Study on electrochemical water splitting : designing efficient oxygen evolution reaction catalysts and Exploring Scientific Issues in activity evaluation of hydrogen evolution reaction

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**NANYANG
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SINGAPORE

Study on Electrochemical Water Splitting: Designing
Efficient Oxygen Evolution Reaction Catalysts and
Exploring Scientific Issues in Activity Evaluation of
Hydrogen Evolution Reaction

Chen Rong

SCHOOL OF CHEMICAL AND BIOMEDICAL ENGINEERING

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Abstract

Developing sustainable and environmental friendly energy and energy storage devices is highly desirable, owing to the increasing demand of energy, limiting storage of fossil energy and rising concerns of environment. Hydrogen is the clean energy carrier with highest energy density and the only product of the conversion is water. Hydrogen produced from electrochemical water splitting has been under intense investigation for several decades. Water splitting involves two half reactions: hydrogen evolution reaction ($\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$) and oxygen evolution reaction ($4\text{OH}^- \rightarrow \text{H}_2\text{O} + 4\text{e}^- + \text{O}_2$). OER is kinetically sluggish and developing highly efficient OER electrocatalysts is essential for sustainable energy.

Three-dimensional NiCo_2O_4 core-shell nanowires made up of NiCo_2O_4 nanowire core and NiCo_2O_4 nanoflake shell have been fabricated by a simple two-step wet chemical method on flexible conductive carbon cloth substrate for oxygen evolution reaction. The combination of high surface area, enhanced mass and charge transport as well as three-dimensional conducting pathway enables superior oxygen evolution reaction. Notably, the NiCo_2O_4 core-shell nanowire electrode exhibits large anodic current and low onset overpotential for OER with an overpotential of ~ 320 mV at a current density of 10 mA/cm^2 . Furthermore, the NiCo_2O_4 core-shell nanowire electrode possesses excellent electrocatalytic stability with long hour electrolysis showing no visible degradation, which is highly desirable for a promising OER electrocatalyst.

In spite of the three-dimensional structure and high surface area of the NiCo_2O_4 core-shell nanowire electrode, more than 300 mV overpotential is still required to drive a current density of 10 mA/cm^2 . Furthermore, we engaged in designing efficient OER electrocatalysts with higher intrinsic activity. We further prepared the stable colloidal NiFe-LDH nanosheets at room temperature with the facile and scalable co-precipitation method. To overcome the poor conductivity

of LDH and weak connection between LDH and conductive support in practical OER applications, we scrolled NiFe-LDH nanosheets into well-aligned multi-walled carbon nanotube (MWCNT) sheets to form binder-free hybrid microfiber electrodes which showed excellent OER activity, reaching 180 mA/cm^2 at a small overpotential of 255 mV with outstanding durability.

For the water electrolyzer to be commercially viable, the other half reaction of water splitting, the hydrogen evolution reaction (HER) is under intense investigation as well, in order to developing catalysts with earth abundant elements and similar activity to Pt. For this reason, sustainable hydrogen generation from water electrolysis has been extensively studied. Unfortunately, in the past studies, much attention has been paid only to the catalyst electrode while neglecting the proper selection of the counter electrode during the measurement of the electrocatalytic activity. We show that the use of widely applied Pt counter electrode without an ion exchange membrane during the HER measurement can cause significant false evaluation on the electrocatalytic activity of non-precious metal catalysts due to the chemical and electrochemical dissolution of platinum from platinum counter electrode and re-deposition of platinum on the hydrogen catalytic electrode.

Overall, we have successfully designed efficient OER electrocatalysts and have addressed the issue easily ignored during evaluation of HER electrocatalysts.

Table of Contents

Acknowledgement.....	I
Abstract	II
Table of Contents.....	IV
List of Figures	VI
List of Tables	XV
Chapter 1 Introduction.....	16
1.1 Perspective of electrochemical water splitting	16
1.2 Water electrolyzers	17
1.3 Oxygen/hydrogen evolution reaction (OER/HER).....	19
1.4 Strategies to improve the performance of OER electrocatalysts	20
1.5 Insight into the OER mechanism.....	20
1.6 Current state of catalysts development for OER	24
1.6.1 Transition-metal oxides	24
1.6.2 Layered double hydroxide (LDH)	28
1.6.3 Non-oxide transitional metal compounds.....	30
1.6.4 Metal-free catalysts.....	30
1.7 Measurement techniques for the study of electrocatalysts	31
1.7.1 Impurity	31
1.7.2 Surface area	33
1.7.3 Uncompensated resistance of the cell.....	37
1.8 Motivation and objective	40
1.9 Organization of the proposal	42
Chapter 2 A Flexible High-Performance Oxygen Evolution Electrode with Three-Dimensional NiCo ₂ O ₄ Core-Shell Nanowires.....	43
2.1 Introduction	43
2.2 Experimental Section.....	44
2.3 Results and discussion.....	50
2.4 Conclusion.....	62
Chapter 3 Achieving Stable and Efficient Water Oxidation by Incorporating NiFe Layered Double Hydroxide Nanosheets into Aligned Carbon Nanotubes	63
3.1 Introduction	63
3.2 Experimental Section.....	64
3.3 Results and discussion.....	67
3.4 Conclusion.....	79
Chapter 4 On the Use of Platinum as the Counter Electrode to Study the Activity of Nonprecious Metal Catalysts for Hydrogen Evolution Reaction?	81
4.1 Introduction	81
4.2 Experimental section	83
4.3 Results and discussion.....	88
4.4 Conclusion.....	106
Chapter 5 Conclusions and outlook.....	108
References	111

Publication list..... 124

List of Figures

Figure 1-1. Schematic of the application of hydrogen.[1] (Copyright © 2017, American Association for the Advancement of Science)

Figure 1-2. Schematic of AEM and PEM electrolyzers

Figure 1-3. Schematic of water electrolysis coupled with photovoltaic device.

Figure 1-4. Schematic illustrations of the transition state theory. $\Delta G^\ddagger$ is the reaction barriers without a catalyst, $\Delta G_A^\ddagger$ and $\Delta G_B^\ddagger$ is the reaction barriers with a catalyst. The presence of stable intermediate states on a catalyst surface effectively reduced the activation barriers for the reaction.[2] (Copyright © 2015, Royal Society of Chemistry)

Figure 1-5. Proposed OER mechanism on bare catalyst surface.[2] (Copyright © 2015, Royal Society of Chemistry)

Figure 1-6. Schematic diagram of Sabatier principle for OER.

Figure 1-7. Sketch of a basic ABO_3 perovskite oxide structure[3]. (Copyright © 2014, Royal Society of Chemistry)

Figure 1-8. The relation between the OER catalytic activity and the occupancy of the e_g -symmetry electron of the transition metal (B in ABO_3).[4] (Copyright © 2011, American Association for the Advancement of Science)

Figure 1-9. (a) Schematic representation of the O p-band for transition metal oxides and (b) Evolution of the iR-corrected potential at 0.5mAcm^{-2} oxide versus the O p-band center relative to E_F (eV).[5] (Copyright © 2013, Rights Managed by Nature Publishing Group)

Figure 1-10. The illustration of obtaining the double layer capacitance based on the double layer charging current.

Figure 1-11. Double-layer capacitance of the uncharged Ni-Fe (oxy)hydroxide films deposited on Au (blue) and FTO (red) electrodes. Obtaining via cyclic

voltammetry (CV, squares) and AC impedance spectroscopy (ZAC, stars). Note: the data points at zero loading corresponding to the values of double-layer capacitance of the substrates (Au/FTO).[6] (Copyright © 2015, American Chemical Society)

Figure 1-12. Integrated voltammetric charge q^* as a function of scan rate v for RuO_2 in 1M KOH.[7] (Copyright © 1990 Published by Elsevier Ltd.)

Figure 1-13. Model of the equivalent circuit of the OER electrodes.[8] (Copyright © 2013, Royal Society of Chemistry)

Figure 1-14. Fitting values of the double layer capacitance of hydrous oxide films as a function of applied potential.[8] (Copyright © 2013, Royal Society of Chemistry)

Figure 1-15. Simplified network of electrochemical test cell

Figure 2-1. FESEM images of NiCo_2O_4 nanowire arrays prepared after different durations of hydrothermal reaction: (a) 1.5 h, (b) 3h, (c) 5h, and (d) polarization curves of NiCo_2O_4 nanowire arrays prepared after different durations of hydrothermal reaction.

Figure 2-2. FESEM images of NiCo_2O_4 core-shell nanowire arrays with nanoflake shell electrochemically deposited for: (a) 100 s (b) 400 s (c) 700 s (d) 1000 s at a current density of 2.5 mA/cm^2 .

Figure 2-3. Cyclic voltammograms in the double layer region at scan rate of 16, 14, 12, 10, 8, 6, 4 mV/s (along the arrow direction) of NiCo_2O_4 core-shell nanowire arrays with different shell electrodeposition time: (a) 100 s, (b) 400 s, and (c) 700 s. (d) Current density as a function of scan rate for NiCo_2O_4 nanowire arrays and NiCo_2O_4 core-shell nanowire arrays with different shell electrodeposition times. (e) Cyclic voltammogram at scan rate of 1 mV/s for NiCo_2O_4 nanowire arrays and NiCo_2O_4 core-shell nanowire arrays with different shell electrodeposition times. (f) Polarization curves of NiCo_2O_4 nanowire arrays

and NiCo₂O₄ core-shell nanowire arrays with different shell electrodeposition times.

Figure 2-4. (a) FESEM image (b) Enlarged view (c) Polarization curves of NiCo₂O₄ core-shell nanowire array with electrodeposition time of 1300s.

Figure 2-5. (a) FESEM image of NiCo₂O₄ nanowire array on carbon cloth. (b) Enlarged view of NiCo₂O₄ nanowires. (c) FESEM image of NiCo₂O₄ core-shell nanowire array on carbon cloth. (d) Enlarged view of NiCo₂O₄ core-shell nanowires.

Figure 2-6. (a) & (b) TEM and HRTEM images of NiCo₂O₄ nanowires. (c) & (d) TEM and HRTEM images of NiCo₂O₄ core-shell nanowires. Insets show enlarged TEM images.

Figure 2-7. (a) XRD patterns of NiCo₂O₄ nanowires and nanoflakes. (b-d) XPS spectra of (b) Ni 2p, (c) Co 2p, and (d) O 1s of NiCo₂O₄ core-shell nanowires.

Figure 2-8. (a) Polarization curves of carbon cloth, Ir/C, NiCo₂O₄ nanowire film and NiCo₂O₄ core-shell nanowire film. Inset: photograph of a flexible NiCo₂O₄ core-shell nanowire electrode. (b) Tafel plots, and (c) Cyclic voltammogram curves at scan rate of 1 mV/s of NiCo₂O₄ nanowire film and NiCo₂O₄ core-shell nanowire film. (d) & (e) Cyclic voltammograms in the double layer region at scan rate of 16, 14, 12, 10, 8, 6, 4 mV/s (along the arrow direction) of (d) NiCo₂O₄ nanowire film and (e) NiCo₂O₄ core-shell nanowire film. (f) Current density as a function of scan rate for NiCo₂O₄ nanowire film and NiCo₂O₄ core-shell nanowire film.

Figure 2-9. (a) Polarization curves (b) Tafel plot of Ir/C.

Figure 2-10. Digital photograph of NiCo₂O₄ core-shell nanowire electrode operated at a current density of 120 mA/cm², showing evolution of O₂ bubbles.

Figure 2-11. (a) Stability tests of NiCo₂O₄ core-shell nanowire film at fixed overpotentials of 320 mV, 340 mV, and 350 mV over 30 h. (b) Polarization

curves before and after 30 h of stability tests. (c) Current density as a function of scan rate before and after 30 h of stability tests. (d) Experimental oxygen volume versus theoretical oxygen volume based on the amount of consumed charge during the course of electrolysis.

Figure 2-12. (a) & (b) FESEM images of NiCo₂O₄ core-shell nanowire film after 30 h of electrolysis. (c-f) XPS spectra of NiCo₂O₄ core-shell nanowires before and after 30 h of electrolysis: (c) Ni 2p, (d) Co 2p, and (e) O 1s. (f) XRD patterns of NiCo₂O₄ core-shell nanowire film before and after 30 h of electrolysis.

Figure 2-13. (a) Plot of electrolysis at constant potentials with currents around 27 mA, 48 mA and 72 mA (sample area 0.5 cm²). (b) Comparison of evolved oxygen volume versus theoretical oxygen volume based on the amount of consumed charges during the course of electrolysis.

Figure 3-1. FESEM images of NiFe-LDH nanosheets with different Fe contents. (a) 10 mol % Fe. (b) 20 mol % Fe. (c) 30 mol % Fe. (d) 40 mol % Fe. Insets: corresponding photographs of NiFe-LDH suspensions.

Figure 3-2. Polarization curves of NiFe-LDH with different Fe contents tested on RDE electrode. The percentage number represents mol% of Fe in NiFe-LDH.

Figure 3-3. (a) FESEM image of as-prepared NiFe-LDH nanosheets. Inset shows a photograph of well-dispersed NiFe-LDH suspension with clear Tyndall effect. (b) TEM and HRTEM images (inset) of NiFe-LDH nanosheets. (c) XRD pattern of NiFe-LDH nanosheets. (d) Size distribution of NiFe-LDH nanosheets obtained from dynamic light scattering (DLS) measurement. (e & f) XPS spectra of Ni 2p and Fe 2p, respectively.

Figure 3-4. FESEM images of NiFe-LDH nanosheets prepared under different conditions: (a) without sonication, (b) sonication at RT, (c) hydrothermal at 100°C, and (d) hydrothermal at 120°C. (e) XRD patterns, and (f) polarization curves of NiFe-LDH nanosheets prepared at different temperatures (performances are tested on RDE electrode).

Figure 3-5. Photographs of NiFe-LDH nanoparticle suspension before and after sonication.

Figure 3-6 (a) Polarization curves, (b) Tafel plots for NiFe-LDH and IrO₂ nanoparticles tested on RDE electrode.

Figure 3-7. Mass activity as a function of the loading amount of NiFe-LDH nanosheets on glassy carbon electrode.

Figure 3-8. (a) Schematic illustration showing the steps of fixing NiFe-LDH nanosheets into MWCNT bundles. (b) FESEM image of a well-aligned MWCNT sheet. (c) Microscope image, (d) FESEM image, and (e) enlarged FESEM image of a NiFe-LDH@MWCNT microfiber electrode.

Figure 3-9. Polarization curves of NiFe-LDH@MWCNT microfiber electrode with varying NiFe-LDH composition from 50% to 95%. Inset shows the surface morphology of 95% NiFe-LDH@MWCNT microfiber electrode. Deteriorating catalytic performance of 95% NiFe-LDH@MWCNT microfiber electrode was due to poor conductivity of too thick NiFe LDH layer. The percentage number represents wt % of NiFe-LDH in the microfiber electrode.

Figure 3-10. (a) Polarization curves of microfiber electrode with 90 wt% of NiFe-LDH nanosheets and bare CNT electrode. (b) Tafel slope of microfiber electrode with 90 wt% of NiFe-LDH nanosheets.

Figure 3-11. Polarization curves of 90 wt % NiFe-LDH@MWCNT microfiber electrode before and after iR correction.

Figure 3-12. AC impedance spectrum of electrode made of several parallel microfibers at an overpotential of 195 mV. Inset shows a photograph of the electrode.

Figure 3-13. (a) Stability test of NiFe-LDH@MWCNT bundle microfiber electrode at fixed overpotential of 240 mV over 24 h. Inset compares current density retention (%) of NiFe-LDH nanosheets on glassy carbon electrode at

fixed overpotential of 265 mV (pink) with NiFe-LDH@MWCNT microfiber electrode over 1 h. (b) Polarization curves before and after 24 h of stability test. (c) Faradaic efficiency measured at constant applied potential over 26 h. (d) Surface morphology of NiFe-LDH@MWCNT bundle microfiber electrode after 24 h of continuous electrolysis.

Figure 3-14. XPS spectra of NiFe-LDH before and after 24 h of electrolysis: (a) wide-scan spectra, (b) high resolution Ni 2P spectra, (c) high resolution Fe 2P spectra, and (d) high resolution O 1s spectra.

Figure 4-1. Published work on hydrogen evolution reaction (HER) in the year of 2015 and 2016. Blue column: number of studies adopting Pt as the counter electrode[9-90] and red column: total number of studies on HER.

Figure 4-2. Schematic illustration showing Pt dissolution and re-deposition during the HER experiment if Pt is applied as the counter electrode.

Figure 4-3. HER polarization curves of carbon cloth in 0.5 M H₂SO₄ with (a) graphite rod and (b) Pt plate as the counter electrode, respectively. CE in (a) and (b) stands for counter electrode. FESEM images of carbon cloth after 600 CV cycles with (c) graphite rod and (d) Pt plate counter electrode.

Figure 4-4. XPS spectra of carbon cloth electrode after 600 CV cycles using Pt plate as the counter electrode. The binding energies of Pt 4f_{7/2} and Pt 4f_{5/2} are 71.6 eV and 74.9 eV, respectively, which are ascribed to metallic Pt.

Figure 4-5. Steady state potential of Pt plate counter electrode in 0.5 M H₂SO₄ during HER together with the corresponding LSV curve of carbon cloth. Steady state measurement of potential of Pt counter electrode was made under potentiostatic condition and recorded in the cathodic direction. E_{WE} and E_{CE} stand for potential on working electrode and counter electrode, respectively.

Figure 4-6. Schematic CV curves of working electrode and counter electrode during HER. Point 2 stands for the maximum potential while point 3 possesses

the minimum potential on counter electrode. “W” stands for working electrode while “C” stands for counter electrode. The current in the circuit has the following relationship: $W3 = - C3$, $W2 = - C2$.

Figure 4-7. (a), (c) and (e) CV curves for carbon cloth electrode, MoS₂ nanoparticles on glassy carbon electrode and Pt plate with varying electrode areas, respectively. Inset of (e) shows the CV curve of Pt plate (dark blue) together with the synchronized potential on Pt counter electrode (orange). (b), (d) and (f) The corresponding potential on the Pt counter electrode. Scan rate: 100 mV/s. E_{WE} and E_{CE} stand for potential on working and counter electrode, respectively.

Figure 4-8. (a), (c) and (e) CV curves with fixed upper potential limit at 0 V vs. Ag/AgCl and different lower potential limit for carbon cloth (2 cm²), MoS₂ (0.196 cm²) and Pt plate (2 cm²), respectively. (b), (d) and (f) The corresponding potential on the Pt counter electrode. Scan rate: 100 mV/s.

Figure 4-9 (a) CV curve of Pt plate (2 cm²) obtained at a scan rate of 100 mV/s in 0.5 M H₂SO₄ without degassing. (b) CV curve of the same Pt plate obtained in degassed 0.5 M H₂SO₄.

Figure 4-10. CV curves of Pt plate (2 cm²) with different potential ranges in 0.5 M H₂SO₄ at a scan rate of 100 mV/s. Note: Different scan ranges will result in different current values of the Pt plate. As a result, it is difficult to determine the potential on Pt counter electrode based on the current density of Pt plate. Nevertheless, we could figure out the measured potential ranges on the Pt counter electrode during catalysis by referring to the CV curves of Pt plate with corresponding potential ranges.

Figure 4-11. Electric double layer at the electrode/electrolyte interface.

Figure 4-12. (a) CV curves of carbon cloth (2 cm²) with fixed lower potential limit at -0.5 V vs. Ag/AgCl and increased upper potential limit varying from -0.2 to 0.2 V vs. Ag/AgCl. (b) The corresponding potential on the Pt counter electrode. Scan rate: 100 mV/s.

Figure 4-13. (a), (c) and (e) CV curves with scanning rate of 100 mV/s and 10 mV/s for carbon cloth (2 cm²), MoS₂ (0.196 cm²) and Pt plate (2 cm²), respectively. Inset of (e) shows the potential on Pt counter electrode vs. potential cycling on the working electrode. (b), (d) and (f) The corresponding potential on the Pt counter electrode.

Figure 4-14. CV curves of (a) carbon cloth (2 cm²) (b) MoS₂ on glassy carbon electrode (0.196 cm²) and (c) Pt plate (2 cm²) obtained at scan rates of 100 mV/s and 10 mV/s.

Figure 4-15. (a) Effect of upper potential limit (E_{UPL}) during potential cycling. CV ranges are from -0.2 V vs. Ag/AgCl to different E_{UPL} of 0.25, 0.45, 0.65, 0.8, 0.97, 1.3, 1.6 V vs. Ag/AgCl. CV curves are obtained for 100 cycles at 100 mV/s in 0.5 M H₂SO₄. (b) Coverage of Pt-O at different E_{UPL} .

Figure 4-16. (a) CV curve of Pt plate obtained at a scan rate of 100 mV/s in 0.5 M H₂SO₄. (b) Amount of dissolved Pt vs. E_{LPL} after 50 cycles of potential cycling at scan rate of 100 mV/s in 0.5 M H₂SO₄. Potential range I: 0.4 to 1.6 V; II: 0.6 to 1.6 V; III: 0.8 to 1.6 V; IV: 1 to 1.6 V; and V: 1.2 to 1.6 V. (c) The corresponding LSV curves of the carbon cloth electrode. Scan rate: 10 mV/s. (d-h) FESEM images of the carbon cloth electrode after potential cycling.

Figure 4-17. (a) HER LSV curves of carbon cloth electrode obtained by applying graphite rod as the counter electrode. Red: in fresh 0.5 M H₂SO₄; black: in 0.5 M H₂SO₄ with immersion of Pt plate for 5 minutes. (b) Low coordinated Pt atoms on Pt (111), which can be quickly dissolved if immersed in H₂SO₄. Red and yellow represent the corner and edge sites, respectively.

Figure 4-18. (a) CV curve of Pt plate obtained at 100 mV/s in 1 M KOH. (b) CV curve of the same Pt plate obtained in 0.5 M H₂SO₄ is included for comparison. (c) Steady state potential of Pt plate as the counter electrode in 1 M KOH within the potential range of HER. Steady state measurement of potential of Pt counter electrode was made under potentiostatic condition and recorded in the cathodic

direction.

Figure 4-19. LSV curves of the carbon cloth electrode after 1st and 600th CV cycles in 1 M KOH with graphite rod and Pt as the counter electrode, respectively. Scan rate: 100 mV/s.

Figure 4-20. FESEM images of the carbon cloth electrode after 600 CV cycles if (a) graphite rod was used as the counter electrode and (b) Pt plate was used as the counter in 1 M KOH. Scan range: -0.8 ~ -1.9 V vs. Ag/AgCl. Scan rate: 100 mV/s.

List of Tables

Table 1-1. Comparison of AEM and PEM electrolyzers

Table 2-1. Comparison of OER performances of NiCo₂O₄ core-shell nanowire arrays with other reported NiCo₂O₄ catalysts.

Table 3-1. Comparison of OER performance of NiFe-LDH in 1 M alkaline electrolyte.

Chapter 1 Introduction

1.1 Perspective of electrochemical water splitting

With the increasing demand of energy, limiting storage of fossil energy and rising concerns of environment, developing sustainable and environmental friendly energy and energy storage devices is highly desirable. Hydrogen can be used as the energy carrier in fuel cells and it is an important chemical raw material in industry for ammonia production and hydrogenation (Figure 1-1).[1] However, more than 90% of hydrogen is produced from fossil fuels, such as natural gas or coal through steam reforming, which produces large amount of CO₂ as a byproduct. CO₂ release should be controlled as the increasing greenhouse effect. Moreover, the purity of the hydrogen produced from the steam reforming is unsatisfying, especially for the field which demands highly pure hydrogen. For instance, the containing CO in the as-prepared hydrogen will poison electrocatalysts of Pt in the proton exchange membrane (PEM) fuel cells. Therefore, the traditional approach for hydrogen production is encountering challenge now. Alternative strategy producing highly pure hydrogen without any pollution release is in great request. Electrochemical conversion of water to hydrogen is a potential solution to solve the energy demand and the environmental concerns since water is abundant on earth. The challenge is to develop the electrocatalysts with high efficiency and stability for electrochemical water splitting, enabling the widespread penetration of clean energy.

Figure 1-1. Schematic of the application of hydrogen.[1] (Copyright © 2017, American Association for the Advancement of Science)

1.2 Water electrolyzers

Water electrolyzers are the integrated devices to split water electrochemically into hydrogen and oxygen. They contain electrocatalysts acting as anode and cathode materials, the membrane and the electrolyte. There are mainly two types of water electrolyzers: the alkaline-exchange membrane (AEM) electrolyzer and proton exchange membrane (PEM) electrolyzer which is also known as polymer electrolyte membrane (PEM) electrolyzer (Figure 1-2). Both electrolyzers have advantages and disadvantages and the detailed comparison are listed in Table 1-1.[91] The AEM electrolyzer is filled with concentrated alkaline while PEM electrolyzer is equipped with the solid polymer electrolyte (Nafion membrane is commonly applied). In PEM, the Nafion membrane is responsible for protons conduction, gas separation and cathode and anode materials insulation. Due to the highly acidic environment next to the membrane, precious metal catalysts (e.g. Pt for hydrogen evolution and IrO_2 for oxygen evolution) are required for the catalysis. The acidic environment enables the large operating current density ($1-3\text{ A/cm}^2$) while enhances the investment costs of PEM electrolyzer. Due to the precious metal catalysts as well as the

titanium structure materials, PEM needs investment costs of about 1900–2300 €/kW. Besides, the insufficient stability of IrO₂ will lead to the short life time of PEM. On the other hand, concentrated sodium hydroxide or potassium hydroxide are applied as an electrolyte and low-priced nickel/stainless-steel mesh is used as electrodes. Currently, these electrodes can be operated at current densities of 100–500 mA/cm² and are stable in hot alkaline (60–80°C). As a result, AEM needs lower investment costs (only 1000–1200 €/kW) compared to PEM. Till now, the high expense of PEM electrolyzer is the major drawback and limits its large-scale application, though the PEM electrolyzer has more merits than AEM electrolyzer. The alkaline electrolyzer is a mature technology and has been used for hydrogen production over a century in industry. The room for improvement of PEM is larger than AEM electrolyzer, while study to enhance the AEM electrolyzer is more related to benefiting the existing industry. To further reduce the energy input of the alkaline electrolyzer, more efficient electrocatalysts with high activity and stability are required. We have made an effort to improve the efficiency of electrocatalysts in alkaline media in the thesis.

Figure 1-2. Schematic of AEM and PEM electrolyzers

Table 1-1. Comparison of AEM and PEM electrolyzers

	AEM		PEM	
	Advantage	Disadvantage	Advantage	Disadvantage
Investment costs	1000–1200 €/kW			1900–2300 €/kW
Current density		below 1 A/cm ²	1–3 A/cm ²	
Lifetime	Longer			Shorter
Membrane		Poor stability and ionic conductivity	Good stability and ionic conductivity	
Differential pressure		Sensitive to differential pressure	Tolerate >100 bar differential pressure	

To reduce the energy input, the water electrolyzers could be further combined with photovoltaic device (Figure 1-3). By coupling a semiconducting light absorber with suitable electrocatalysts for hydrogen and oxygen evolution, it becomes possible to mimic photosynthesis by using solid, inorganic materials to convert sunlight into hydrogen and oxygen.

Figure 1-3. Schematic of water electrolysis coupled with photovoltaic device.

1.3 Oxygen/hydrogen evolution reaction (OER/HER)

Water splitting involves two half reactions: hydrogen evolution reaction ($\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$) and oxygen evolution reaction ($4\text{OH}^- \rightarrow \text{H}_2\text{O} + 4\text{e}^- + \text{O}_2$). Electrocatalysts for HER and OER are designed to increase the efficiency and selectivity during water electrolysis. OER is the bottleneck of the water splitting since it requires four electrons transfer and usually needs 250–450 mV onset

overpotential to drive the reaction. Hence, we have done work aiming for designing efficient OER catalysts design in this thesis. HER is also widely studied since the large-scale application of the Pt, which is the most efficient HER catalyst, is restricted by the skyrocketing prices. Thus, many researchers have engaged in developing earth abundant HER catalysts with comparable activity to Pt. Unfortunately, a large number of studies have neglected the proper selection of counter electrode during HER catalysts study and the forged performances are reported. We have addressed this problem in the later chapter and revealed that Pt dissolution and re-deposition is the origin of the misleading performances.

1.4 Strategies to improve the performance of OER electrocatalysts

The efficient OER electrocatalysts play the key role in the water electrolyzer because they increase the efficiency of the reaction. For the last decades, researchers have engaged in developing the efficient electrocatalysts with low overpotential, large current density and satisfied stability. Generally, there are two strategies to improve the activity of electrocatalysts. One is to increase the number of active sites of the catalyst and the other is to enhance the intrinsic activity of the active site. Raising the loading amount of electrocatalysts (nanoparticles) may enable more exposed surface to electrolyte (number of active sites). Nevertheless, the large loading amount may sacrifice the conductivity and reduce the overall performance. Preparing catalysts with large surface area, e.g. the three-dimensional core shell structure is the efficient tactics to solve the contradiction. Besides, to enhance the intrinsic activity of the active site is more important. Enabling the catalysts with less crystalline structure and/or more defects is among the numerous approaches concerning raising the intrinsic activity. Moreover, the reaction mechanism is introduced in the next section to direct the design the electrocatalysts with improved intrinsic activity.

1.5 Insight into the OER mechanism

In order to design efficient OER catalysts, it is essential to understand the

mechanism during OER catalysis. Marcus theory indicates that transfer of two electrons simultaneously requires four times larger activation energy than that of a single electron transfer.[92] Thus, electrons transfer will proceed one by one by forming the stable intermediate states. Catalysts could provide the reaction path with intermediates on the surface. Thus, the activation barriers for the reaction is effectively reduced on the catalyst surface (Figure 1-4).[2]

Figure 1-4. Schematic illustrations of the transition state theory. $\Delta G^\ddagger$ is the reaction barriers without a catalyst, $\Delta G_A^\ddagger$ and $\Delta G_B^\ddagger$ is the reaction barriers with a catalyst. The presence of stable intermediate states on a catalyst surface effectively reduced the activation barriers for the reaction.[2] (Copyright © 2015, Royal Society of Chemistry)

The mechanism of OER is complex due to the four-electron transfer process ($4\text{OH}^- \rightarrow \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^-$) and a series of intermediates (M-OH, M-O, M-OOH) on the catalyst surface. The most prevalent mechanism as demonstrated in Figure 1-5 is proposed based on the bare catalyst surface (the same as the metal surface).

Figure 1-5. Proposed OER mechanism on bare catalyst surface.[2] (Copyright © 2015, Royal Society of Chemistry)

The current understanding of the OER mechanism is based on the Sabatier principle, which involves the surface metal cations (M) as the active sites for OER. The principle claims that the activity can be described by M-O bond strength. The optimum catalyst has neither too strong nor too weak M-O binding energy (Figure 1-6). However, based on the thermodynamic point of view, energetic relationships exist between intermediates (the reaction involves more than one intermediates). This is called the scaling relationship. It can be explained by quantum-chemical theory of chemical bonding. For OER, it is found that the scaling relation is between OH and OOH. The energy difference between the OH and OOH intermediates is always 3.2 ± 0.2 eV while the ideal energy difference between the two intermediates should be 2.46 eV. Thus, even the M-O bond strength reaches the optimum value according to the Sabatier principle, the catalysts still have 250-350 mV $((3.2 \pm 0.2 - 2.46 \text{ eV})/2e)$ onset overpotential. The universal scaling relation involving more than one catalytic intermediates (e.g. OER/ORR) was first realized by Koper [92] and later confirmed by a series of different catalyst surfaces [93-96]. Understanding the thermodynamic origin of the underlying OER overpotential is a key step to understand the performance/limitation of catalysts. The electrocatalysts under consideration in this thesis are probably in the scope of scaling relation, according to the onset overpotential.

Figure 1-6. Schematic diagram of Sabatier principle for OER.

Mastering the kinetic of the reaction is crucial to improve the performance of the catalysts. Kinetic study toward the mechanistic pathway of the interfacial reaction is based on establishing the relationship between the driving force (the applied potential) and the rate of the electron transfer reaction (the measured current). Tafel slope provides the insight of reaction mechanism. Before the foundation of the electron transfer kinetics theory, the Tafel equation ($\eta = a + b \log j$, where η is the overpotential, b is the Tafel slope) was deduced experimentally. The theoretical validity was later confirmed by Butler-Volmer equation where the reversal reaction could be ignored. Meanwhile, the physical implications of a and b are revealed based on the Butler-Volmer equation. For example, for anodic polarization, $a = -\frac{2.3RT}{\beta F} \log j_0$, $b = \frac{2.3RT}{\beta F}$ (β is the transfer coefficient). Since the Tafel equation is established by considering that the reverse reaction rate is negligible compared to the forward reaction rate, it is applicable to the region with high polarization (at the low polarization region, the dependence of current on overpotential is usually linear). The Tafel plots deviate from linearity at the region with large current density, mainly due to the extra resistance caused by bubbles on the surface. Moreover, dual Tafel slopes are also observed with higher slopes at large current densities. Few studies have been conducted toward the dual Tafel slope, the extra barriers of electron/mass transport or different mechanism may be involved.[8]

The experimentally measured Tafel slopes could be correlated with the reaction mechanism for OER on metal oxide surface. In Figure 1-5, if step 1 is turnover limiting, a Tafel slope of 120 mV/dec is predicted. When considering step 2 as the turnover limiting, the expected Tafel slope will be 40 mV/dec. While step 3 is turnover limiting, the Tafel slope is expected to be 24 mV/dec (all assuming $\beta = 0.5$). [97]

In addition, measuring the Tafel slope properly is necessary to explore the reaction mechanism. As we know, the measured current may comprise both the double layer charging current and the faradic current. When investigating the kinetics of reaction, we only consider the current arising from the interfacial reaction of interest. Therefore, to measure the Tafel slope, we must ensure that a true steady state has been achieved. Seeing that the charge which can be stored in the double layer is finite, it may decay in an exponential fashion approaching zero. Accordingly, scanning with quite slow scan rate or holding at constant potentials are feasible to study the rate of catalytic reaction.

1.6 Current state of catalysts development for OER

1.6.1 Transition-metal oxides

Transition-metal oxides are the most widely studied materials for OER in alkaline, mainly due to the decent activity as well as stability. The most promising non-noble metal oxides often contain 3d elements (Mn, Fe, Ni and Co). Co_3O_4 with the spinel structure is the typical candidate for OER. [98] The performance of Co_3O_4 deposited on different substrates, [99] with different particle sizes (surface area) [100, 101] or with different crystallinity (crystal or amorphous) [102] were investigated. Performances on different crystal planes have been researched through both theoretical calculations and experiments analyses. [103, 104] The spinels are stable under OER conditions with only the surface participating in the reaction. [105] Researchers further improved the performance of Co_3O_4 by doping with a third element such as Li, Ni, Cu, Zn, etc. [106-108] Doping Co_3O_4 with Ni (NiCo_2O_4) showed enhancement in conductivity as well as the catalytic

performance. Several studies have been carried out to improve the performance of NiCo_2O_4 as the OER electrocatalysts, as introduced in chapter 2.

The spinel structures contain two octahedral and one tetrahedral in one unit with the formulation of AB_2O_4 . Thus, it is desired to figure out the site occupation of the catalyst in spinel structures. The oxygen anions arrange the octahedral and tetrahedral in the lattice and the cations A and B occupy the central site of the octahedral/tetrahedral. For normal spinels, the formulation can be written as $\text{A}^t\text{B}_2^o\text{O}_4$, with A^{2+} occupying the tetrahedral and B^{3+} occupying octahedral site. If the A^{2+} occupies the octahedral site, the formulation should be written as $\text{B}^t(\text{AB})^o\text{O}_4$, leading to the inverse spinel structure. For non-transition metal systems, the cations usually adopt the normal spinel structure, e.g. MgTi_2O_4 . For spinels contain the first-row transition metals, the cation distribution is affected by the partial occupancy of d-orbitals. The excess octahedral stabilization energy (the difference between crystal field stabilization energy in octahedral and tetrahedral) is the indicator to determine the transition metal occupation. For example, the excess octahedral stabilization energy of Fe^{3+} and Fe^{2+} is 0 and 17 kJ/mol, respectively, so Fe^{2+} would rather occupy the octahedral site, giving inverse spinel $(\text{Fe}^{3+})^t(\text{Fe}^{2+}, \text{Fe}^{3+})^o\text{O}_4$. Similarly, the excess octahedral stabilization energy of Ni^{2+} is 86 kJ/mol. It indicates that the Ni^{2+} prefers octahedral site, leading to the inverse spinel structure of NiCo_2O_4 . Nevertheless, we should keep in mind that the above statement is based on the thermodynamic stable state. The site occupation of as synthesized catalysts may be more complicated, owing to the preparation process and the existence of metastable state.

The work in our group has demonstrated that in spinel Co_3O_4 , Co ion in the tetrahedral site is active toward OER while that occupying the octahedral site is relatively inactive.[109] The work may have some indications toward NiCo_2O_4 concerning the active site. However, Ni has different electronic structure from Co and the conclusion may not fit for the NiCo_2O_4 . Further work is needed to reveal the active site/mechanism.

Perovskite oxide is the more complex metal oxide system. The activity and stability of perovskite is identified to be rationalized with the electronic structures.[2] This correlation may provide useful information towards the design of other metal oxides. Thus, it is worthwhile to review the perovskite family as the OER catalysts.

ABO_3 is the basic structure of perovskite, where A is the larger cation, such as an alkaline earth element or a lanthanide, and B is the smaller cation, generally a transition metal surrounded by 6 oxygen atoms forming a BO_6 octahedral (Figure 1-7).[3] In most cases, the A ions are not essential in determining the perovskite electronic properties, while the BO_6 octahedral accounts the catalytic performance.

Figure1-7. Sketch of a basic ABO_3 perovskite oxide structure[3]. (Copyright © 2014, Royal Society of Chemistry)

e_g orbital of surface transition metal ions participate in σ -bonding with a surface-anion adsorbate, its occupancy can greatly influence the binding of oxygen related intermediate species on B-sites and thus the OER activity. Yang et al. have published a design principle for high activity perovskite catalyst based on orbital principles.[4] They have demonstrated a volcano-shaped dependence on the occupancy with the 3d electron (e_g symmetry) of surface transition metal cations in an oxide. The peak OER activity was predicted to be at an e_g occupancy close to unity (Figure 1-8).[4] Based on the theory, $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\sigma}$ (BSCF) with e_g occupancy close 1 shows the most efficient activity.

Figure 1-8. The relation between the OER catalytic activity and the occupancy of the e_g -symmetry electron of the transition metal (B in ABO_3). [4] (Copyright © 2011, American Association for the Advancement of Science)

Two years later, the same group published double perovskites ($\text{Ln}_{0.5}\text{Ba}_{0.5}$) $\text{CoO}_{3-\delta}$ (with $\text{Ln}=\text{Pr}$, Sm , Gd and Ho) which showed comparable activities to BSCF. [5] O p-band center relative to Fermi level is utilized to predict the OER activity, which is easier accessed experimentally. They demonstrated that moving the computed O p-band center closer to the Fermi level could enhance the OER activities (Figure 1-9). [5]

Figure 1-9. (a) Schematic representation of the O p-band for transition metal oxides and (b) Evolution of the iR-corrected potential at 0.5mAcm^{-2} oxide versus the O p-band center relative to E_F (eV). [5] (Copyright © 2013, Rights Managed)

by Nature Publishing Group)

Researchers have also developed methods to rationalize the bulk stability of perovskites. Goldschmidt tolerance factor[110] is one of the effective method, which is written as: $\tau = \frac{r_A + r_O}{\sqrt{2}(r_B + r_O)}$, where r_A , r_O and r_B is the ionic radii for A site, O ion and B site, respectively. When $\tau = 1$, the ideal cubic structure is most stable. When $\tau < 1$, tilted BO_6 octahedra is stable. When $\tau > 1$, hexagonal structure is preferred. In addition, the bulk stability can also be related to the O p-band center. For example, when the O p-band center is closer to the Fermi level, it will be easier to form the oxygen vacancy, resulting in destabilizing the perovskite structure (Figure 1-9b).[111-114]

1.6.2 Layered double hydroxide (LDH)

LDHs are a class of synthetic 2D nanostructured anionic clays, which can be represented by the general formula $[\text{M}_{1-x}^{2+} \text{M}_x^{3+} (\text{OH})_2]^{x+} [\text{A}_{x/n}]^{n-} \cdot z\text{H}_2\text{O}$, where M^{2+} may be Ni^{2+} , Mg^{2+} or Zn^{2+} and M^{3+} may be Al^{3+} , Fe^{3+} or Mn^{3+} . A^{n-} is a non-framework charge compensating inorganic or organic anion, e.g. CO_3^{2-} , NO_3^- , Cl^- , SO_4^{2-} , RCO_2^- , and x is normally between 0.2–0.4.[115-117] LDH has been known for over 150 years since the discovery of the mineral hydrotalcite.[118] The LDH structure has been intensely studied in OER catalysts since the discovery of NiFe-LDHs, which exhibit the most efficient catalytic performance toward OER.

NiFe-LDH OER catalysts have been known for over 30 years. [119-123] However, they been barely studied for OER catalyst until recently, owing to its poor conductivity (a commonly encountered problem with hydroxides). Boettcher and coworkers have confirmed that the conductivity of hydroxides was largely enhanced after oxidized to higher valent state (e.g. $\text{Ni}^{2+} \rightarrow \text{Ni}^{3+}$) by in-situ electrical conductivity measurements.[124] Thus, the conductivity of NiFe-LDH is not the limiting factor when the loading amount is low. However, large loading amount is needed to achieve robust current in industry since the catalytic current

is proportional to the loading amount/electrochemical surface area. Consequently, coupling the NiFe-LDH with highly conductive substrate is the effective strategy to tackle the conductivity versus loading problem.

Dai and coworkers coupled ultrathin NiFe-LDH with CNT to form interconnected electrically conducting networks and showed onset overpotential of 220 mV in 1 M KOH at a loading of 0.25 mg/cm². [125] Yang and co-workers coupled NiFe-LDH with reduced graphene, which showed the onset potential of 195mV. [126] Combining the ultrathin NiFe-LDH and conductive CNT or graphene results in more abundant edge sites as well as satisfied conductivity.

Synthesis ultra-thin NiFe-LDHs with more exposed active sites and enhanced conductivity is an alternative optimization strategy. Exfoliation of the layered materials has been the most well-developed method for obtaining ultra-thin or single layer materials, involving exchanging the interlayer anions with larger spacing and sonicating in highly polarized solvent (e.g. formamide). [127] The layered structure of NiFe-LDH facilitates this strategy. Song and Hu exfoliated NiFe-LDH to single-layered NiFe-LDH by first exchanging the interlayer anion of CO₃²⁻ with Cl⁻ and then ClO₄⁻, finally sonicating in the formamide. The exfoliated NiFe-LDHs single layers outperforms the bulk counterpart. [128] Preparing ultra-thin NiFe-LDH without the need of interlayer anion exchange or utilizing of organic solvent is rarely reported and remains challenging. We have demonstrated a facile strategy for synthesis of ultra-thin NiFe LDH with high activity in Chapter 3.

Due to the surprisingly synergic performance of the NiFe based materials toward OER, researchers have engaged in figuring out the origin of the enhancement and the active site of the NiFe based materials. Boettcher and co-workers revealed that though Fe could increase the conductivity of NiOOH by >30-fold, this enhancement in conductivity was not sufficient to explain the improvement in activity. Instead, Fe enables partial charge transfer of Ni, resulting in activation of Ni centers as the efficient active site. [124] The

activation of the Ni site by nearby Fe is similar to the effect that Au as the substrate with large electronegativity exerts on Ni. The viewpoint was prevalent until the paper published next year by Daniel Friebe and co-workers.[129] Combining in-situ high energy resolution fluorescence detection (HERFD) operando X-ray absorption spectroscopy (XAS) with DFT+U calculations, they figured out that FeO_6 octahedra in NiFeOOH possesses short Fe–O bond distances, resulting in the near optimal adsorption energies of OER intermediates. Consequently, they claimed that Fe was the active site while Ni was not the active site in NiFe (oxy)hydroxide for OER. Recently, the synergistic effect between Ni and Fe was proposed to account for the superior performance of NiFe based catalysts. They considered that the Fe^{3+} promoted the formation of Ni^{4+} , which in turn correlated with the activity enhancement.[130]

1.6.3 Non-oxide transitional metal compounds

Expect for the large efforts devoted to transition metal oxide/hydroxide, some researchers have engaged in developing non-oxide compounds, including sulfide ($\text{MoS}_2/\text{Ni}_3\text{S}_2$, Ni_3S_2)[75, 131], selenide ($\text{Ni}_x\text{Fe}_{1-x}\text{Se}_2$)[132], nitride (Ni_3N , Co_4N)[133, 134], phosphide (Ni_2P , Ni_5P_4 , Co-P)[135-137] and carbide(Ni_3C)[138]. The merit of the non-oxide compounds is the superior conductivity. As we mentioned above, conductivity is also an essential factor in determining the catalyst. However, the contradictory of the design is that the non-oxide compound will completely converted into (oxy)hydroxides after long time of catalysis, indicating that metal hydroxides/oxyhydroxides are the active phase toward catalysis and the merit of the superior conductivity vanishes.[132]

1.6.4 Metal-free catalysts

Non-metal catalysts only contain cheap earth-abundant elements C, N, O, H and could have comparable performance of noble metal catalysts.[139] Recently, N-doped carbon materials have emerged as efficient OER catalysts.[140] Tested in pH=13 KOH electrolyte, this N-doped carbon nanomaterials generated a

current density of 10 mA/cm² at the overpotential of 380 mV, which was among the best OER catalysts. The high oxygen evolution activity of the nitrogen doped carbon materials arise from the quaternary-nitrogen- and/or pyridinic-nitrogen-related active sites.[140] Qiao's group have done a series researches of carbon based catalysts for OER.[139, 141, 142] They have designed the N,O-dual doped graphene-CNT hydrogel film which is easily fabricated by filtration of graphene and CNT with layer-by-layer strategy. The synergy effect of graphene and CNT brought about the current density of 5 mA cm⁻² at the overpotential of 368 mV (0.1 M KOH).[141] g-C₃N₄/CNT catalyst is developed since it has promising good performance due to the high N concentration of g-C₃N₄ (large amount of active sites).[139] It exhibits low overpotential of 300 mV and small Tafel slope of 83 mV/dec (IrO₂ with overpotential of 280 mV and Tafel slope of 90 mV/dec, 0.1 M KOH). They further doped the g-C₃N₄ with phosphorus (P-g-C₃N₄). The flower-like P-g-C₃N₄ directly deposited on carbon fiber paper exhibits high activity and stability in reversibly catalyzing oxygen reduction and evolution reactions, ascribing to N, P dual action, enhanced mass/charge transfer, and high active surface area.[142]

1.7 Measurement techniques for the study of electrocatalysts

1.7.1 Impurity

The trace loadings of adventitious metal ions which can give high activity is a major hazard for obtaining the intrinsic activity/activity trend of the catalyst under consideration. It takes a long time for researchers to realize the impurities in the alkaline electrolyte (the commercial NaOH/KOH electrolyte) and the influence towards the characterization of electrocatalysts. The effect of Fe impurities on Ni(OH)₂ was initially found in Ni-based alkaline batteries.[143-145] The iron contamination leads to lower OER overpotential, resulting in reduced capacity and poorer cycling performance of the alkaline batteries. When water splitting attracted the interest of research, Corrigan et. al. first demonstrated that Fe impurities greatly enhanced the OER performance of NiO in 1987.[146] In

2014, Boettcher and coworkers revisited the issue and attracted the attention concerning the affect of incidental Fe incorporation toward Ni(OH)_2 for OER. Consequently, Fe is now a widely known impurity in KOH/NaOH and the activation towards OER, especially in Ni or Co based electrocatalysts. Purification of KOH/NaOH with Ni(OH)_2 is proposed to remove the Fe impurities. Isolda Roger and coworkers further identified that fluorine-doped tin oxide (FTO) exhibited a steady rise of current when applied a potential of 1.4 V vs NHE in potassium borate buffer.[147] ICP-MS detected that it was the adventitious nickel (the concentration as low as 17 nM) existed in the electrolyte and further deposited on the FTO during electrolysis contributed the activity. Thus, contamination by adventitious metal ions must be excluded when studying the performance of electrocatalysts. Also, the materials for preparation of electrocatalysts should have high purity as well.

The metal ions impurities may be incorporated during the preparation of NaOH/KOH in the industry, which are mainly produced by electrolysis of saturated NaCl. The electrolysis includes the anode reaction ($2\text{Cl}^- - 2\text{e}^- = \text{Cl}_2 \uparrow$) and cathode reaction ($2\text{H}^+ + 2\text{e}^- = \text{H}_2 \uparrow$). The latter reaction utilizes the iron gauze as the electrode and iron may dissolve into the alkaline during the electrolysis. Besides, utensil made of iron or nickel may be applied to store the concentrated NaOH/KOH and slight amount of iron/nickel ions may contaminate the NaOH/KOH.

The hazards induced by the metal ions impurity has caused serious problems, for example, the inconsistency activity trends among Mn, Fe, Ni and Co. Trasatti claimed that activity trend is $\text{MnO}_2 > \text{NiO} > \text{Co}_3\text{O}_4 > \text{Fe}_3\text{O}_4$, correlating with the energy change from the lower to higher valence state transition.^[148, 149] Markovic's group have revealed that the activity trends are $\text{Mn} < \text{Fe} < \text{Co} < \text{Ni}$, which is governed by the strength of OH-M ($\text{Ni} < \text{Co} < \text{Fe} < \text{Mn}$).^[150] Shannon's group have established a new activity trend by claiming that Fe-based (oxy)hydroxide is intrinsically highly active and the poor activity is due to its

poor conductivity with a large film thickness.^[151] The above studies all neglected the metal ion impurities in the electrolyte as well as the materials for catalyst preparation, thus, inconsistency activity trends were reported.

The impurity of the electrolyte may also come from the dissolution of the counter electrode and redeposit onto the working electrode. Pt dissolution from the Pt counter electrode during HER is the major problem when measuring the activity of HER electrocatalysts. We systematically studied this problem in Chapter Four and declared that counter electrode in any form of Pt (Pt plate or wire) should be avoided or used together with an ion-exchange membrane to prevent Pt re-deposition during the study of HER catalysis.

1.7.2 Surface area

To compare the intrinsic activity between different catalysts is quite difficult due to the complex difference of catalysts, e.g. the loading amounts, the morphologies of catalysts and/or substrates, the components/phases/facets of the catalysts. Normalizing the current to the surface area of catalysts provides a feasible solution for accurate activity comparisons between different catalysts. Surface area measured by BET is commonly applied. However, the surface of catalysts may be altered when undergo potential cycling or exposed to electrolyte. Therefore, researchers usually apply the surface double layer capacitance to determine the surface area of catalysts.

Cyclic voltammetry in the region without any faradaic redox current is the most prevalent strategy for measuring the electrochemically active surface area. The theoretical support of this method is shown as follows:

$$\text{Capacitance formula: } C = \frac{Q}{E}$$

Where C is the double layer capacitance, Q is the charge stored on each plate. E is the voltage applied to the plates. Differential of the formula leading to:

$$\frac{dQ}{dt} = C \frac{dE}{dt}$$

assuming that C is constant. This formula can also be written as:

$$i = C v$$

where v is the scan rate. Thus, the plot of double layer charging current i vs. different scan rates v (e.g. from 5mV/s to 30 mV/s) results in a linear plot with a slope equal to C (Figure 1-10). The method is efficient when the surface of the catalyst remains stable with potential applied. Metal oxide surfaces could meet the requirement.

Figure 1-10. The illustration of obtaining the double layer capacitance based on the double layer charging current.

This method encounters problem when measuring the catalysts with poor conductivity (e.g. hydroxide) or the hydrous oxide. Many catalysts exhibit poor conductivity before they are oxidized. Measuring the double layer capacitance usually lies in the potentials sufficiently cathodic of redox peak. Boettcher and coworkers[6] identified that the measured capacitance of the catalyst (Ni-Fe oxy-hydroxide) with poor conductivity is similar to that of the underlying substrate (Figure 1-11).

Figure 1-11. Double-layer capacitance of the uncharged Ni-Fe (oxy)hydroxide films deposited on Au (blue) and FTO (red) electrodes. Obtaining via cyclic voltammetry (CV, squares) and AC impedance spectroscopy (ZAC, stars). Note: the data points at zero loading corresponding to the values of double-layer capacitance of the substrates (Au/FTO).[6] (Copyright © 2015, American Chemical Society)

Furthermore, this method is not easily applied to hydrous oxides, owing to the penetration of ion and solvent through the film and causing the formation of an electric double layer at the underlying interface between the catalyst and the conductive support.[97] As such, the double-layer capacitance measurement returns a value similar to that of the substrate regardless of the thickness of the hydrous oxide layer.[97]

Another electrochemical approach to surface area estimations could be based on the integration of the CVs and the integrated area (q) provides an estimate of the surface-active sites.[7] This technique is suitable to catalysts where all sites give rise to the surface redox process are also responsible for the turnover catalysis. As a result, this approach is applicable to both dry/hydrous oxides as well as hydroxide with poor conductivity. The integrated charge varies at different scan rates, as shown in Figure 1-12, suggesting that the redox reaction is limited by slow mass diffusion. Furthermore, by measuring the integrated

charge versus the scan rate of the redox peak, one can obtain the outer surface area as well as the inner-surface area (cracks or pores). In the rate of limit zero, the outer and inner surface are both involved, and only the outer surface accounts for current at infinite scan rate.[7]

Figure 1-12. Integrated voltammetric charge q^* as a function of scan rate v for RuO_2 in 1M KOH.[7] (Copyright © 1990 Published by Elsevier Ltd.)

The double capacitance can also be measured by impedance. By generating the equivalent circuit, double layer capacitance could be extracted from the impedance. As shown in Figure 1-13, the equivalent circuit is utilized to model the OER electrodes. It is obvious that the fitting values of the double layer capacitance of hydrous oxide films are potential-dependent, as demonstrated in Figure 1-14.[8]

Figure 1-13. Model of the equivalent circuit of the OER electrodes.[8] (Copyright © 2013, Royal Society of Chemistry)

Figure 1-14. Fitting values of the double layer capacitance of hydrous oxide films as a function of applied potential.[8] (Copyright © 2013, Royal Society of Chemistry)

1.7.3 Uncompensated resistance of the cell

Uncompensated resistance is an important factor during electrochemical tests, especially when the current is large. For basic understanding of this technical factor, we need to figure out the following questions:

1) Where does the Uncompensated resistance come from?

Figure 1-15. Simplified network of electrochemical test cell

As shown in Figure 1-15, the potentiostat can only control the voltage between

points H & I, however, we need to control the voltage between points E & F, which can be described by

$$V = V_f - V_e;$$

Point G is equivalent to H except for the offset of open circuit voltage V_{oc} . So we can get

$$V_{measured} = V_i - V_h = V_f - V_d + V_{oc};$$

Point E equals to point D without R_u , $V_e - V_d = iR_u$. Finally, we can obtain the important formula:

$$V = V_f - V_e = V_{measured} - iR_u - V_{oc};$$

$$V_{iR} = iR_u;$$

As a result, whenever a current is passed through the circuit, there is always a potential control error due to the uncompensated resistance.

2) How to minimize the uncompensated resistance?

Use an electrolyte with high conductivity and/or reduce the current passing through the working electrode (the size of the working electrode). Besides, applying a Luggin capillary is efficient to reduce the uncompensated resistance, owing to the nearer distance between the reference electrode and the working electrode.

Even R_u could be minimized, it still needed to be eliminated since kinetics study only correlates to the driving force exerted on the interfacial reaction.

a) How to measure iR ?

We apply high frequency technique here. High frequency will pass through

the capacitor without any voltage drop, so the drop the voltage is due to R_u , thus we can get the value of R_u . Then multiply it by the current, we can get the uncompensated iR .

1.8 Motivation and objective

Since all electrochemical processes are occurred on the interface, the surface area of the interface is a key consideration in the design of practical electrodes. Thus, preparation of an anode with three-dimensional structure and high surface area is essential of the catalyst material, regardless of the intrinsic (specific) activity. Moreover, the requirements for catalyst specific activity can be dramatically reduced if the oxide layer can be prepared in a porous 3D architecture. The objective is to achieve highly stable and active electrode towards OER with porous architecture.

Furthermore, we attempted to design efficient OER electrocatalysts with higher intrinsic activity. NiFe-LDH nanosheets is known to be among the most efficient OER catalysts. The aim is to synthesis NiFe-LDH with facile and scalable method and realize its application as active and stable OER catalysts. Furthermore, in order to overcome the poor conductivity of LDH and weak connection between LDH and conductive support in practical OER applications, well-aligned multi-walled carbon nanotube (MWCNT) sheets were applied to form the binder-free hybrid microfiber electrodes.

HER is the other half reaction of water splitting and is also under intense investigation. Researchers dedicated to developing catalysts with earth abundant elements and similar activity to Pt. Unfortunately, according to our literature survey, around 50% of the published HER studies adopted Pt as the counter electrode without the use of ion-exchange membrane during the last two years. The aim is to arouse the awareness of the results in those recently published papers by systematic studies concerning the dissolution behavior of Pt as the counter electrode during the electrochemical measurement of HER activity.

The overall objective is to achieve water splitting with lower energy input, by designing highly efficient and stable OER electrodes, which suffer from sluggish kinetics and high overpotential. On the other hand, the reported

performance of HER electrocatalysts should be true for industry application, so we explored the scientific issues in activity evaluation of HER, expecting that researchers measuring HER electrocatalysts are all aware of the counter electrode influence on the electrocatalysts.

1.9 Organization of the proposal

The dissertation contains 5 chapters, and is organized as follows:

Chapter 1 provides a general introduction of the topics in this dissertation, including the background and significance of water splitting technologies, the mechanisms of OER and the current states of catalysts towards OER, the measurement techniques for the study of electrocatalysts.

Chapter 2 demonstrates the research towards highly efficient OER catalyst NiCo_2O_4 , enabling large surface area with three-dimensional core shell structure.

Chapter 3 displays the fabrication of ultra-thin NiFe LDH nanosheets. Further, the well-aligned multi-walled carbon nanotube (MWCNT) sheets were utilized to solve the conductivity issue and adhesion problem.

Chapter 4 conducts the evaluation of the influence of Pt counter electrode during HER measurement. The influence in alkaline and acidic media are investigated. Electrochemical pretreatment (usually cyclic voltammetry method) during HER measurement was simulated with different area ratios of HER catalysts, CV scan ranges and scan rates. The results were presented and analyzed.

Chapter 5 summarizes a general conclusion of this PhD project, and provides recommendation of directions for future research in the field of water splitting.

Chapter 2 A Flexible High-Performance Oxygen Evolution Electrode with Three-Dimensional NiCo₂O₄ Core-Shell Nanowires

2.1 Introduction

Developing efficient oxygen evolution reaction (OER) catalysts with low overpotential and sufficient stability for OER is highly demanded. To enhance the electrocatalytic performance and achieve full utilization of the active material, it is important to design nanostructured OER electrocatalysts with high active surface area and good electrical conductivity. It is well known that 1D nanomaterial can facilitate the electrical transport along the axial direction [152] and 2D nanostructures offer high active surface area for electrocatalysis [153-155]. Thus, it is highly desirable to combine the 1D and 2D OER electrocatalysts together to make hierarchical nanostructures for enhanced electrocatalytic activity.

Transition metal oxides acting as oxygen evolution anodes in alkaline media have been widely studied and shown suitable overpotential and stability. [150, 156-159] Of which, the spinel NiCo₂O₄ is a promising OER electrocatalyst, because of its excellent electrical conductivity, fairly low overpotential and corrosion-resistivity in alkaline solution.[104, 160] In this work, spinel NiCo₂O₄ has been applied as the OER electrocatalysts to demonstrate the efficiency of the core-shell structure design.

NiCo₂O₄ has been used as an electrocatalyst in oxygen evolution since 1970s. The early researches studied NiCo₂O₄ electrodes for OER, which were prepared by applying Teflon to bind NiCo₂O₄ powders on conducting substrates. However, the polymer binder influenced the conductivity of electrode by adding extra contact resistances and undesirable interfaces, thus limiting the OER performance.[106, 161, 162] To improve the OER performance of NiCo₂O₄, Qiao's group applied 3D structure of NiCo₂O₄ by assembling NiCo₂O₄ with

graphene/MnO₂ or nitrogen-doped graphene film. [163, 164] The hybrid structures to some extent improved the catalytic performance. Nevertheless, the NiCo₂O₄ assembled into the framework exhibited limited active surface area and poor catalytic stability due to weak mechanical strength especially at high operating current densities. Yang et al. synthesized NiCo₂O₄ nanowires for OER, [165] however the powder sample and thus poor electrical contact limited the OER performance. Wu et al. synthesized freestanding Ni_xCo_{3-x}O₄ nanowire arrays on Ti substrate. Ni doping in Co₃O₄ increased the roughness factor of nanowires, and thus improved catalytic performance.[166] However, the performance was still far from satisfactory.

In this work, a simple two-step wet chemical method based on a hydrothermal synthesis and an electrochemical deposition was developed to fabricate three-dimensional NiCo₂O₄ core-shell nanowire arrays on flexible conductive carbon cloth substrate. Carbon cloth was chosen as the substrate owing to its high porosity, good electrical conductivity, light weight and excellent flexibility. [167] The as-prepared NiCo₂O₄ core-shell nanowire arrays have high surface area arising from the ultrathin and highly porous NiCo₂O₄ nanoflake shell, as well as offer three-dimensional conducting pathways. Consequently, the NiCo₂O₄ core-shell nanowire arrays show much improved electrocatalytic activity for oxygen evolution reaction.

2.2 Experimental Section

Synthesis of NiCo₂O₄ core-shell nanowire arrays on carbon cloth: All chemicals were purchased from Sigma-Aldrich and used without further purification. NiCo₂O₄ core-shell nanowire arrays were grown on carbon cloth using a two-step wet chemical method. Firstly, self-supported NiCo₂O₄ nanowire arrays were grown on carbon cloth by a facile hydrothermal method. The precursor solution was prepared by dissolving 1.5 mmol Co(NO₃)₂, 0.75 mmol Ni(NO₃)₂ and 7.5 mmol CO(NH₂)₂ in 50 mL of deionized water. Carbon cloth was vertically placed in the reaction solution to grow NiCo₂O₄. The hydrothermal reaction was

conducted at 110 °C for different time (1.5 to 5 h) in an electric oven to optimize the electrocatalytic performance (Figure 2-1). After reaction, the carbon cloth substrate was taken out, rinsed with deionized water, dried, and annealed at 350 °C in air for 2 h at a heating rate of 1 °C/min. In the second step, NiCo_2O_4 nanoflake shell was electrochemically deposited on NiCo_2O_4 nanowires in a standard three-electrode glass cell at 25 °C. During electrochemical deposition, the as-prepared NiCo_2O_4 nanowire array was used as the working electrode, saturated calomel electrode (SCE) and a Pt foil were used as the reference and counter electrode, respectively. The electrolyte was composed of 0.2 mol/L $\text{Co}(\text{NO}_3)_2$ and 0.1 mol/L $\text{Ni}(\text{NO}_3)_2$. A constant cathodic current of 2.5 mA/cm^2 was applied to the working electrode. The deposition time was varied from 100 s to 1000 s to optimize the shell morphology and electrochemical properties (see Figure 2-2, 2-3). Longer deposition time will lead to intimate contact of NiCo_2O_4 nanoflake with no open space between each NiCo_2O_4 nanowire and thus deteriorated electrocatalytic performance (Figure 2-4).

Figure 2-1. FESEM images of NiCo_2O_4 nanowire arrays prepared after different durations of hydrothermal reaction: (a) 1.5 h, (b) 3h, (c) 5h, and (d) polarization curves of NiCo_2O_4 nanowire arrays prepared after different durations of hydrothermal reaction.

Figure 2-2. FESEM images of NiCo_2O_4 core-shell nanowire arrays with nanoflake shell electrochemically deposited for: (a) 100 s (b) 400 s (c) 700 s (d) 1000 s at a current density of 2.5 mA/cm^2 .

Figure 2-3. Cyclic voltammograms in the double layer region at scan rate of 16, 14, 12, 10, 8, 6, 4 mV/s (along the arrow direction) of NiCo₂O₄ core-shell nanowire arrays with different shell electrodeposition time: (a) 100 s, (b) 400 s, and (c) 700 s. (d) Current density as a function of scan rate for NiCo₂O₄ nanowire arrays and NiCo₂O₄ core-shell nanowire arrays with different shell electrodeposition times. (e) Cyclic voltammogram at scan rate of 1 mV/s for NiCo₂O₄ nanowire arrays and NiCo₂O₄ core-shell nanowire arrays with different shell electrodeposition times. (f) Polarization curves of NiCo₂O₄ nanowire arrays and NiCo₂O₄ core-shell nanowire arrays with different shell electrodeposition

times.

Figure 2-4. (a) FESEM image (b) Enlarged view (c) Polarization curves of NiCo_2O_4 core-shell nanowire array with electrodeposition time of 1300s.

Ir/C electrode preparation: Ir/C (20% Ir on Vulcan XC-72) was purchased from Premetek. 5mg of Ir/C nanoparticles were dispersed in 1 mL solution (containing 0.45 mL DI water, 0.45 mL isopropanol and 0.1 mL nafion) and sonicated in an ultrasonic water bath. Pretreated carbon cloth substrate was drop-casted with the mixed solution at the loading of $0.2\text{mg}/\text{cm}^2$ (loading area: 0.5 cm^2).

Materials characterization: The phase composition of the as-prepared film was analyzed by X-ray diffraction (XRD, Bruker AXS D8 Advance) with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406\text{ \AA}$). Morphological and lattice structural information were examined with field-emission scanning electron microscopy (FESEM, JEOL, JSM6700F) and transmission electron microscopy (TEM, FEI Tecnai G2 30). Detailed chemical composition of samples was obtained by X-ray photoelectron spectroscopy (XPS) measurements on an ESCALAB 250 photoelectron spectrometer (Thermo Fisher Scientific) at 2.4×10^{-10} mbar using a monochromatic Al $\text{K}\alpha$ X-ray beam (1486.60 eV). All binding energies were referenced to the C 1s peak (284.60 eV) arising from adventitious hydrocarbons.

Surface area was measured based on BET method using Autosorb 6B at liquid-nitrogen temperature.

Electrochemical measurements: All electrochemical measurements were carried out in a standard three-electrode cell using a Pt plate as the counter electrode and a SCE (in saturated KCl) as the reference electrode. The electrochemical cell was controlled by a CHI 760D electrochemical workstation. All potentials were calculated with respect to reversible hydrogen electrode (RHE) using the following equation: $E(\text{RHE}) = E(\text{Hg}/\text{Hg}_2\text{Cl}_2) + 0.059\text{pH} + 0.241\text{V}$. The overpotential (η) was computed via $\eta(\text{V}) = E(\text{RHE}) - 1.23\text{ V}$. Working electrode was cycled between 1.07 and 1.58 V for 5 cycles at a scan rate of 5 mV/s and electrolyte was purged by O_2 for at least 30 min before data collection. Linear sweep voltammetry (scan rate: 1 mV/s) and AC impedance spectroscopy (at zero overpotential, frequency range from 100 kHz to 1 Hz, amplitude = 0.01 V) were recorded. Double-layer capacitance was derived from the slope of capacitive current versus scan rate plot. Cyclic voltammetry (CV) measurement was performed in the potential region without redox processes (1.22 ~ 1.27 V vs. RHE). The Faraday efficiency was estimated using volumetric method. The actual-evolved oxygen gas on NiCo_2O_4 core-shell nanowire electrode was collected in a precise 15ml graduated tube, which was filled with the electrolyte. Controlled potential electrolysis was carried out at three different currents (~ 27 mA, 48 mA and 72 mA) sequentially for about 3 h under standard conditions (25 °C, 1 atm). The time points at each 0.5 ml of collected gaseous were recorded. Meanwhile, the accumulated charges passed through the working electrode were recorded using electrochemistry workstation. In order to determine the composition and purity of the product, the collected gas was sampled with a Hamilton syringe and then analysed using gas chromatograph (Agilent GC 490). From the GC spectra, O_2 was the only detected gaseous product throughout the test, while peaks associated with impurities were absent. After the test, we plotted the actual collected volume of gaseous product against the theoretical oxygen produced based on Faraday's law. The electrolyte was 1 M NaOH aqueous

solution; we also tested our sample in 0.1 M KOH for comparison as listed in Table 1. All data were corrected for a small ohmic drop ($\sim 4.5 \Omega$). Current density was calculated based on the geometric area of carbon cloth.

2.3 Results and discussion

NiCo₂O₄ nanowires were grown on conductive carbon cloth substrate using a hydrothermal method. Figure 2-5 a & b show the FESEM images of NiCo₂O₄ nanowires, which closely and uniformly cover the entire carbon cloth with a mean diameter of ~ 80 nm and length of $\sim 4 \mu\text{m}$ (Figure 2-1). A thick layer of NiCo₂O₄ nanoflake was grown on the surface of NiCo₂O₄ nanowires to form a core-shell nanostructure using electrochemical deposition followed by a gentle annealing (Figure 2-5c & d and Figure 2-2). It is worth mentioning that the nanoflake shell is very thin and highly porous, which significantly improves the external surface area of NiCo₂O₄ nanowires. The measured BET surface area was increased from $61 \text{ m}^2/\text{g}$ to $208 \text{ m}^2/\text{g}$ after depositing a shell of NiCo₂O₄ nanoflakes on NiCo₂O₄ nanowires.

Figure 2-5. (a) FESEM image of NiCo₂O₄ nanowire array on carbon cloth. (b) Enlarged view of NiCo₂O₄ nanowires. (c) FESEM image of NiCo₂O₄ core-shell nanowire array on carbon cloth. (d) Enlarged view of NiCo₂O₄ core-shell nanowires.

The detailed microstructures of NiCo_2O_4 nanowires were examined by transmission electron microscopy (TEM). As shown in Figure 2-6 a, NiCo_2O_4 nanowires are composed of strings of closely connected nanoparticles (2-4 nm in size). The spacing between adjacent fringes is ~ 0.44 nm (Figure 2-6 b), very close to the theoretical interplanar spacing of spinel NiCo_2O_4 (111). [168, 169] Figure 2-6 c and d show TEM images of NiCo_2O_4 core-shell nanowires in which NiCo_2O_4 nanoflakes uniformly cover the surface of NiCo_2O_4 nanowires. The thickness of the shell is around 200 nm, corresponding to the size of NiCo_2O_4 nanoflakes. The low contrast of the nanoflakes indicates their ultrathin feature (Figure 2-6c inset). Furthermore, the nanoflakes are highly porous with numerous mesopores distributed evenly on the nanoflake surface. Thus, a large amount of exposed surface and full utilization of electrocatalytically active materials could be expected, which are beneficial for OER as discussed shortly. HRTEM image of nanoflakes grown on NiCo_2O_4 nanowires shows a lattice spacing of 0.28 nm, corresponding to the (220) plane of spinel NiCo_2O_4 . [170]

Figure 2-6. (a) & (b) TEM and HRTEM images of NiCo_2O_4 nanowires. (c) & (d) TEM and HRTEM images of NiCo_2O_4 core-shell nanowires. Insets show

enlarged TEM images.

The spinel crystal structure of NiCo_2O_4 nanowires was further confirmed by X-ray diffraction. Figure 2-7a shows the XRD patterns of as-prepared NiCo_2O_4 nanowires and nanoflakes. Besides the diffraction peaks (marked with *) corresponding to carbon cloth, the rest peaks can be well assigned to spinel NiCo_2O_4 . The broadening of XRD peaks suggests the small crystallite size. The valence states of nickel and cobalt in NiCo_2O_4 were examined with X-ray photoelectron spectroscopy (XPS). As shown in Figure 2-7 b, binding energies of Ni $2p_{3/2}$ photoelectrons were measured at 854.1 eV and 855.8 eV, which correspond to Ni^{2+} and Ni^{3+} , respectively. Similarly, the Co $2p$ peaks can be deconvoluted into Co^{2+} and Co^{3+} (Figure 2-7 c). [171] The O $1s$ spectrum shows three oxygen contributions, denoted as O1 (529.5 eV), O2 (531.0 eV) and O3 (532.4 eV), which are associated with metal–oxygen bonds in metal oxide [170, 172], the defect sites with low oxygen coordination in the material with small particle size [173, 174], and the multiplicity of physi/chemisorbed water [171, 173], respectively.

Figure 2-7. (a) XRD patterns of NiCo₂O₄ nanowires and nanoflakes. (b-d) XPS spectra of (b) Ni 2p, (c) Co 2p, and (d) O 1s of NiCo₂O₄ core-shell nanowires.

The electrocatalytic activity of as-prepared NiCo₂O₄ nanowire films were evaluated in a typical three-electrode cell setup with 1M NaOH electrolyte. Figure 2-8 a shows the polarization curves of of NiCo₂O₄ nanowire film and NiCo₂O₄ core-shell nanowire film, respectively. It can be seen that the core-shell nanowire film exhibits higher catalytic activity across the entire potential window by showing higher current densities, indicating a clear advantage of the core-shell nanostructure. The activity of NiCo₂O₄ nanowire film and NiCo₂O₄ core-shell nanowire film was then compared with a state-of-the-art precious catalyst, Ir/C (loading: 0.2 mg/cm²), as shown in Fig. 2-8 a and Figure 2-9. Both showed comparable onset overpotential with Ir/C, however, much larger current density. Figure 2-10 show the evolution of O₂ bubbles on NiCo₂O₄ core-shell nanowire electrode. The overpotentials of core-shell nanowire film required to drive anodic current densities of 10, 20, 50 mA/cm² are 320 mV, 344 mV, and 370 mV, respectively, which are among the most active NiCo₂O₄ electrocatalysts. Table 2-1 compares electrocatalytic activities of different forms of NiCo₂O₄ electrocatalysts reported so far. In Figure 2-8 b, the corresponding Tafel plots obtained from low overpotential region (0.3 - 0.4 V) reveal small Tafel slopes of 47.4 mV/dec and 63.1 mV/dec for NiCo₂O₄ nanowire film and NiCo₂O₄ core-shell nanowire film, respectively, suggesting a similar surface chemistry in OER. At high overpotential region (0.57 ~ 0.77 V), deviations from Tafel behavior occurs in both samples (data not shown), which are attributed to ohmic drop in the electrolyte solution as well as strong evolution of gas bubbles from the oxide surface. [162]

Table 2-1. Comparison of OER performances of NiCo₂O₄ core-shell nanowire arrays with other reported NiCo₂O₄ catalysts.

References	Overpotential (mV) @ current density of 10 mA/cm ²	Tafel slope (mV/dec)	Onset overpotential (mV)	Stability	Double layer capacitance (roughness factor)	BET surface area (m ² g ⁻¹)	Electrode	Experimental conditions
Our work	320	63.1	290	Fixed potential electrolysis in the current density range of 10.7 to 23.6 mA/cm ² for 30 h, showing less than 0.2% degradation	5.2×10 ³	208	Core-shell nanowire arrays on carbon cloth	1 M NaOH, RT
Our work	350	74.0	290				Core-shell nanowire arrays on carbon cloth	0.1 M KOH, RT
Jasem, S. M.; et al., <i>J. Electrochem. Soc.</i> 1979, 126, 1353.	NA	33	345	NA	NA	69	Teflon-bonded film on nickel screen	5 M KOH, RT
Nikolov, I.; et al., <i>J. Electroanal. Chem.</i> 1997, 429, 157	572	44	399	NA	11.5×10 ³	14	Teflon-bonded film on nickel screen	3.5 M KOH, RT
Li, Y.; et al., <i>Adv. Mater.</i> 2010, 22, 1926.	NA	64	436	NA	2.8×10 ³	NA	Ni _x Co _{3-x} O ₄ nanowire arrays on Ti foil	1 M NaOH, RT
Lee, D. U.; et al., <i>J. Mater. Chem.</i> 2013, 1, 4754.	471	161	331	99.6% current retention after 1000 CV cycles	NA	77	NiCo ₂ O ₄ /graphene powder coated on glassy carbon disk	0.1 M KOH, RT
Jin, C.; et al., <i>J. Mater. Chem.</i> 2013, 1, 12170.	412	NA	337	Electrolysis at 20 mA/cm ² for 12.5 h, 4.8% attenuation	NA	124	Nanowire powder coated on glassy carbon disk	0.1 M KOH, RT
Chen, S.; et al., <i>ACS Nano</i> 2013, 7, 10190.	434	156	310	Electrolysis at 334 mV (~ 1.75 mA/cm ²) for 10 h, less than 10% attenuation	NA	155	NiCo ₂ O ₄ /nitrogen doped graphene hybrid film	0.1 M KOH, RT
Chen, S.; et al., <i>Chem. Commun.</i> 2014, 50, 207.	NA	371.3	321	Electrolysis at 6 mA/cm ² for 12 h, ~ 16.7% attenuation	NA	70	NiCo ₂ O ₄ /Graphene/MnO ₂ on nickel foam	0.1 M KOH, RT

To understand the better performance of core-shell NiCo₂O₄ nanowire films, CV measurements were conducted at a scan rate of 1 mV/s (Figure 2-8 c). Both nanowire and core-shell nanowire sample show an anodic peak and a corresponding cathodic peak, assignable to the redox couples of Ni²⁺/Ni³⁺ and Co³⁺/Co⁴⁺ due to overlapped potentials of these two redox couples. Co²⁺ in the tetrahedral sites of NiCo₂O₄ is electrochemically inactive, thus no anodic peak associated with Co²⁺/Co³⁺ at E = 1.26 V vs. RHE was observable. The oxidation peak of Ni³⁺/Ni⁴⁺ (E = 1.54 V vs. RHE) is overlapped with the rising OER current. [175] As a result, the transitions on the surface of NiCo₂O₄ can be summarized according to the following equations [176]:

where M is cobalt or nickel cation. The peak current density as well as enclosed area is dramatically increased for core-shell nanowire sample, indicating much larger surface area for core-shell nanowire film. [166, 177] Electrochemically active surface area is further determined via capacitance measurements, as shown in Figure 2-8 c-f. The calculated capacitance of NiCo₂O₄ core-shell nanowire film and NiCo₂O₄ nanowire film are 0.313 F/cm² and 0.036 F/cm², respectively. Based on these values, the roughness factors of the two samples are estimated to be around 5.2×10^3 and 0.6×10^3 , respectively. Clearly, core-shell nanowire film shows more than 8 times larger active surface area than the nanowire film, which contributes to the better electrocatalytic performance for NiCo₂O₄ core-shell nanowires.

Figure 2-8. (a) Polarization curves of carbon cloth, Ir/C, NiCo₂O₄ nanowire film and NiCo₂O₄ core-shell nanowire film. Inset: photograph of a flexible NiCo₂O₄ core-shell nanowire electrode. (b) Tafel plots, and (c) Cyclic voltammogram curves at scan rate of 1 mV/s of NiCo₂O₄ nanowire film and NiCo₂O₄ core-shell nanowire film. (d) & (e) Cyclic voltammograms in the double layer region at scan rate of 16, 14, 12, 10, 8, 6, 4 mV/s (along the arrow direction) of (d) NiCo₂O₄ nanowire film and (e) NiCo₂O₄ core-shell nanowire film. (f) Current density as a function of scan rate for NiCo₂O₄ nanowire film and NiCo₂O₄ core-shell nanowire film.

Figure 2-9. (a) Polarization curves (b) Tafel plot of of Ir/C.

Figure 2-10. Digital photograph of NiCo₂O₄ core-shell nanowire electrode operated at a current density of 120 mA/cm^2 , showing evolution of O₂ bubbles.

Aside from a stringent requirement for high activity, excellent durability is another key factor for electrocatalyst selection. To probe the durability of the NiCo₂O₄ core-shell nanowires, electrolysis at three different fixed overpotentials

(320 mV, 340 mV, and 350 mV) was performed sequentially over 30 h. At overpotentials of 320 mV, 340 mV and 350 mV, the current density remains stable at around 10.7 mA/cm², 16.8 mA/cm², and 23.6 mA/cm² over each 10 h period (Figure 2-11 a). After 30 h of stability test, the linear sweep voltammetry and capacitance measurement were collected as shown in Figure 2-11 b&c. It can be seen from Figure 2-11 b that the polarization curve of NiCo₂O₄ core-shell nanowire film before and after 30 h of electrolysis almost overlap with each other, especially at low overpotential region. Also, as indicated by Figure 2-11 c, the electrochemically active surface area maintained well after 30h of electrolysis. The stability of NiCo₂O₄ core-shell nanowires was greatly improved as compared with other reported NiCo₂O₄ samples, for instance, NiCo₂O₄ nanowires coated on rotating disk (in 0.1 M KOH, RT, electrolysis at fixed potential with current density around 20 mA/cm² for 12.5 h with 4.8% attenuation) [178] and 3D hybrid paper of N-doped grapheme/NiCo₂O₄ (in 0.1 M KOH, RT, electrolysis at current density of 1.75 mA/cm² for 10 h with current loss close to 10%) [163]. To gain insight into the good stability of NiCo₂O₄ core-shell nanowires, morphology and crystal structure of core-shell nanowires before and after electrolysis were examined with FESEM, XPS and XRD. As shown in Figure 2-12, the morphology, valence states of nickel and cobalt and crystal structure of NiCo₂O₄ core-shell nanowire film remain almost unchanged after 30 h of continuous electrolysis, indicating excellent stability of the film. To confirm the currents were associated with water oxidation, we also carried out Faradaic efficiency measurements at constant potentials electrolysis with three different currents (~ 27 mA, 48 mA and 72 mA) sequentially for about 3 h, as shown in Figure 2-11 d (~ 27 mA) and Figure 2-13, all showed near 100% Faradaic efficiency.

Figure 2-11. (a) Stability tests of NiCo₂O₄ core-shell nanowire film at fixed overpotentials of 320 mV, 340 mV, and 350 mV over 30 h. (b) Polarization curves before and after 30 h of stability tests. (c) Current density as a function of scan rate before and after 30 h of stability tests. (d) Experimental oxygen volume versus theoretical oxygen volume based on the amount of consumed charge during the course of electrolysis.

Figure 2-12. (a) & (b) FESEM images of NiCo₂O₄ core-shell nanowire film after 30 h of electrolysis. (c-f) XPS spectra of NiCo₂O₄ core-shell nanowires before and after 30 h of electrolysis: (c) Ni 2p, (d) Co 2p, and (e) O 1s. (f) XRD patterns of NiCo₂O₄ core-shell nanowire film before and after 30 h of electrolysis.

Figure 2-13. (a) Plot of electrolysis at constant potentials with currents around 27 mA, 48 mA and 72 mA (sample area 0.5 cm²). (b) Comparison of evolved oxygen volume versus theoretical oxygen volume based on the amount of consumed charges during the course of electrolysis.

We ascribe the excellent electrocatalytic performance of the NiCo₂O₄ core-shell nanowire film to the unique architecture including the porous NiCo₂O₄ nanowire core, porous and ultrathin NiCo₂O₄ nanoflake shell, and ordered array on 3D conductive carbon cloth. Firstly, the open space between the ultrathin nanoflake and the mesopores within the nanoflake enable the full exposure of active materials to the electrolyte, and thus enhance both mass and electron transport. Secondly, large surface area of the core-shell nanowire arrays provides efficient contact between active materials and electrolyte, thus benefits electrocatalysis. Thirdly, the 1D array structure ensures good mechanical adhesion and electrical connection to the 3D current collector and, therefore,

avoids the use of polymer binders and conductive additives. The direct contact of nanowires with the conductive carbon cloth substrate and the intrinsic electrical conductivity enable fast electron transport. Lastly, the NiCo_2O_4 has excellent electrochemical stability towards oxygen evolution reaction in alkaline electrolyte. In short, 1D NiCo_2O_4 core-shell nanostructures ensure fast mass and electron transport, sufficient contact between catalysts and electrolyte, finally leading to enhanced electrocatalytic performance.

2.4 Conclusion

In summary, a two-step wet chemical method has been developed for the fabrication of NiCo_2O_4 core-shell nanowire arrays on 3D conductive carbon cloth substrate. Owing to the high surface area, ultrathin porous nanoshell, and enhanced mass and charge transport, the resultant NiCo_2O_4 core-shell nanowire array electrode exhibits excellent OER performance with a small overpotential of ~ 320 mV at a current density of 10 mA/cm^2 . Furthermore, the NiCo_2O_4 core-shell nanowires are able to drive large anodic current at low overpotential and stably function over an extended period. Our study provides a promising way for achieving efficient OER electrocatalysis using inexpensive, earth-abundant and easily prepared electrocatalyst on flexible electrodes.

Chapter 3 Achieving Stable and Efficient Water Oxidation by Incorporating NiFe Layered Double Hydroxide Nanosheets into Aligned Carbon Nanotubes

3.1 Introduction

Though the efficiency of the structure design has been confirmed in chapter 2, the intrinsic activity of the spinel NiCo_2O_4 still needs improvement to achieve more efficient OER electrodes. As far as we know, NiFe layered double hydroxide (NiFe-LDH) showed the best OER performance in the alkaline medium.[179, 180] The LDH structure is attractive for OER, which allows easy intercalation of water molecules and anions in-between different layers.[115, 117, 181, 182] However, NiFe-LDH suffers from the poor conductivity in OER electrocatalysis. Over the past few years, great efforts have been made to overcome this problem by preparing ultra-thin nanosheets and further coupling NiFe-LDH with conductive supports, such as carbon nanotubes or graphene.[125, 126, 183] But, most of the reported NiFe-LDH hybrid catalysts are in the form of powders, which have to be mixed with binders such as Nafion and casted onto conductive substrate to prepare OER electrodes. Binder, to some extent, can improve the adhesion of the electrocatalysts to substrate. Nevertheless, it decreases the electrocatalytic surface area of the catalyst as well as increases dead weight without contributing to catalytic reactions, leading to decreased overall electrocatalytic performances. Furthermore, the stability of the electrode is relatively poor due to loss in contact between electrocatalysts and substrate during electrocatalysis, especially under large current densities.

Herein, we develop a facile and scalable method to prepare stable colloidal NiFe-LDH nanosheets by rapid co-precipitation of Ni^{2+} and Fe^{3+} ions followed by sonication at room temperature. The as-prepared NiFe-LDH nanosheets exhibited a high catalytic activity towards OER with a low Tafel slope of 21.2

mV/dec and a high mass activity of 200 mA/mg at an overpotential of 260 mV. To construct efficient OER electrodes with good durability, we incorporated NiFe-LDH nanosheets into well-aligned MWCNTs. The thus-obtained NiFe-LDH@MWCNT microfiber electrode exhibited outstanding OER activity and durability owing to the synergistic integration between these two types of functional nanomaterials. Furthermore, the microfiber electrode is highly flexible and could be woven into arbitrary fabric patterns for a large variety of electrochemical and catalytic applications.

3.2 Experimental Section

Synthesis of NiFe-LDH nanosheets: All chemicals were purchased from Sigma-Aldrich and used without further purification. The NiFe-LDH nanosheets were prepared through fast co-precipitation of Ni^{2+} and Fe^{3+} followed by sonication at room temperature. Briefly, a mixed solution containing 1.5 mmol of metal ions with different ratios of $\text{Ni}(\text{NO}_3)_2$ to $\text{Fe}(\text{NO}_3)_3$ (different metal cation ratios were studied to optimize the composition of NiFe-LDH for OER (Figure 3-1& 3-2, marked as 10 mol% – 40 mol% Fe in NiFe-LDH) were quickly added into 20 mL of NaOH aqueous solution (0.15 M) under vigorous stirring. The precipitate was then centrifuged and washed three times with deionized (DI) water. Subsequently, after sonicating over night at room temperature, a stable homogenous suspension was obtained. The homogenous feature was attributable to the positive zeta potential of ~ 32 mV. The suspension was stable in DI water, ethanol or dimethylformamide (DMF). For comparison, hydrothermal treatments were also carried out at 100 °C to 120 °C for 24 h instead of sonication at room temperature.

Figure 3-1. FESEM images of NiFe-LDH nanosheets with different Fe contents. (a) 10 mol % Fe. (b) 20 mol % Fe. (c) 30 mol % Fe. (d) 40 mol % Fe. Insets: corresponding photographs of NiFe-LDH suspensions.

Figure 3-2. Polarization curves of NiFe-LDH with different Fe contents tested on RDE electrode. The percentage number represents mol% of Fe in NiFe-LDH.

Materials characterization: The morphology and structure of as-obtained catalysts were studied with field-emission scanning electron microscopy (FESEM, JEOL, JSM6700F) and transmission electron microscopy (TEM, JEOL 2100F). X-ray diffraction (XRD) patterns were recorded on Bruker AXS D8 Advance with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). Detailed compositional information was probed by X-ray photoelectron spectroscopy (XPS) on an ESCALAB 250 photoelectron spectrometer (Thermo Fisher Scientific) at 2.4×10^{-10} mbar using a monochromatic Al K α X-ray beam (1486.60 eV). All binding energies were referenced to the C 1s peak (284.60 eV) arising from adventitious hydrocarbons. Particle size distribution and zeta potential were determined by dynamic light scattering (DLS, Zeta PALS) using BI-200SM (Brookhaven, USA).

Electrochemical measurement: Electrochemical measurements were performed in a standard three-electrode cell using CHI 760D electrochemical workstation. Pt plate was used as the counter electrode and a saturated calomel electrode (in saturated KCl) as the reference electrode. All potentials were calculated with respect to reversible hydrogen electrode (RHE) based on: $E(\text{RHE}) = E(\text{Hg}/\text{Hg}_2\text{Cl}_2) + 0.059 \times \text{pH} + 0.241\text{V}$. The overpotential (η) was calculated by $\eta(\text{V}) = E(\text{RHE}) - 1.23\text{V}$. The working electrode was prepared by loading 3 μL of the catalyst suspension onto glassy carbon electrode with area of 0.196 cm^2 (catalyst loading: 0.05 mg/cm^2). The catalyst suspension was prepared by mixing 980 μL of 3.5 mg/mL NiFe-LDH suspension with 20 μL of 5 wt% Nafion solution under sonication for 1 h. To construct a microfiber electrode, well-dispersed NiFe-LDH nanosheets in DMF were drop-casted onto a multi-walled carbon nanotube (MWCNT) sheet on a polytetrafluoroethylene (PTFE) substrate, which was grown by a chemical vapor deposition method as described previously.[184] Subsequently after drying in vacuum, the NiFe-LDH@MWCNT sheet was peeled off and twisted into a fiber at a twisting speed of 200 rpm in 3 min. As MWCNT sheet is very thin and porous, NiFe-LDH nanosheets can easily penetrate into the sheet. The NiFe-LDH nanosheets will be

located both inside and outside of the MWCNT bundles. During electrochemical testing, the working electrode was cycled at a rate of 20 mV/s until achieving stable cyclic voltammetry scans. The current density was calculated by dividing as-measured current with the geometric area of the microfiber electrode ($A = \pi Dh$, where D and h are the diameter and length of the microfiber electrode, respectively). All electrochemical tests were performed in 1 M NaOH electrolyte, which was purged by O_2 for at least 30 min before data collection. Linear sweep voltammetry (LSV) and cyclic voltammetry (CV) measurements were recorded at a scan rate of 1 mV/s. AC impedance spectroscopy was acquired in a frequency range from 100 kHz to 0.1 Hz at an amplitude of 10 mV. Faraday efficiency was measured using volumetric method as described before.[185]

3.3 Results and discussion

Figure 3-3 displays the FESEM image of as-prepared NiFe-LDH nanosheets, which show uniform size distribution of around 33 nm (Figure 3-3). The nanosheets could be dispersed in DMF to form a stable colloidal suspension with clear Tyndall effect (inset in Figure 3-3). The detailed structure was further examined by transmission electron microscopy (TEM) as shown in Figure 3-3, which confirms the uniform size of NiFe-LDH nanosheets. HRTEM (inset in Figure 3-3) reveals a clear lattice spacing of around 0.23 nm, corresponding to (015) planes of NiFe-LDH. Figure 3-3 shows the XRD pattern with all peaks matching well with the LDH structure.[186] The observed peak broadening is resulted from the small crystal domain size of the nanosheets, particularly in the (00 l) direction.[187] X-ray photoelectron spectroscopy (XPS) spectra of Ni 2p_{3/2} and Fe 2p_{3/2} indicate that the Ni and Fe species exist in the +2 and +3 oxidation states, respectively (Figure 3-3 e & f). Ultrasonication plays an important role here not only to confine the size and crystallinity of NiFe-LDH nanosheets (Figure 3-4, but also to disperse them in solution to form stable suspensions (Figure 3-5, which could benefit their subsequent applications in electrocatalysis.

Figure 3-3. (a) FESEM image of as-prepared NiFe-LDH nanosheets. Inset shows a photograph of well-dispersed NiFe-LDH suspension with clear Tyndall effect. (b) TEM and HRTEM images (inset) of NiFe-LDH nanosheets. (c) XRD pattern of NiFe-LDH nanosheets. (d) Size distribution of NiFe-LDH nanosheets obtained from dynamic light scattering (DLS) measurement. (e & f) XPS spectra of Ni 2p and Fe 2p, respectively.

Figure 3-4. FESEM images of NiFe-LDH nanosheets prepared under different conditions: (a) without sonication, (b) sonication at RT, (c) hydrothermal at 100°C, and (d) hydrothermal at 120°C. (e) XRD patterns, and (f) polarization curves of NiFe-LDH nanosheets prepared at different temperatures (performances are tested on RDE electrode).

Figure 3-5. Photographs of NiFe-LDH nanoparticle suspension before and after sonication.

The electrocatalytic activity of as-prepared NiFe-LDH nanosheets towards OER was evaluated by rotating disk electrode (RDE) measurement in alkaline electrolyte. Figure 3-6 depicts the OER polarization curves of the NiFe-LDH nanosheets and the state-of-the-art IrO₂ nanoparticles (as a reference), which show that the overpotential required to drive a 10 mA/cm² OER current density (η_{10}) for NiFe-LDH nanosheets (~ 260 mV) is significantly lower than that for IrO₂ nanoparticles (~ 360 mV). Additionally, the NiFe-LDH nanosheets display lower onset potential and smaller Tafel slope (~ 21.2 mV/dec) as compared with that of IrO₂ nanoparticles (Tafel slope ~ 42.8 mV/dec). It is worth mentioning that the Tafel slope of our NiFe-LDH nanosheets is one of the smallest as reported in the literature (Table 3-1). Furthermore, the OER activity could be tuned by changing the Ni to Fe ratio in NiFe-LDH (Figure 3-2). The water oxidation reaction in basic electrolyte involves four elementary charge transfer steps, as described below:[104]

where M is the active site. The Tafel slope of 21.2 mV/dec indicates that the third electron transfer is the rate-limiting step for our NiFe-LDH nanosheets, once again verifying the favorable catalytic kinetics towards OER. The superior OER performance of our NiFe-LDH nanosheets as compared with those conventionally synthesized at higher temperatures could be attributable to the smaller size and defect-rich structure resulting from poorer crystallinity, which should offer more abundant active sites for OER (Figure 3-4). The mass activity could reach as high as 200 mA/mg at an overpotential of 260 mV by optimizing the catalyst loading (Figure 3-7).

Table 3-1. Comparison of OER performance of NiFe-LDH in 1 M alkaline electrolyte.

References	Tafel slope (mV/dec)	$\eta@10$ mA/cm ² (mV)	$\eta@30$ mA/cm ² (mV)	Loading amount (mg/cm ²)	Electrode
This work	21	260	—	0.05	NiFe-LDH nanosheets on glassy carbon electrode
This work	33	215	235	—	NiFe-LDH@MWCNT microfiber electrode
Ma, W.; et al. <i>ACS Nano</i> 2015, 9, 1977.	40	240	—	0.25	Alternately stacked NiFe-LDH nanosheets & Graphene on glassy carbon electrode
Lu, X.; et al. <i>Nat. Commun.</i> 2015, 6.	28	215	~ 250	—	Amorphous NiFe hydroxide electrodeposited on Ni foam [®]
Long, X.; et al. <i>Angew. Chem. Int. Ed.</i> 2014, 53, 7584.	39	206	~ 220	0.25	FeNi-rGO LDH on Ni foam [®]

Song, F.; Hu, X. <i>Nat. Commun.</i> 2014, 5.	40	302	—	0.07	Exfoliated NiFe-LDH nanosheets on glassy carbon electrode
Gong, M.; et al. <i>J. Am. Chem. Soc.</i> 2013, 135, 8452.	31	232	~ 260	0.2	NiFe-LDH/CNT on glassy carbon electrode

©Note: Ni foam is a three-dimensional conductive support, with thickness typically in the range of millimeters, which is much thicker than that of our microfiber electrode.

Figure 3-6 (a) Polarization curves, (b) Tafel plots for NiFe-LDH and IrO₂ nanoparticles tested on RDE electrode.

Figure 3-7. Mass activity as a function of the loading amount of NiFe-LDH nanosheets on glassy carbon electrode.

Note: The enhanced mass activity of the low loading amount is ascribed to gathering of the catalysts suspension, which is caused by the small amount of Nafion (extra ions caused the aggregation of the colloid).

However, insufficient long-term stability (Figure 3-13a inset) resulting from the poor electrical conductivity of LDH and weak contact between LDH and conductive support restricts the practical applications of our NiFe-LDH nanosheets. To overcome this problem and construct an efficient and stable OER electrode, we incorporated NiFe-LDH nanosheets into well-aligned and highly conductive multi-walled carbon nanotubes (MWCNTs) to form weavable microfiber electrodes. As schematically illustrated in Figure 3-8a, this could be achieved by twisting MWCNT sheets with the top surface casted with a thin layer of NiFe-LDH nanosheets. The MWCNT bundle offers a porous, flexible and conductive support for NiFe-LDH nanosheets towards OER electrocatalysis. Additionally, the entangled structure of MWCNT bundles creates numerous intimate contacts between NiFe-LDH nanosheets and MWCNTs. Figure 3-8b shows a MWCNT sheet made of many aligned MWCNTs. The long and aligned

MWCNTs could ensure good electrical conductivity and mechanical strength. Figure 3-8c displays a typical hybrid microfiber electrode with uniform diameter around 30 μm . After twisting, the NiFe-LDH nanosheets were uniformly distributed across the entire matrix of MWCNT bundles both inside and outside, resulting in homogeneous and smooth surfaces of MWCNT microfibers (Figure 3-8d). Enlarged FESEM image in Figure 3-8e clearly shows individual NiFe-LDH nanosheets, which binds firmly on the surface of MWCNT bundles, forming a thin layer. The loading amount of NiFe-LDH nanosheets could be adjusted by changing the concentration of NiFe-LDH nanosheets in the casting solution.

Figure 3-8. (a) Schematic illustration showing the steps of fixing NiFe-LDH nanosheets into MWCNT bundles. (b) FESEM image of a well-aligned MWCNT sheet. (c) Microscope image, (d) FESEM image, and (e) enlarged FESEM image of a NiFe-LDH@MWCNT microfiber electrode.

To investigate the OER performance of the microfiber electrode, a single fiber with length of around 5 mm was constructed and applied as the working electrode. The loading amount of NiFe-LDH nanosheets in the microfiber electrode could significantly affect the OER performance. Thus, we systematically optimized the loading and found that with 90 wt % of NiFe-LDH, the microfiber electrode had the best OER performance (Figure 3-9). Figure 3-10 shows the OER performance of an optimized microfiber electrode at a scan rate of 1 mV/s. It is found that the overpotential required to drive an anodic current density of 10 mA/cm² is as low as 215 mV (the current density was calculated based on the geometric area of the microfiber $A = \pi Dh$, where D and h are the diameter and length of the microfiber electrode, respectively). The OER current ramps up quickly with increasing applied voltage, reaching 180 mA/cm² at an overpotential of 255 mV, which to the best of our knowledge is the smallest among all reported values. The OER contribution from bare CNTs is negligible as shown in the control experiment in Figure 3-10a. The microfiber electrode has a Tafel slope of 33.3 mV/dec and an onset overpotential of ~ 195 mV, which are also among the lowest values reported in the literature. Because of micron-sized diameter, the microfiber electrode showed a large Ohmic loss during electrocatalysis (Figure 3-11). However, this Ohmic loss could be minimized by connecting a few microfiber electrodes in series for practical applications (Figure 3-12). Furthermore, the microfiber electrodes are highly flexible and thus they could be woven into fabrics with arbitrary patterns which should be beneficial for a large variety of electrochemical and catalytic applications.

Figure 3-9. Polarization curves of NiFe-LDH@MWCNT microfiber electrode with varying NiFe-LDH composition from 50% to 95%. Inset shows the surface morphology of 95% NiFe-LDH@MWCNT microfiber electrode. Deteriorating catalytic performance of 95% NiFe-LDH@MWCNT microfiber electrode was due to poor conductivity of too thick NiFe LDH layer. The percentage number represents wt % of NiFe-LDH in the microfiber electrode.

Figure 3-10. (a) Polarization curves of microfiber electrode with 90 wt% of NiFe-LDH nanosheets and bare CNT electrode. (b) Tafel slope of microfiber electrode with 90 wt% of NiFe-LDH nanosheets.

Figure 3-11. Polarization curves of 90 wt % NiFe-LDH@MWCNT microfiber electrode before and after iR correction.

Figure 3-12. AC impedance spectrum of electrode made of several parallel microfibers at an overpotential of 195 mV. Inset shows a photograph of the electrode.

The durability of the microfiber electrode was further tested to highlight its potential applications. For a single microfiber electrode with length of 5 mm at

an applied external potential of 1.47 V vs. RHE, the current density remained stable at around 38 mA/cm² over 24 h of continuous electrolysis (Figure 3-13a). The current jump mainly stemmed from bubbles detachment from the electrode. After 24 h of electrolysis, the linear sweep voltammetry curve was collected again as shown in Figure 3-13b, which almost overlapped with the one collected before stability testing, indicating excellent stability of the microfiber electrode. Furthermore, the morphology and elemental chemical states were probed before and after stability testing, which also showed minor changes. The shift of binding energy for Ni 2p, Fe 2p and O 1s towards lower values (Figure 3-14) was resulted from formation of OOH on the surface of NiFe-LDH during OER.[188, 189] The microfiber electrode had a high selectivity to oxygen by showing a nearly 100% Faradaic efficiency (Figure 3-13c). The high activity and durability renders the NiFe-LDH@MWCNT bundle microfiber electrode as an excellent candidate for practical OER applications in metal-air batteries and electrolysis cells.

Figure 3-13. (a) Stability test of NiFe-LDH@MWCNT bundle microfiber electrode at fixed overpotential of 240 mV over 24 h. Inset compares current density retention (%) of NiFe-LDH nanosheets on glassy carbon electrode at fixed overpotential of 265 mV (pink) with NiFe-LDH@MWCNT microfiber electrode over 1 h. (b) Polarization curves before and after 24 h of stability test.

(c) Faradaic efficiency measured at constant applied potential over 26 h. (d) Surface morphology of NiFe-LDH@MWCNT bundle microfiber electrode after 24 h of continuous electrolysis.

Figure 3-14. XPS spectra of NiFe-LDH before and after 24 h of electrolysis: (a) wide-scan spectra, (b) high resolution Ni 2P spectra, (c) high resolution Fe 2P spectra, and (d) high resolution O 1s spectra.

3.4 Conclusion

In summary, we have developed a facile and scalable co-precipitation method to prepare stable colloidal NiFe-LDH nanosheets at room temperature. The as-prepared NiFe-LDH nanosheets showed outstanding water oxidation activity in basic electrolyte with a low Tafel slope of 21.2 mV/dec and a high mass activity of 200 mA/mg at an overpotential of 260 mV. To overcome the poor conductivity of LDH and weak connection between LDH and conductive support in practical OER applications, we incorporated NiFe-LDH nanosheets into well-aligned MWCNT sheets to form hybrid microfiber electrodes. The microfiber

electrode showed excellent OER activity, reaching 180 mA/cm^2 at an overpotential of 255 mV with outstanding durability. Furthermore, the microfiber electrodes are highly flexible and could be woven into fabrics with arbitrary patterns. Our work could provide a general strategy to couple active electrocatalysts with porous, flexible and conductive carbon nanotubes for a wide range of electrochemical and catalytic applications.

Chapter 4 On the Use of Platinum as the Counter Electrode to Study the Activity of Nonprecious Metal Catalysts for Hydrogen Evolution Reaction?

4.1 Introduction

While we have engaged in developing efficient OER electrocatalysts in the last two chapters to enhance the efficiency of the water electrolyzer, the other half reaction hydrogen evolution reaction (HER) is also under intense investigation. Earth abundant HER electrocatalysts are being developed, in order to replace the noble metal Pt which is the most efficient electrocatalysts for water reduction. For example, molybdenum carbide coupled with reduced graphene oxide was prepared, which exhibits almost overlapped hydrogen evolution reaction (HER) activity with Pt/C.[28] Ni–C-based catalyst synthesized from carbonization of Ni-based metal organic frameworks (MOFs) was also reported to show similar HER performance as that of Pt.[38] However, by carefully studying these published works, it was noticed that Pt was unexceptionally chosen as the counter electrode without applying an ion-exchange membrane across the working and counter electrode during the electrochemical measurements. We therefore conducted a thorough literature survey and found that around 50% of the published HER studies adopted Pt as the counter electrode without the use of ion-exchange membrane (Figure 4-1).

Figure 4-1. Published work on hydrogen evolution reaction (HER) in the year of

2015 and 2016. Blue column: number of studies adopting Pt as the counter electrode[9-90] and red column: total number of studies on HER.

Note: Nature group includes: Nat. Mater., Nat. Chem., Nat. Energy, Nat. Commun.; Wiley includes: Angew. Chem., Int. Ed., Adv. Mater., Adv. Funct. Mater., Adv. Energy Mater.; ACS includes: J. Am. Chem. Soc., ACS Catal., Nano Lett., ACS Nano; RSC includes: Energy Environ. Sci.

Pt is considered as an inert metal towards oxidation. Therefore, it has been prevalently applied as the counter electrode in various electrochemical tests. However, from the aspect of thermodynamics, it is known that Pt can be oxidized and dissolved under certain chemical or electrochemical circumstances. For example, the presence of chloride in the acidic solution will enhance both the chemical and electrochemical dissolution of Pt due to the formation of stable chloride complexes (e.g. PtCl_3^- , PtCl_4^{2-} or PtCl_6^{2-}). [190, 191] Thus, it raises a question “can Pt be used as the counter electrode during the measurement of HER activity?”. To answer this question, we carried out a series of well-controlled experiments, which showed that the counter Pt electrode during HER would be unavoidably dissolved and re-deposited onto the HER catalyst, making the measured HER activity of the catalyst close or comparable to that of Pt, if no ion-exchange membrane was applied to separate the working from the counter electrode (Figure 4-2). The most severe dissolution of Pt occurs when the potential on the Pt counter electrode enables both Pt oxidation and reduction, while repetitive oxidation and reduction of Pt can further intensify the Pt dissolution. During HER measurements, cyclic voltammetry (CV) scans are typically applied to pre-treat the surface of electrocatalysts, where repetitive oxidation and reduction of Pt are highly possible, depending on the potential on the Pt counter electrode. The potential on the Pt counter electrode is not controlled by electrochemical workstation but determined by the current density passing through it. During HER measurements, the current density of Pt counter electrode is influenced by the characteristic/type of electrocatalysts, the relative

catalytic area of the working to the counter electrode, the potential scan range and the scan rate on the working electrode. The Pt dissolution and re-deposition is more severe in acidic medium as compared with the alkaline medium since reduction potential of Pt in alkaline medium is below 0 V vs. Ag/AgCl. Besides potential cycling during HER measurements, a small amount of Pt can be dissolved in both acidic and alkaline medium through Pt chemical dissolution. Therefore, counter electrode in any form of Pt (Pt plate or wire) should be avoided or used together with an ion-exchange membrane to prevent Pt re-deposition during the study of HER catalysis.

Figure 4-2. Schematic illustration showing Pt dissolution and re-deposition during the HER experiment if Pt is applied as the counter electrode.

4.2 Experimental section

Preparation of working electrodes: Carbon cloth was used as the HER working electrode to study the effect of Pt dissolution from the counter electrode. Carbon cloth was first immersed in Piranha solution overnight to make it hydrophilic and then thoroughly washed with DI water and kept in it before use. When applied as the working electrode, hot melt adhesives were applied to fix the area of carbon cloth. The most widely studied HER catalysts such as MoS₂ and Pt were also studied for comparison. To prepare the MoS₂ electrode, commercial MoS₂ powders (Sigma-Aldrich) were dispersed in a mixed solution of 980 μ L (1:1 DI water and isopropanol) with 20 μ L of 5 wt% Nafion solution and sonicated for 1

h. The mixed MoS₂ ink was loaded onto glassy carbon electrode (area of 0.196 cm² and 2 cm², respectively) with loading amount of 0.15 mg/cm². Polycrystalline Pt plates were purchased from Tian Jin Ai Da with area of 1 and 2 cm², respectively.

Characterization: The morphology of carbon cloth was characterized by field-emission scanning electron microscopy (FESEM, JEOL, JSM6700F). The re-deposited Pt nanoparticles were probed by X-ray photoelectron spectroscopy (XPS) with an ESCALAB 250 photoelectron spectrometer (Thermo Fisher Scientific) at 2.4×10^{-10} mbar using a monochromatic Al K α X-ray beam (1486.60 eV). The binding energies were calibrated against the C 1s peak (284.60 eV) arising from adventitious hydrocarbons.

Electrochemical measurements: A polycrystalline platinum plate (2 cm²) was used as the counter electrode for HER and the working electrode for studying its dissolution behavior. The roughness factor for Pt plate was determined to be around 1.6 from under potential deposition of hydrogen (H_{UPD}).^[192] Electrochemical experiments were carried out both in 0.5 M H₂SO₄ and 1 M KOH. The volume of the electrolyte was kept at 50 mL in all conditions. Current densities of Pt plate as well as carbon cloth were normalized to the projected geometric area (Pt plate and carbon cloth electrodes are double-sided while MoS₂ on glassy carbon electrode in single-sided). Graphite rod was used as the counter electrode for HER measurement. As surface state of working/counter electrode could be altered after electrochemical test, so for each measurement, the working and Pt counter electrode were freshly prepared as well as the electrolyte. The reference electrode was Ag/AgCl (saturated KCl, 0.198 V vs. RHE at room temperature) with salt bridge. To mimic the pretreatment condition during HER measurement (typically, several cycles of cyclic voltammetry would be performed until a relative steady curve was achieved), fast cyclic voltammetry (CV) scans at the rate of 100 mV/s were applied. Scan rate of 10 mV/s was also applied for comparison. The concentration of dissolved Pt was detected by

inductively coupled plasma mass spectrometry (ICP-MS) (Perkin-Elmer ELAN DRC-e). Coverage of Pt-O with different upper potential limit (E_{UPL}) was obtained through integrating the reduction peak of Pt-O during each CV cycle by considering the charge density of one monolayer of O chemisorption on Pt surface as $440 \mu\text{C}/\text{cm}^2$. [193]

Background

Measurement of potential on counter electrode

Potential on counter electrode (E_{CE}) is not widely taken care of since it just functions as the auxiliary part in the circuit. To study the dissolution effect of Pt, we tracked the potential on the Pt counter electrode using open circuit potential (OCP) mode with another electrochemical work station. The OCP is measured between the Pt counter electrode and Ag/AgCl reference electrode. Thus, $E_{\text{measure}} = E_{CE} + iR_u$. R_u is the uncompensated resistance in the circuit, including resistance of the electrolyte, the interface and Pt electrode itself. The measured R_u is about 1.5Ω in this work with distance of about 3 cm between Pt counter electrode and Ag/AgCl reference electrode. When compared with E_{measure} (usually above 0.6 V), the value of iR_u is negligible (especially for the charge/discharge current of double layer), so for simplicity, we just considered the E_{measure} as E_{CE} in our work.

Description of cyclic voltammetry

For ideally polarizable electrode, the voltage sweep will create current:

$$Q = CE \quad (1)$$

$$\frac{dQ}{dt} = C \frac{dE}{dt} \quad (2)$$

$$i = C v \quad (3)$$

where C is the capacitance of the electrode, v is the scan rate. i in the circuit is linearly proportional to the capacitance and scan rate, and the direction of current is in accordance with scan rate. For the same material, faster scan rate or larger

surface area (larger C) will result in larger current in the circuit. Ideally, the current remains constant and the shape of CV curve should be a rectangle. However, in reality, equivalent series resistance (including resistances in electrodes, electrical contacts and electrolyte) causes slow rise in current. Thus, we could observe slight current increase/decrease in the electric double layer region. As a result, the slight current change leads to potential variation of Pt counter electrode.

Background of the electrode system

Electrode potential is derived from the difference of internal potential between electrode and electrolyte, which is mainly determined by the electric double layer (EDL) at the phase boundary. When the current passes through the electrode, the current can either be consumed by electrode reaction or establish/change the electric double layer. If the current through the electrode is nonfaradaic current (the electrode is ideally polarizable) as stated above, the potential is determined by:

$$E = i \cdot t / C \quad (4)$$

When the current is consumed by electrode reaction (anodic polarization), the electrode potential is determined by Butler – Volmer equation (electron transfer step is the limiting step of the reaction):

$$\eta = -\frac{2.3 RT}{\beta F} \log i^0 + \frac{2.3 RT}{\beta F} \log i \quad (5)$$

Mechanism of Pt dissolution/re-deposition during HER

Pt dissolution can be induced chemically and/or electrochemically. Specifically, during the anodic scan, the oxidation of Pt is attributed to the adsorption of oxygenated species. The oxidation of Pt can be described by the following equations, where the oxidation products (PtO or PtO_2 , both are denoted as Pt-O) depend on the applied anodic potential (Figure 4-15b).

We evaluated the coverage of Pt-O as a function of E_{UPL} while fixing E_{LPL} at -0.2 V vs. Ag/AgCl (Figure 4-15b). The adsorption begins at around 0.8 V vs. Ag/AgCl with Pt-O coverage of 0.08 and increases with raising E_{UPL} . Complete coverage of Pt-O is achieved at around 1.1 V vs. Ag/AgCl. The Pt-O coverage reaches 3.76 as E_{UPL} increases to 1.6 V vs. Ag/AgCl. Above the complete coverage point, the electronegative O adsorption layer will induce occupation of sub surface sites, termed as the place-exchange (Pt-O_{ex}). Place exchange between the adsorbed O and surface Pt has been confirmed through X-ray scattering.[194] The place exchange effect can generate the exposure of oxidized Pt atoms (Pt-O_{ex}) at the surface and enable chemical dissolution at the unstable Pt-O_{ex} sites during anodic scan (Equation 8 & 9). More importantly, during the cathodic scan, Pt-O_{ex} sites can be reduced (Equation 10 & 11), resulting in low-coordinated Pt_{ex} that is much more prone to be dissolved than chemical dissolution during anodic scan (electrochemical dissolution, Equation 12). Therefore, Pt dissolution becomes more severe with increasing E_{UPL} and/or decreasing E_{LPL} .

Based on the above studies, it is clear to see that Pt can be dissolved from the Pt electrode during HER measurement if it is applied as the counter electrode (the potential on Pt electrode during HER is less than 0.6 V vs. Ag/AgCl). The dissolved Pt species are expected to re-deposit onto the working electrode (Equation 13 & 14) as shown in Figure 4-3d, which will greatly enhance the HER performance with much better catalytic activity than the catalyst itself and even

close to Pt, depending on the potential cycling process.

$$E = E^0 - \frac{RT}{2F} \ln \frac{1}{a_{Pt^{2+}}} = 1.188 + 0.0296 \log a_{Pt^{2+}} \quad (\text{vs. RHE}) \quad (13)$$

$$E = E^0 - \frac{RT}{4F} \ln \frac{1}{a_{Pt^{4+}}} = 1.15 + 0.0148 \log a_{Pt^{4+}} \quad (\text{vs. RHE}) \quad (14)$$

4.3 Results and discussion

To reveal the effect of Pt counter electrode on HER activity during electrochemical measurements, bare carbon cloth - a poor HER catalyst was chosen as the working electrode. Figure 4-3 a & b compare the HER performance of the carbon cloth electrode when graphite rod or Pt was separately applied as the counter electrode without adding an ion-exchange membrane to separate the working from the counter electrode. In the first case, the carbon cloth showed poor HER activity with a large HER onset of about 0.65 V vs. RHE. The HER activity maintained stable with increasing numbers of CV cycles (Figure 4-3a). However, when using Pt plate as the counter electrode instead, the HER performance of the carbon cloth electrode was continuously improved (Figure 4-3b). After 600 CV cycles, the performance of carbon cloth became comparable to that of Pt with nearly zero onset potential and robust current density. We further compared the morphology of the working electrode after 600 CV cycles as displayed in Figure 4-3 c & d. The carbon cloth electrode maintained the smooth surface if graphite rod was used as the counter electrode during water electrolysis, while plenty of bright nanodots were formed on the surface of carbon fiber if Pt counter electrode was used during the CV cycling. Those nanodots were identified as platinum by XPS as indicated in Figure 4-4. The same phenomenon has been previously reported by Dong and co-workers.[195]

Figure 4-3. HER polarization curves of carbon cloth in 0.5 M H_2SO_4 with (a) graphite rod and (b) Pt plate as the counter electrode, respectively. CE in (a) and (b) stands for counter electrode. FESEM images of carbon cloth after 600 CV cycles with (c) graphite rod and (d) Pt plate counter electrode.

Figure 4-4. XPS spectra of carbon cloth electrode after 600 CV cycles using Pt plate as the counter electrode. The binding energies of $\text{Pt } 4f_{7/2}$ and $\text{Pt } 4f_{5/2}$ are 71.6 eV and 74.9 eV, respectively, which are ascribed to metallic Pt.

Measurement of potential on the Pt counter electrode: To probe the formation process of Pt nanodots on carbon cloth, we need to figure out the

potential on the Pt counter electrode during HER measurement. It is known that the potential of counter electrode is not controlled by electrochemical workstation but automatically adjusted to enable the electric double layer (EDL)/chemical reactions on the counter electrode surface. It is easy to understand that the potential on the counter electrode increases with current density under potentiostatic condition (Figure 4-5). During HER measurement, CV scans are typically applied to clean or “activate” the surface of electrocatalysts. Different from potentiostatic measurement (steady state), CV is a transient technique, which consists of both faradaic and non-faradaic (EDL charging/discharging) current. It is more complicated to predict the potential range on Pt counter electrode during CV scans, since it is determined by the current passing through the counter electrode at points C2 and C3 (Figure 4-6). The potential on Pt counter electrode (carbon cloth, MoS₂ and Pt have been applied as the working electrode) is studied in detail during CV scans with varying relative catalytic areas of working and counter electrodes, CV scan ranges and scan rates.

Figure 4-5. Steady state potential of Pt plate counter electrode in 0.5 M H₂SO₄ during HER together with the corresponding LSV curve of carbon cloth. Steady state measurement of potential of Pt counter electrode was made under potentiostatic condition and recorded in the cathodic direction. E_{WE} and E_{CE} stand

for potential on working electrode and counter electrode, respectively.

Effect of relative catalytic area: The relative catalytic area of the working to the counter electrode is essential to determine the potential on Pt counter electrode during HER and thus Pt dissolution since different relative electrode area will lead to different currents at points C2 and C3 (Figure 4-6). In our experiments, we fixed the Pt counter electrode with an area of 2 cm² and varied the areas of the working electrodes. Larger area leads to both larger forward and backward current and finally results in larger potential range on the Pt counter electrode (Figure 4-7). Unlike carbon cloth or MoS₂, which has only double layer charging/discharging behavior before the hydrogen evolution reaction, Pt shows a redox feature, arising from H desorption (Figure 4-7e). The inset in Figure 4-7e shows the synchronized potential on Pt counter electrode when potential cycling is performed on the working electrode of Pt plate. During the anodic scan where H desorption takes place, the potential on the Pt counter electrode (2 cm²) declines to around 0.46 V vs. Ag/AgCl which is much smaller than the region without redox peak. The enhancement of anodic current is ascribed to the electrochemical desorption of adsorbed atomic hydrogen. Larger H desorption current (larger surface area) at the working electrode would result in larger reduction current at the counter electrode, therefore more negative potential of the counter electrode (Figure 4-7f). To figure out the relationship between current and the potential on Pt counter electrode, we further conducted CV scans on Pt plate (as working electrode) with varying scanning ranges (Figure 4-9 and Figure 4-10). Larger currents at both points W2 and W3 (Figure 4-6) reflect larger potential range (points C2 and C3, Figure 4-6) of the CV curve of Pt. Therefore, for the same HER catalyst, it is clear that increase in the relative catalytic area of the working electrode can lead to larger range of potential on the Pt counter electrode, which will accelerate the dissolution of Pt.

Figure 4-6. Schematic CV curves of working electrode and counter electrode during HER. Point 2 stands for the maximum potential while point 3 possesses the minimum potential on counter electrode. “W” stands for working electrode while “C” stands for counter electrode. The current in the circuit has the following relationship: $W3 = -C3$, $W2 = -C2$.

Note: For the working electrode, if the cathodic scan reaches W2, the largest current is achieved, leading to maximum potential on Pt counter electrode as stated in Figure 4-5. Furthermore, when the anodic scan reaches EDL region, discharging of EDL takes place (working electrode), resulting in the minimum potential on Pt counter electrode if reaches point C3.

Figure 4-7. (a), (c) and (e) CV curves for carbon cloth electrode, MoS₂ nanoparticles on glassy carbon electrode and Pt plate with varying electrode areas, respectively. Inset of (e) shows the CV curve of Pt plate (dark blue) together with the synchronized potential on Pt counter electrode (orange). (b), (d) and (f) The corresponding potential on the Pt counter electrode. Scan rate: 100 mV/s. E_{WE} and E_{CE} stand for potential on working and counter electrode, respectively.

Effect of scan range: The ranges of CV scan can influence the potential on the counter electrode. As shown in Figure 4-8a, if we fix the CV upper potential limit of the carbon cloth working electrode at 0 V vs. Ag/AgCl and vary the lower potential limit from -0.3 to -1.1 V vs. Ag/AgCl, the upper potential limit on Pt counter electrode will increase with CV scans having more negative values of the lower potential limit. The amplification of upper potential limit on Pt counter electrode varies in different catalyst systems (Figure 4-8b, d & f), which can be figured out with the aid of the CV curve of Pt (Figure 4-9). The maximum current

of carbon cloth is an order of magnitude larger than that of MoS₂ (Figure 4-8a & c). The large maximum current (at point W2 in Figure 4-6) of carbon cloth enables Pt counter electrode in the OER region (point C2 in Figure 4-6), indicating that large current change in the circuit only leads to small potential difference of Pt counter electrode (Figure 4-8b). On the other hand, the current of MoS₂ is on the plateau (oxygen adsorption) region in the Pt CV curve, suggesting that small current variation will cause large potential change on Pt counter electrode (Figure 4-8d). CV curve of Pt (Figure 4-8e) exhibits even larger maximum current, so the increase of the maximum potential vs. current increase on Pt counter electrode is slow (comparable to carbon cloth). More interestingly, when the potential scan reaches more negative values while fixing the upper potential limit at 0 V vs. Ag/AgCl on working electrode, the lower potential limit on Pt counter electrode (point C3 in Figure S5) decreases as shown in Figure 4-8b, d & f. This decrease is due to the larger current on the backward scan (point W3, Figure 4-8a, c & e). The observed phenomena could be explained by the polarization of the working electrodes, which arises from slower reaction rate than the electron transport rate. Large current or poor catalytic property can lead to severe electrode polarization. For the same material such as carbon cloth, more negative potential causes more intense polarization, so the current during the backward scan becomes larger with more negative scanning (Figure 4-8a), thus, smaller minimum potential on Pt counter electrode (Figure 4-8b). For different materials, carbon cloth has inferior catalytic property towards HER as compared to MoS₂, and the minimum potential of Pt counter electrode decreases faster when carbon cloth is applied as the working electrode. The mechanism of polarization can be further explained by the interface structure (electric double layer) between electrode and electrolyte (Figure 4-11). Furthermore, if we fix the lower CV potential limit and increase the upper potential limit, larger current will be obtained at point W3/C3, leading to a decreased minimum potential on Pt counter electrode (Figure 4-12).

Figure 4-8. (a), (c) and (e) CV curves with fixed upper potential limit at 0 V vs. Ag/AgCl and different lower potential limit for carbon cloth (2 cm²), MoS₂ (0.196 cm²) and Pt plate (2 cm²), respectively. (b), (d) and (f) The corresponding potential on the Pt counter electrode. Scan rate: 100 mV/s.

Figure 4-9 (a) CV curve of Pt plate (2 cm²) obtained at a scan rate of 100 mV/s in 0.5 M H₂SO₄ without degassing. (b) CV curve of the same Pt plate obtained in degassed 0.5 M H₂SO₄.

Note 1: For Pt electrodes, the electric double layer (EDL) region is ideally polarizable and the current is determined by equation 3 as shown in the Supporting Information. H_{UPD} desorption/adsorption is reversible and the external charge supplied will only cause changes in the surface condition. O adsorption/desorption is irreversible with reaction products Pt-O formed on surface. The latter two regions have much higher capacitance than the EDL capacitance since both the electrochemical adsorption/desorption of atomic hydrogen and electrochemical oxygen adsorption/desorption contribute to the total current. For the oxygen evolution reaction (OER) region, the current is derived from electrons consumed for oxygen evolution except for EDL charging/discharging. Based on the above analysis, it can be seen that the processes taking place on Pt electrode is quite complicated. Thus, CV curves of Pt (Figure 4-6) are needed to estimate the potential on Pt counter electrode during HER since different scan ranges will result in different CV curves.

Note 2: As displayed in Figure 4-5b, H_{UPD} desorption/adsorption current as well as double layer current moves towards the positive direction if the electrolyte is degassed by nitrogen to remove dissolved molecular oxygen. The current derived from the oxygen reduction reaction (ORR) on Pt contributes to more negative current when applied external potential is smaller than ~ 0.86 V vs. Ag/AgCl. When the external potential is larger than 0.86 V vs. Ag/AgCl, the CV curves overlap well (no ORR on Pt when potential is larger than 0.86 V vs. Ag/AgCl in 0.5 M H_2SO_4).

Figure 4-10. CV curves of Pt plate (2 cm^2) with different potential ranges in $0.5 \text{ M H}_2\text{SO}_4$ at a scan rate of 100 mV/s . Note: Different scan ranges will result in different current values of the Pt plate. As a result, it is difficult to determine the

potential on Pt counter electrode based on the current density of Pt plate. Nevertheless, we could figure out the measured potential ranges on the Pt counter electrode during catalysis by referring to the CV curves of Pt plate with corresponding potential ranges.

Figure 4-11. Electric double layer at the electrode/electrolyte interface.

Note: Electrode (HER) with inferior catalytic performance has slower reaction rate and more adsorbed hydrogen surface will be accumulated in electrolyte and more electrons within the catalyst material, when backward scan is applied and reaches the double layer region, the surplus adsorbed hydrogen will diffuse into the electrolyte and more electrons will be transported towards the counter electrode, thus smaller potential will be resulted on Pt counter electrode.

Figure 4-12. (a) CV curves of carbon cloth (2 cm²) with fixed lower potential limit at -0.5 V vs. Ag/AgCl and increased upper potential limit varying from -0.2 to 0.2 V vs. Ag/AgCl. (b) The corresponding potential on the Pt counter electrode. Scan rate: 100 mV/s.

Effect of scan rate: Scan rate can also influence the electrochemical measurements. Only with the aid of the Pt CV curve at different scan rates, we can predict the potential on the Pt counter electrode. We compared the potential of the Pt counter electrode measured at a scan rate of 100 mV/s (which is applied elsewhere in this work) with that obtained at a scan rate of 10 mV/s for the three different working electrodes (Figure 4-13). Figure 4-14 displays the Pt CV curves obtained at scan rates of 100 mV/s and 10 mV/s, respectively. To illustrate the result, carbon cloth as the working electrode is described in detail. As shown in Figure 4-13a, the current of the carbon cloth working electrode at point W3 is 0.077 mA and 0.006 mA at scan rates of 100 mV/s and 10 mV/s, respectively. Referring to the CV curve of the Pt counter electrode, as indicated in the inset of Figure 4-14a, the current at point C3 of Pt counter electrode is around -0.006 mA at 1.3 V vs. Ag/AgCl at a scan rate of 10 mV/s and -0.04 mA at a scan rate of 100 mV/s. To reach -0.077 mA, lower potential should be applied. As expected, we observe that the scan rate of 100 mV/s results in smaller lower potential limit on the Pt counter electrode as shown in Figure 4-13b. The results from the MoS₂ and

Pt working electrodes (Figure 4-13c~f) are also well fitted with the corresponding Pt CV curves (Figure 4-14b, c).

Figure 4-13. (a), (c) and (e) CV curves with scanning rate of 100 mV/s and 10 mV/s for carbon cloth (2 cm²), MoS₂ (0.196 cm²) and Pt plate (2 cm²), respectively. Inset of (e) shows the potential on Pt counter electrode vs. potential cycling on the working electrode. (b), (d) and (f) The corresponding potential on the Pt counter electrode.

Figure 4-14. CV curves of (a) carbon cloth (2 cm²) (b) MoS₂ on glassy carbon electrode (0.196 cm²) and (c) Pt plate (2 cm²) obtained at scan rates of 100 mV/s and 10 mV/s.

Potential-dependent Pt dissolution: The potential on the Pt counter electrode is critical for Pt dissolution. Figure 4-16a shows the typical CV curve of Pt in 0.5 M H₂SO₄ with peaks corresponding to under-potential electro-adsorption/desorption of H and the formation/reduction of Pt oxide. We investigated the influence of both the upper and lower potential limit during potential cycling on Pt dissolution. Specifically, as shown in Figure 4-15, when the lower potential limit (E_{LPL}) is fixed at -0.2 V vs. Ag/AgCl, the amount of Pt dissolution increases with increase of the upper potential limit (E_{UPL}). The dissolution amount abruptly increases at E_{UPL} larger than 0.8 V vs. Ag/AgCl, which is consistent with the potential of the Pt oxidation onset. However, during the potential cycling of HER tests, the value of E_{UPL} is not critical since the potential of counter electrode usually lies above the onset potential of Pt oxidation as indicated in Figure 4-7~4. E_{LPL} is more essential since it determines whether Pt-O can be reduced. Subsequently, we fixed the E_{UPL} at 1.6 V vs. Ag/AgCl, and varied the E_{LPL} from 0.4 to 1.2 V vs. Ag/AgCl with Pt as the work electrode and carbon cloth as the counter electrode. The amount of dissolved Pt vs. E_{LPL} was evaluated by ICP-MS as shown in Figure 4-16b. It is clear to see that the concentration of dissolved Pt dramatically increases with decrease of E_{LPL} . The corresponding LSV curves of the carbon cloth electrode as shown in Figure 4-16c exhibit evidently larger current densities when E_{LPL} is below 0.6 V vs. Ag/AgCl (Figure 4-16b). FESEM images (Figure 4-16d-h) show more deposition of Pt nanoparticles on carbon cloth when E_{LPL} is less than 0.6 V, verifying the trend of Pt dissolution.

Figure 4-15. (a) Effect of upper potential limit (E_{UPL}) during potential cycling. CV ranges are from -0.2 V vs. Ag/AgCl to different E_{UPL} of 0.25, 0.45, 0.65, 0.8, 0.97, 1.3, 1.6 V vs. Ag/AgCl. CV curves are obtained for 100 cycles at 100 mV/s in 0.5 M H_2SO_4 . (b) Coverage of Pt-O at different E_{UPL} .

Note: The amount of dissolved Pt in -0.2 to 1.6 V is much less than that in the scan range from 0.4 to 1.6 V, which is due to the fact that Pt can be more easily electro-deposited if the applied potential is more negative.

Figure 4-16. (a) CV curve of Pt plate obtained at a scan rate of 100 mV/s in 0.5 M H_2SO_4 . (b) Amount of dissolved Pt vs. E_{LPL} after 50 cycles of potential cycling at scan rate of 100 mV/s in 0.5 M H_2SO_4 . Potential range I: 0.4 to 1.6 V; II: 0.6 to 1.6 V; III: 0.8 to 1.6 V; IV: 1 to 1.6 V; and V: 1.2 to 1.6 V. (c) The corresponding LSV curves of the carbon cloth electrode. Scan rate: 10 mV/s. (d-h) FESEM images of the carbon cloth electrode after potential cycling.

Chemical Pt dissolution: Additionally, it is important to point out here that even without undergoing potential cycling, Pt is unstable to serve as the counter electrode for HER tests. Figure 4-17a compares the LSV curves of carbon cloth electrode tested in a freshly prepared 0.5 M H_2SO_4 with and without Pt plate immersion for just five minutes. We could clearly observe improved HER performance, which should be mainly resulted from Pt chemical dissolution of those low coordinated Pt atoms (e.g. corner or edge sites at kinks, steps and/or vacancies) as illustrated in Figure 4-17b. The dissolved Pt in solution reaches 0.49 ng/mL as confirmed by ICP-MS. We can imagine that the dissolution of standard Pt/C catalysts will be more severe due to their nanoscale sizes and higher degrees of defects. Thus, the electrolyte after testing Pt samples will be highly contaminated by Pt and should not be reused for other electrochemical tests.

Figure 4-17. (a) HER LSV curves of carbon cloth electrode obtained by applying graphite rod as the counter electrode. Red: in fresh 0.5 M H_2SO_4 ; black: in 0.5 M H_2SO_4 with immersion of Pt plate for 5 minutes. (b) Low coordinated Pt atoms on Pt (111), which can be quickly dissolved if immersed in H_2SO_4 . Red and yellow represent the corner and edge sites, respectively.

Pt dissolution in alkaline medium: Besides acidic media, alkaline electrolyte has been increasingly employed during water electrolysis. We further studied the effect of Pt dissolution in 1 M KOH (Figure 4-18~S4-15), chemical dissolution of Pt will enhance the performance of working electrode. Figure 4-18a displays a CV curve of Pt in 1 M KOH (0.5 M H_2SO_4 as electrolyte is included for reference as shown in Figure 4-18b). Although the oxidation and

reduction potential of Pt are similar in both electrolytes, the reduction potential of oxidized Pt is below 0 V vs. Ag/AgCl in 1 M KOH, which indicates that the electrochemical dissolution of Pt might not be that severe in alkaline media (Figure 4-18c). However, the use of Pt as the counter electrode during HER can still improve the HER activity of the working electrode (Figure 4-19,15), suggesting that chemical dissolution cannot be avoided even in alkaline electrolyte (the measured dissolved Pt species reach 0.54 ng/mL after Pt plate immersed in for five minutes).

Figure 4-18. (a) CV curve of Pt plate obtained at 100 mV/s in 1 M KOH. (b) CV curve of the same Pt plate obtained in 0.5 M H₂SO₄ is included for comparison. (c) Steady state potential of Pt plate as the counter electrode in 1 M KOH within the potential range of HER. Steady state measurement of potential of Pt counter electrode was made under potentiostatic condition and recorded in the cathodic direction.

Figure 4-19. LSV curves of the carbon cloth electrode after 1st and 600th CV cycles in 1 M KOH with graphite rod and Pt as the counter electrode, respectively. Scan rate: 100 mV/s.

Note 1: The current of carbon cloth exhibits tiny enhancement when graphite rod is applied as counter electrode. On the other hand, when Pt is applied as the counter electrode, the increase is more obvious with both earlier onset and larger current density.

Note 2: Here, we measured the LSV curves immediately after Pt/graphite rod counter electrode immersed in, so the initial LSV curves are quite similar. The performance enhancement after 600th CV cycles with Pt as counter electrode is ascribed to Pt chemical dissolution of fresh Pt plate (the same mechanism as shown in Figure 4-17b and the dissolved Pt species reached 0.54 ng/mL after Pt plate immersed in for just five minutes) as well as chemical dissolution of unstable Pt-O_{ex} during anodic scan.

Figure 4-20. FESEM images of the carbon cloth electrode after 600 CV cycles if (a) graphite rod was used as the counter electrode and (b) Pt plate was used as the counter in 1 M KOH. Scan range: $-0.8 \sim -1.9$ V vs. Ag/AgCl. Scan rate: 100 mV/s.

Note: The CV scan range in 1 M KOH is the same as that in 0.5 M H_2SO_4 after being converted to the potential vs. RHE.

4.4 Conclusion

In conclusion, we carefully studied the dissolution behavior of Pt as the counter electrode during the electrochemical measurement of HER activity. Our results show that both electrochemical and/or chemical dissolution of Pt in acidic or alkaline electrolyte cause re-deposition of Pt on the working electrode of interest, which significantly improves the HER activity. As a result, Pt should not be selected as the counter electrode for measuring the activity of HER unless it is coupled with an ion-exchange membrane, which is commonly ignored during the past research. Additionally, Pt is also susceptible to sulfur compounds (e.g., sulfide), nitrogen compounds (e.g., cyanide) and CO, leading to Pt poisoning due to the strong chemisorption.[196] Therefore, electrolyte purification to remove those poisonous impurities is necessary if Pt is chosen as the counter electrode. Considering how to choose the right counter electrode for electrochemical measurements, we provide the following suggestions: firstly, the counter electrode must be both chemically and electrochemically stable, for example

glassy carbon or graphite for oxidation reaction (counter electrode for HER or ORR) and Pt for reduction reaction (counter electrode for OER, little amount of Pt dissolution will not affect OER performance since Pt is prone to re-deposit onto cathode). Secondly, the half-reaction occurring at the counter electrode should be fast enough to enable the reaction at the working electrode. Regarding this point, alternative strategies can be adopted. One approach is to choose counter electrode with high catalytic activity and another is to render the counter electrode with larger surface area than that of the working electrode to make up the large energetic barrier. Our work provides a complete understanding of the Pt counter electrode effect during HER characterization and should arouse the awareness of the results in those recently published papers.

Chapter 5 Conclusions and outlook

Earth abundant OER electrocatalysts with Fe, Co and Ni are reported. In the first part, NiCo_2O_4 with three-dimensional core-shell nanowire arrays were fabricated and showed the overpotential of ~ 320 mV at a current density of 10 mA/cm^2 . The electrode functioned stably during an extend period. The NiCo_2O_4 OER electrode developed in this thesis outperforms other reported NiCo_2O_4 , owing to the high surface area, ultrathin porous nanoshell, and enhanced mass and charge transport. Based on this work, we provided a promising way for achieving efficient OER electrocatalysis using inexpensive, earth-abundant and easily prepared electrocatalyst on flexible electrodes.

To further enhance the performance of the OER electrode, we have studied the NiFe-LDH, which is among the most efficient OER catalysts. We developed a facile and scalable co-precipitation method to prepare stable colloidal NiFe-LDH nanosheets at room temperature. The as-prepared NiFe-LDH nanosheets showed outstanding water oxidation activity in basic electrolyte with a low Tafel slope of 21.2 mV/dec and current density of 10 mA/cm^2 at an overpotential of 260 mV. To overcome the poor conductivity of LDH and weak connection between LDH and conductive support in practical OER applications, we incorporated NiFe-LDH nanoparticles into well-aligned MWCNT sheets to form hybrid microfiber electrodes. The microfiber electrode showed excellent OER activity, reaching 180 mA/cm^2 at an overpotential of 255 mV with outstanding durability. Furthermore, the microfiber electrodes are highly flexible and could be woven into fabrics with arbitrary patterns. Our work provided a general strategy to couple active electrocatalysts with porous, flexible and conductive carbon nanotubes for a wide range of electrochemical and catalytic applications.

Our attention has also been diverted to the measurement techniques in HER, owing to the Pt dissolution/re-deposition issues that have been easily ignored by researchers. Our results show that the most severe dissolution of Pt occurs when

the potential on the Pt counter electrode enables both Pt oxidation and reduction, while repetitive oxidation and reduction of Pt can further intensify the Pt dissolution. The Pt dissolution and re-deposition is more severe in acidic medium as compared with the alkaline medium since reduction potential of Pt in alkaline medium is below 0 V vs. Ag/AgCl. Besides potential cycling during HER measurements, a small amount of Pt can be dissolved in both acidic and alkaline medium through Pt chemical dissolution. As a result, Pt should not be selected as the counter electrode for measuring the activity of HER unless it is coupled with an ion-exchange membrane, which is commonly ignored during the past research. Our work provides a complete understanding of the Pt counter electrode effect during HER characterization and should arouse the awareness of the results in those recently published papers.

Owing to the merit of hydrogen production through electrochemical water splitting, more research is required concerning the development of highly efficient and cost effective electrocatalysts. Proton exchange membrane (PEM) electrolyzer is promising for large-scale industry application. The challenge is that the electrocatalysts which are able to work efficiently in acidic media are limited to iridium and ruthium oxide, which are expensive and suffer from instability over long time. Alkaline-exchange membrane (AEM) electrolyzer needs lower investment costs and is competitive for large scale industry application. As a result, electrocatalysts which are capable to work at large current density (100-500 mA/cm²) and are stable in hot alkaline (60-80°C) are highly desired. The study is best to be conducted by applying the most efficient electrocatalysts. By now, the NiFe LDH developed in chapter 3 is highly efficient and is among the optimum electrocatalysts, including low overpotential as well as stable performance over dozens of hours. However, it remains questionable whether the stability that accessed for that limited number of hours could provide the basis upon which one could judge the long term performance of a catalyst in a real device over a number of years. For long time inspection of a certain

electrocatalysts, measuring the concentration of the dissolved metal ions through ICP-MS in the electrolyte after a certain duration of electrolysis could provide the information of stability. The different concentration during different measuring time could inform us whether the electrocatalysts are stable or not. Consequently, further optimization of the NiFe based electrocatalysts to achieve desirable adsorption energy of reaction intermediates as well as the evaluation of its stability on application in industry conditions are recommended for the future research.

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