalyst after OER. The bottom spectra were collected after Ar plasma etching for 300 s.

Figure 3.10 Faradaic efficiency measured at a constant applied current of 50 mA.

3.3.4 Adsorption of intermediates analysis

To probe the origin of the enhanced and reduced OER activity of NiFeMoB and NiFeMnB as compared to NiFeB, we compared their specific surface area, electrochemically active surface area (ECSA) and conductivity. It can be concluded that the comparable values of slopes indicate nearly the same ECSA in Figure 3.11, the adsorption-desorption isotherms give nearly the same BET surface area in Figure 3.12a, and the comparable slopes of U-I curves show high conductivity for all three catalysts in Figure 3.12b. Furthermore, Tafel plots also give close Tafel slopes of around 24 mV/dec for all alloy catalysts (Figure 3.13), suggesting that OER should be rate-limited at the same elementary reaction.^{244,245}

Figure 3.11 Determination of electrochemically active surface area (ECSA). (a), (b), (c), CV curves of amorphous NiFeMnB, NiFeB and NiFeMoB alloy catalysts

acquired in the potential range from 1.00 to 1.05 V vs. RHE. (d), The corresponding double layer capacitance.

Figure 3.12 Brunauer–Emmett–Teller (BET) surface area and conductivity. (a), (b), (c), Adsorption-desorption isotherms of NiFeMnB, NiFeB, and NiFeMoB. (d), U-I curves of the three catalysts.

Figure 3.13 Tafel slope study. (a), LSV curves acquired via backward scan at 1 mV/s avoiding the influence of capacitance. (b), The corresponding Tafel plots.

However, the three amorphous alloy catalysts show distinctively different redox peak positions in the polarization curves (Figure 3.15a), in which, the redox peak of NiFeMoB appears much later, but it shows the best OER activity. We further conducted a methanol oxidation reaction (MOR) tests to confirm that the redox peaks resulted from $^*\text{OH}$ adsorption (Figure 3.15b).^{246,248} Therefore, the lowest OER activity of NiFeMnB as compared to NiFeB and NiFeMoB can be attributed to the too strong adsorption of $^*\text{OH}$ intermediate. Because of re-hybridization of the d and s, p states among Ni, Fe, and Mn (Mo), the d band center of NiFeMnB (NiFeMoB) moves close to (away from) the Fermi level (E_f), thus enhances (weakens) the binding of oxygenated species (Figure 3.14).^{275,291,292}

Figure 3.14 Schematic illustration showing the formation of a chemical bond between the OH^* adsorbate valence level and the d-states of amorphous alloy surface.

To gain an in-depth understanding of the OER energetics, we extracted adsorption energies for each oxygenated OER intermediate based on an associative OER pathway as displayed in Figure 3.16 by applying a recently developed MOR test²⁴⁸ together with the microkinetic model (density functional theory calculations are

impeded because of the poorly defined amorphous structure of the alloy catalysts).²⁹³ As shown in Figure 3.15c and d, the extracted potential determining step (PDS) for all three alloy catalysts are at the third electron transfer (ET) step ($\text{O}^* + \text{OH}^- \rightarrow \text{OOH}^* + \text{e}^-$). Among the three amorphous alloy catalysts, Mo incorporation into NiFeB makes NiFeMoB possess near-optimal adsorption energies for oxygenated OER intermediates (Figure 3.15d), resulting in the best OER activity.

Figure 3.15 Binding energies of oxygenated OER intermediates. (a), Redox potential and OER potential assessed at 10 mA/cm² for NiFeB, NiFeMnB and NiFeMoB. (b), CV curves of MOR collected at a scan rate of 20 mV/s. Inset in (b) shows the enlarged view. (c), LSV (collected via backward scan at 1 mV/s) curves (dots) and the corresponding electrochemical fitting curves (lines) to extract binding energies of oxygenated OER intermediates. (d), The free energy diagram for OER. Inset in (d) shows the activity volcano plot.

Detailed methods of extracting the adsorption energies of the oxygen intermediates are described in the previous work.²⁴⁸ For the highly irreversible process of OER, the

back reaction of the rate-determining step (RDS) is neglected. Therefore, the overall kinetics can be described by RDS (the elemental steps are shown in Figure 3.16).

Figure 3.16 The mechanism of OER. A well-adopted associative mechanism is used to describe the pathway of OER.

The velocities of RDS for the 1st, 2nd and 3rd elemental reaction are given by:

$$v_1 = k_1 \theta_{M^*} \quad (3.2)$$

$$v_2 = k_2 \theta_{OH^*} \quad (3.3)$$

$$v_3 = k_3 \theta_{O^*} \quad (3.4)$$

where θ_{OH^*} , θ_{O^*} , and θ_{M^*} represent the surface coverage of OH*, O* and empty sites.

The absolute value of the steady state current density of the overall reaction is described by:

$$j_{ET}^i = 4Fv_i \quad (3.5)$$

where k_i is:

$$k_i = k_i^0 \cdot e^{\frac{-\alpha F(E_i^0 - E)}{RT}} \quad (3.6)$$

Based on an associative OER pathway as shown in Figure 3.16, if the 1st elementary reaction is in equilibrium (K is equilibrium constant):

$$\frac{\theta_{OH^*}}{\theta_{M^*}} = K_1^0 e^{\left(\frac{-F(E_1^0 - E)}{RT}\right)} \quad (3.8)$$

If the 2nd elementary reaction is in equilibrium:

$$\frac{\theta_{O^*}}{\theta_{OH^*}} = K_2^0 e^{\left(\frac{-F(E_2^0 - E)}{RT}\right)} \quad (3.10)$$

where K_i is:

$$K_i = K_i^0 \cdot e^{\frac{-F(E_i^0 - E)}{RT}} \quad (3.11)$$

The total coverage can be calculated as:

If the 1st elementary reaction is the RDS:

$$\theta_{M^*} = 1 \quad (3.12)$$

If the 2nd elementary reaction is the RDS:

$$\theta_{M^*} + \theta_{OH^*} = 1 \quad (3.13)$$

If the 3rd elementary reaction is the RDS:

$$\theta_{M^*} + \theta_{OH^*} + \theta_{O^*} = 1 \quad (3.14)$$

From equation (3.8) and (3.13), we can get:

$$\theta_{OH^*} = \frac{K_1^0 e^{\left(\frac{-F(E_1^0 - E)}{RT}\right)}}{1 + K_1^0 e^{\left(\frac{-F(E_1^0 - E)}{RT}\right)}} \quad (3.15)$$

From equation (3.8), (3.10) and (3.14), we can get:

$$\theta_{O^*} = \frac{K_1^0 K_2^0 e^{\left(\frac{-F(E_1^0 + E_2^0 - 2E)}{RT}\right)}}{1 + K_1^0 e^{\left(\frac{-F(E_1^0 - E)}{RT}\right)} + K_1^0 K_2^0 e^{\left(\frac{-F(E_1^0 + E_2^0 - 2E)}{RT}\right)}} \quad (3.16)$$

From equation (3.2), (3.5) and (3.12), we can get:

$$j_{ET}^1 = 4Fk_1^0 e^{\left(\frac{-\alpha F(E_1^0 - E)}{RT}\right)} \quad (3.17)$$

From equation (3.3), (3.5) and (3.15), we can get:

$$j_{ET}^2 = \frac{4Fk_2^0 K_1^0 e^{\left(\frac{-F(E_1^0 + \alpha E_2^0 - E - \alpha E)}{RT}\right)}}{1 + K_1^0 e^{\left(\frac{-F(E_1^0 - E)}{RT}\right)}} \quad (3.18)$$

From equation (3.4), (3.5) and (3.16), we can get:

$$j_{ET}^3 = \frac{4Fk_3^0 K_1^0 K_2^0 e^{\left(\frac{-F(E_1^0 + E_2^0 + \alpha E_3^0 - 2E - \alpha E)}{RT}\right)}}{1 + K_1^0 e^{\left(\frac{-F(E_1^0 - E)}{RT}\right)} + K_1^0 K_2^0 e^{\left(\frac{-F(E_1^0 + E_2^0 - 2E)}{RT}\right)}} \quad (3.19)$$

Considering the mass transport limitation, we obtain:

$$\frac{1}{j_{ET}^1} = \frac{1}{4Fk_1^0 e^{\left(\frac{-\alpha F(E_1^0 - E)}{RT}\right)}} + \frac{1}{j_{MT}} \quad (3.20)$$

$$\frac{1}{j_{ET}^2} = \frac{1}{\frac{4Fk_2^0 K_1^0 e^{\left(\frac{-F(E_1^0 + \alpha E_2^0 - E - \alpha E)}{RT}\right)}}{1 + K_1^0 e^{\left(\frac{-F(E_1^0 - E)}{RT}\right)}}} + \frac{1}{j_{MT}} \quad (3.21)$$

$$\frac{1}{j_{ET}^3} = \frac{1}{\frac{4Fk_3^0 K_1^0 K_2^0 e^{\left(\frac{-F(E_1^0 + E_2^0 + \alpha E_3^0 - 2E - \alpha E)}{RT}\right)}}{1 + K_1^0 e^{\left(\frac{-F(E_1^0 - E)}{RT}\right)} + K_1^0 K_2^0 e^{\left(\frac{-F(E_1^0 + E_2^0 - 2E)}{RT}\right)}}} + \frac{1}{j_{MT}} \quad (3.22)$$

According to a number of experimental results from both literature and our laboratory,²⁴⁸ we find the parameters in scaling relationship as:

$$\Delta G_{OOH^*} - \Delta G_{OH^*} = 2.8 \text{ eV} \quad (3.23)$$

$$\Delta G_{O^*} = 1.65 \cdot \Delta G_{OH^*} + 0.58 \text{ eV} \quad (3.24)$$

And the relationships between ΔG and E_i^0 are given by:

$$-FE_1^0 = \Delta G_{OH^*} \quad (3.25)$$

$$-FE_2^0 = \Delta G_{O^*} - \Delta G_{OH^*} \quad (3.26)$$

$$-FE_3^0 = \Delta G_{OOH^*} - \Delta G_{O^*} \quad (3.27)$$

$$-FE_4^0 = -\Delta G_{OOH^*} \quad (3.28)$$

Based on our definition of the binding energy of kinetic-relevant intermediates, the range of initial values for k_i^0 , K_i^0 , α , j_{MT} of OER are properly set in the kinetic modeling. Furthermore, according to a recently developed methanol oxidation reaction (MOR) test, the adsorption energy of OH^* intermediate could be

experimentally acquired by the onset potential of methanol oxidation (E_{MOR}), which was used as the initial E_1^0 for the kinetic modeling.

Figure 3.17 Surface adsorption study. (a), (b), (c), CV curves of methanol oxidation (pink) and OER (cyan) for amorphous NiFeMnB, NiFeB, and NiFeMoB.

Table 3.5 Binding strength of oxygenated intermediates obtained from MOR test and microkinetic modeling.

Parameter	NiFeMnB	NiFeB	NiFeMoB
E_1^0 (V) ^a	1.347	1.385	1.410
E_1^0 (V)	1.35	1.38	1.40
E_2^0 (V)	1.36	1.38	1.43
E_3^0 (V)	1.53	1.46	1.42
E_4^0 (V)	0.68	0.7	0.67

^aResults obtained from MOR test.

Subsequently, we fit equation (3.20), (3.21) and (3.22) to our experimental steady-state LSV data. The obtained results are shown in Figure 3.17 and Table 3.5,. It reveals that the RDS of the three catalysts is at the third electron transfer (ET) step (Figure 3.18). Figure 3.18a shows a transition of Tafel slope from 24 mV/dec to 44 mV/dec for all three amorphous alloy catalysts with increasing current density. This

transition can be explained by the saturated adsorption of OH* intermediate (Figure 3.18b) due to the strong bindings of oxygenated species on metallic alloys. This phenomenon is consistent with our theoretical model. According to equation (3.19), the Tafel slope of a catalyst whose RDS at the 3rd ET step can be determined by: ²⁴⁸

$$b = \frac{\partial E}{\partial \log(i)} = \frac{60}{2 + \alpha} \text{ (mV/dec)} \quad (3.29)$$

After the saturation of OH* intermediate, according to equation (14) and (18), we will obtain a new Tafel slope:

$$b = \frac{\partial E}{\partial \log(i)} = \frac{60}{1 + \alpha} \text{ (mV/dec)} \quad (3.30)$$

Typically, we take the symmetry factor α as 0.5, and Tafel slope transits from 24 to 40 mV/dec. Figure 3.18b shows the change of coverage of OH* and O* intermediates with potential. The potential where OH* saturates shifts positively from NiFeMnB to NiFeMoB accompanied by decreased coverage, which is consistent with the decreased adsorption strength on the three catalysts.

Figure 3.18 Microkinetic modeling. a, Tafel plots. b, Coverage of OH* and O* intermediates.

3.3.5 Long-term stability for overall water splitting

To test the practical application potential, we assembled an alkaline water electrolysis cell made of a NiFeMoB oxygen-evolving anode and a NiB hydrogen-evolving cathode (Figure 3.7d). As shown in Figure 3.19, the complete alkaline electrolyzer is composed of a crystalline NiB (on Ni foam) cathode and an amorphous NiFeMoB (on Ni foam) anode. A membrane (e.g., PTFE membrane) is used to separate the hydrogen from the oxygen. But we want to point out that schematic illustration as shown in Figure 3.19 is an alkaline water electrolyzer stack, while the digital photograph as shown in Figure 3.7d inset is a single alkaline water electrolysis cell for performing long-term stability test.

Figure 3.19 The alkaline electrolyzer.

The cathodic catalyst NiB was simply prepared by sequentially dropping transition metal salt solution and NaBH_4 solution onto nickel foam, then annealing at 500°C for 2 hours under the nitrogen atmosphere. The morphology of the cathodic catalyst NiB was displayed in Figure 3.20, the HRTEM image and SAED pattern (inset in Figure 3.20a) indicated the well crystalline phase of NiB. Although the Tafel slope during HER is very large (Figure 3.20b), NiB electrode (on Ni foam) showed much better HER activity than Pt foil. Therefore, to drive the water splitting more efficiently, we used the NiB electrode (on Ni foam) as the anode rather than Pt foil.

Figure 3.20 Activity of HER electrode in 1 M KOH. (a), TEM image, HRTEM image and SAED pattern (inset) of crystalline NiB. (b), HER polarization curve and the corresponding Tafel plot (inset) acquired on the glassy carbon electrode. (c), Comparison of HER polarization curve between crystalline NiB electrode (on Ni foam) and Pt foil electrode. (d), Chronopotentiometric curve of NiB electrode (on Ni foam) at a constant current density of $500 \text{ mA}/\text{cm}^2$ and room temperature.

Finally, the homemade single cell (Figure 3.7d) only requires an external voltage of ~ 1.72 V to reach a current density of 500 mA/cm^2 without correcting solution resistance (~ 1.63 V with 95% solution resistance correction) in 1 M KOH at room temperature, which can be stably operated for over 40 h. Increasing electrolyte concentration to 6 M KOH and operating temperature to 80°C (to meet the industrial standards), the cell voltage can be further decreased to ~ 1.57 V without correcting solution resistance (~ 1.48 V with 95% solution resistance correction) at 500 mA/cm^2 (Figure 3.21). The slight increase in cell voltage along with operation time is caused by the slow deactivation of the crystalline NiB hydrogen-evolving cathode (Figure 3.20d).

Figure 3.21 The potential step (P_{step}) method and acquired polarization curve (inset) with amorphous NiFeMoB as anode and crystalline NiB as the cathode. (a), in 1 M KOH at 80°C . (b), in 6 M KOH at room temperature. (c), in 6 M KOH at 80°C . (d),

Chronopotentiometric curve of overall water splitting (~ 1.57 V without correcting solution resistance and ~ 1.48 V with correcting solution resistance) at a constant current density of 0.5 A/cm^2 in 6 M KOH at 80°C .

3.3.6 Tafel slope study at higher current density

To gain a deeper understanding of the outstanding performance of our designed catalyst, Tafel slope is studied at higher current density. It has been known that the Tafel slope is a measure of how efficiently the electrode can respond to an applied potential to produce current. In this respect, a smaller Tafel slope usually indicates a better performance of the catalyst with a smaller overpotential to increase the current density, which means faster kinetics on the reaction. Therefore, to reach a high current density ($>500 \text{ mA/cm}^2$), the smaller Tafel slope, the lower applied potential, However, most of the OER electrocatalysts (Table 3.6) show stable and low Tafel slopes below the current density of 20 mA/cm^2 , which indicates that much more overpotentials are required to drive a higher current density. While in our work, due to the strong adsorption of OH^* intermediates on the surface, the kinetics of OER keeps at the faster step, NiFeMoB shows a Tafel slope of 46 mV/dec even at 100 mA/cm^2 , which ensure the small overpotential at high current density. This phenomenon provides extra evidence for driving a high current density at a small overpotential.

Figure 3.22 Turning point of Tafel slope. The turning point of Tafel slope appearing at much higher current density for amorphous NiFeMoB alloy as compared to the reported catalysts in the literature (Table 3.6) makes NiFeMoB an ideal OER catalyst to reach high current density at low applied potential.

Table 3.6 Comparison of various OER catalysts studied on a glassy carbon electrode.

Catalyst	Tafel slope (mV/dec)	Electrolyte	Turning point ^a (mA/cm ²)	Reference
NiFeMoB	23	1M KOH	100	This work
LiNi _{0.8} Al _{0.2} O ₂	44	0.1 M KOH	0.01	Ref. ²⁹⁴
G-FeCoW	37 (-/+2)	1 M KOH	16	Ref. ¹⁴⁷
NiFe-NS	40	1 M KOH	10	Ref. ²⁹⁵
La _{0.5} Sr _{1.5} Ni _{1-x} Fe _x O _{4±δ}	50	0.1 M KOH	10	Ref. ²⁹⁶
2.5H-PHNCMs	45.7	1 M KOH	10	Ref. ²⁹⁷
LSMO	50	0.1 M KOH	1	Ref. ²⁹⁸

IrO _x /SrIrO ₃	40	0.5 M H ₂ SO ₄	10	<i>Ref.</i> ²⁹⁹
NiFe-LDH/CNT	35	1 M KOH	15	<i>Ref.</i> ²⁹⁰
Co(OH) ₂	60	1 M KOH	8	<i>Ref.</i> ³⁰⁰

^aThe current density where Tafel slope changes to more than 100 mV/dec.

3.4 Conclusion

In summary, we have successfully developed a room temperature solution synthesis to prepare amorphous molybdenum incorporated nickel-iron boron alloy for efficient and stable water oxidation. The high-valent molybdenum with high electron affinity could effectively reduce electron density near the Fermi level in nickel iron boron alloy and thus optimize its adsorption to the oxygenated OER intermediates. Our findings demonstrate the importance of modulating 3d electronic states in transition-metal based OER catalysts towards optimizing their catalytic performance.

Chapter 4 Conclusion and Future Works

4.1 Conclusion

In-depth understanding of the structure-performance relationship for OER on amorphous alloy catalysts. In the first work, amorphous nickel iron alloy with the Ni : Fe ratio of 3 was successfully synthesized by reduction of nickel and iron ions in solution at room temperature using the sodium borohydride. The corresponding crystalline nickel iron alloy without change of composition and phase degradation was obtained by annealing the as-prepared amorphous nickel iron alloy at 600 °C under nitrogen atmosphere. Both of the well-defined amorphous and crystalline catalysts were elected as the typical structures to investigate the mechanism on amorphous alloy for OER outperforming than the crystalline counterpart. Based on the HAADF-STEM, SAED and EXAFS, the amorphous nickel iron alloy demonstrated the unique structure of long-range disordering and short-range ordering while the crystalline nickel iron alloy displayed typical features of metal with the clear and strict lattice. The amorphous catalyst exhibited far higher OER performance under small anodic overpotential than the crystalline alloy. Based on the cyclic voltammetry and electrochemical impedance spectroscopy studies, and further evidence from ex situ isotope (^{18}O) labeling experiments and in situ EXAFS analysis, it revealed that amorphous nickel iron alloy catalyst could be electrochemically activated to expose active sites in the bulk by applying a positive anodic potential due

to the short-range ordering of the amorphous structure, which greatly increased the number of active sites and thus significantly improved the water oxidation activity. Apart from the investigation of mechanism, the amorphous nickel iron alloy demonstrated an extremely high activity toward oxygen evolution reaction with a low overpotential of 260 mV at 10 mA/cm² on glassy carbon electrode in 1 M KOH. By in situ depositing the amorphous nickel iron alloy onto the nickel foam, the amorphous alloy exhibited long-term stability above 200 h at a current density of 40 mA/cm² and showed ignorable dissolution after 20 h water oxidation at 500 mA/cm² in 80 °C alkalines of 1 M KOH. This work successfully figures out the mechanism of enhancing OER performance of amorphous catalyst compared to the crystalline counterpart, which offers the fundamental guidance to design and develop amorphous electrocatalyst for oxygen evolution reaction in the future.

In-depth understanding of the electronic-performance relationship for OER on amorphous alloy catalysts. In the second work, based on the understanding of the mechanism of OER on amorphous structure, we acquired the homogeneous amorphous multimetal alloy with fine-regulated composition against directional tuning the binding energy of oxy intermediates. Based on the characterization methods of HAADF, SAED, EXAFS, trace Mo and Mn-doped amorphous nickel iron alloys were obtained in success by demonstrating the unique long-range disordering but short-range ordering structure. In the analysis of XPS, XNES, Valence band, electrochemical simulation, and using methanol as a probing molecule to determine the binding energy of OH on the catalyst surface. It revealed that the optimal binding

strength to OH was achieved by trace doped Mo into amorphous nickel iron alloy (amorphous NiFeMoB), resulting in the best activity at the top of the volcanic plot. Finally, the developed amorphous NiFeMoB offered an exceeding low overpotential of 220 mV at 10 mA/cm² on glassy carbon electrode ranking as the best water oxidation electrocatalyst in recent years. Besides, by casting the amorphous NiFeMo alloy onto nickel foam, the OER only required 220 mV to reach a current density of 500 mA/cm². To test the practical application, we assembled an alkaline water electrolysis cell with amorphous NiFeMoB as anode and crystalline NiB as the cathode. The cell only requires an external voltage of ~ 1.7 V to reach a current density of 500 mA/cm² without correcting solution resistance (~1.60 V with 95% solution resistance correction) in 1 M KOH at room temperature, operating stably over 40 h. Further increasing electrolyte concentration to 6 M KOH and operating temperature to 80 °C to meet the industrial standards, the cell voltage can be further decreased to ~ 1.48 V (with 95% solution resistance correction) at 500 mA/cm² exhibiting extensive potential for industrial application. In a conclusion, this work succeeded developing the homogeneous amorphous NiFeMo alloy as electrocatalyst demonstrating the excellent performance for water oxidation. And the work provided an effective strategy to tune the electronic structure of amorphous alloy by incorporation of the third element.

In a conclusion, in this thesis, we successfully established the structure-performance relationships for OER on amorphous alloy catalysts by revealing that the amorphous nickel iron alloy catalyst could be electrochemically activated to expose

active sites in the bulk under an anodic potential due to the short-range ordering structure. And we further gain deep comprehension of the electronic-performance relationship for OER on amorphous alloy catalysts by tuning the electronic structure for the optimal binding energy of the intermediates.

4.2 Future Work

To gain an in-depth understanding of the substrate-durability relationship for OER on amorphous alloy catalysts. Although in the second work, a highly stable amorphous alloy for OER was obtained by in situ synthesizing the amorphous alloy on the nickel foam substrate. Few studies were put into the origin of the durability-substrate relationship in order to achieve amorphous electrocatalysts with both high catalytic performance and stability for application in a large scale. Among the reported substrates, generally, carbon-based materials including carbon powder, graphene and CNT offered a high conductivity and BET-surface area as substrates for highly efficient oxygen evolution. Besides, the more common substrates for OER electrocatalysts including Ti foil, FTO, ITO presented higher physical and chemical stability than the carbon-based substrates but offer small surface area. Apart from that, transition metal carbides nanoparticles including TiC, TaC, were allowed for loading electrocatalysts by offering both high conductivity and stability. Finally, metal foam including nickel foam, iron foam, gold foam, copper foam could be more suitable options affording high surface area and conductivity. Aside from the properties of substrates, the interactions between electrocatalysts and substrates showed an important effect on both the physical and chemical stability. It should be pointed out that a stronger interaction could be achieved by in situ fabricating the electrocatalysts on the substrates. In light of these, our future work would concentrate on both the physical and chemical stability of OER for amorphous alloy on different substrates by both in situ and ex situ preparations.

To gain an in-depth understanding of the structure and electronic-performance relationship for HER on amorphous alloy catalysts. It has been discovered in the second work that the crystalline NiB showed much excellent activity of hydrogen evolution than the amorphous counterpart in alkaline. It could be inferred that the hydrogen evolution reaction for amorphous alloy observed a different mechanism on structure compared with the oxygen evolution reaction. On the other hand, the different oxidized degrees of surface for amorphous and crystalline could lead to different numbers of active sites for HER, where metal rather than metal oxide was regarded as an active site reported by many works. Finally, the ratio of boron demonstrated a significant effect on the electronic structure of metal which could cause unequal binding energy to the intermediates of HER. In this work, the method of obtaining the crystalline counterpart by annealing could lead to the change of the ratio of B in the alloy. Therefore, our further work should be put into the structure and electronic-performance relationship for HER on amorphous alloy catalysts by studying the structure, surface oxidizing, boron ratio difference.

To conduct extensive studies on amorphous alloy catalysts. On the basis of the two works and another merit of amorphous alloy that it is benefited to develop the amorphous surface with identical active sites toward a purposed selected catalytic activity for the reaction with multi byproducts, while there are always several kinds of sites on different crystalline planes resulting a lot of unwanted products. Amorphous alloy could be promising in electrochemical nitrogen reduction reaction and carbon

dioxide reduction reaction with more than one product. By directional regulation of the active sites on the amorphous surface, a selective single product could be achieved.

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