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**EXPLORATION OF THE SPIN RELATED REACTION
MECHANISMS OF OXYGEN
ELECTROCATALYSIS**

CHEN RUIXI

Interdisciplinary Graduate School

Energy Research Institute @NTU

2022

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**Interdisciplinary Graduate School
Energy Research Institute @NTU**

A thesis submitted to the Nanyang Technological University in partial
fulfillment of the requirement for the degree of
Doctor of Philosophy

2022

Statement of Originality

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

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I have reviewed the content and presentation style of this thesis and declare it is free of plagiarism and of sufficient grammatical clarity to be examined. To the best of my knowledge, the research and writing are those of the candidate except as acknowledged in the Author Attribution Statement. I confirm that the investigations were conducted in accord with the ethics policies and integrity standards of Nanyang Technological University and that the research data are presented honestly and without prejudice.

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Prof XU ZHICHUAN, JASON

Authorship Attribution Statement

This thesis contains material from two papers published in the following peer-reviewed journals where I was the first or co-first author.

Chapter 4 is published as Chen, Riccardo Ruixi, Yuanmiao Sun, Samuel Jun Hoong Ong, Shibo Xi, Yonghua Du, Chuntai Liu, Ovadia Lev, and Zhichuan J. Xu. "Antiferromagnetic Inverse Spinel Oxide LiCoVO₄ with Spin-Polarized Channels for Water Oxidation." *Advanced Materials* 32, no. 10 (2020): 1907976. DOI: 10.1002/adma.201907976.

The contributions of the co-authors are as follows:

- Assoc. Prof Zhichuan J. Xu and I provided the initial project idea and Assoc. Prof Zhichuan J. Xu supervised the entire project.
- I prepared the manuscript drafts. The manuscript was revised by Assoc. Prof Zhichuan J. Xu and me. Prof Chuntai Liu and Prof Ovadia Lev provided valuable suggestions which helped to polish the manuscript.
- I synthesized all the catalysts, conducted all electrochemical measurements and analyzed the data.
- Dr Yuanmiao Sun conducted the DFT simulation.
- Samuel Jun Hoong Ong took the TEM images and helped to polish the manuscript.
- Dr Y. Du and Dr S. Xi assisted in the collection of the X-ray absorption fine structure data in Singapore Synchrotron Light Source. Dr Shibo Xi and I analyzed the data together.
- The XPS measurement was conducted by the Facility for Analysis, Characterization, Testing and Simulation (FACTS), Nanyang Technological University, Singapore. Dr. Teddy Salim and I analyzed the XPS data.

Chapter 5 is published as Jingjie Ge, Riccardo Ruixi Chen (co-first author), Xiao Ren, Jiawei Liu, Samuel Jun Hoong Ong, Zhichuan J. Xu. "Ferromagnetic–Antiferromagnetic Coupling Core–Shell Nanoparticles with Spin Conservation for Water Oxidation." *Advanced Materials*, 2021, DOI: 10.1002/(ISSN)1521-4095 (In press).

The contributions of the co-authors are as follows:

- Assoc. Prof Zhichuan J. Xu suggested the initial project direction and designed the experiment with Dr Jingjie Ge and I. Assoc. Prof Zhichuan J. Xu supervised the entire project.
- I wrote the manuscript drafts. Assoc. Prof Zhichuan J. Xu and Dr Jingjie Ge and I discussed and analyzed the experimental data. The manuscript was revised by Assoc. Prof Zhichuan J. Xu, Dr Jingjie Ge and me.
- Dr Jingjie Ge synthesized the catalysts and conducted the electrochemical measurements.
- I led the project and analyzed the electrochemical data. There were intensive discussions between Dr Jingjie Ge and me.
- Dr Xiao Ren assisted with vibrating sample magnetometer (VSM) measurements and collected VSM data. The VSM data was analyzed by Dr Xiao Ren, Dr Jingjie Ge and me.
- The XPS measurement was conducted in the Facility for Analysis, Characterization, Testing and Simulation (FACTS), Nanyang Technological University, Singapore by Jiawei Liu. Dr Jingjie Ge and I analyzed the XPS data.
- Samuel Jun Hoong Ong helped to polish the manuscript.

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CHEN RUIXI

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Summary

Exploring highly efficient catalysts for the oxygen evolution reaction (OER) is essential for water electrolysis. Cost-effective transition-metal oxides with reasonable activity are raising attention. This thesis presents in-depth studies to explore spin-dependent OER mechanisms for transition metal oxide catalysts and proposes a new rational design for highly efficient OER catalysts. This thesis firstly investigates the significance of spin channels for water oxidation. A layered antiferromagnetic inverse spinel oxide LiCoVO_4 , which possesses spin-polarized edge-shared Co^{2+} octahedra channels, is synthesized. I demonstrate that these spin-polarized channels facilitate spin-selective electron transfer during OER and promote triplet oxygen generation. Besides that, I design bi-magnetic core-shell nanoparticles (NPs) with different core sizes and shell thicknesses that mimic surface reconstructed catalysts to investigate the effect of magnetic domain structure on direct magnetic field induced OER catalytic activity enhancement phenomena. In these studies, I find that the interfacial FM-AFM coupling of these core-shell catalysts facilitates selective removal of electrons with spin direction opposing the magnetic moment of their FM cores, improving OER kinetics. Also, the FM core's domain structure is critical for the spin-selective electron transport process. I, therefore, propose a magnetism/OER activity model that depends on two main parameters: interfacial spin coupling and domain structure. Lastly, I apply the findings from these studies to design a good OER catalyst, $\text{SmCo}_5/\text{CoO}_x\text{H}_y$ core-shell particle, for high temperature practical applications. It maintained the magnetic field induced OER activity enhancement even at an elevated temperature of 60 °C. This catalyst's unique property grants it huge potential to utilize spin-

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Abbreviations

OER	Oxygen Evolution Reaction
ORR	Oxygen Reduction Reaction
RDE	Rotating Disk Electrode
CV	Cyclic Voltammetry
CP	Chronopotentiometry
TOF	Turnover Frequency
VSM	Vibrating-sample Magnetometer
SEM	Scanning Electron Microscope
TEM	Transmission Electron Microscopy
HRTEM	High-Resolution Transmission Electron Microscopy
XRD	X-ray Diffraction
XAS	X ray Absorption Spectroscopy
XANES	Extended X Ray Absorption Fine Structure
XPS	X-ray Photoelectron Spectroscopy
ICP-ms	Inductively Coupled Plasma mass spectrometry
DFT	Density Functional Theory

List of Publication

1 **Riccardo Ruixi Chen**, Yuanmiao Sun, Samuel Jun Hoong Ong, Shibo Xi, Yonghua Du, Chuntai Liu, Ovadia Lev, and Zhichuan J. Xu. "Antiferromagnetic Inverse Spinel Oxide LiCoVO₄ with Spin - Polarized Channels for Water Oxidation." *Advanced Materials* 32, no. 10 (2020): 1907976.

2 Jingjie Ge, **Riccardo Ruixi Chen (co-first author)**, Xiao Ren, Jiawei Liu, Samuel Jun Hoong Ong, Zhichuan J. Xu. "Ferromagnetic–Antiferromagnetic Coupling Core–Shell Nanoparticles with Spin Conservation for Water Oxidation." *Advanced Materials*, 2021, DOI: 10.1002/(ISSN)1521-4095 (In press).

3 Chen, Gao, Yuanmiao Sun, **Riccardo Ruixi Chen**, Chiara Biz, Adrian Fisher, Matthew P. Sherburne, Joel W. Ager, Jose Gracia, and Zhichuan J. Xu. "A discussion on the possible involvement of singlet oxygen in oxygen electrocatalysis." *Journal of Physics: Energy* (2021).

Chapter 1

Introduction

1.1 Background and hypothesis

Since the late eighteenth century, fossil fuels have powered industrialization and human activities. However, the massive consumption of fossil fuels causes severe environmental impacts on our planet. Utilizing clean and renewable energy sources to meet increasing global energy demand and mitigate the environmental impact is becoming necessary. The intermittent nature of renewable energy sources requires suitable energy conversion and storage technologies. Electrochemical water splitting, which stores the harvested renewable energy in the form of H₂ gas, is one prominent energy conversion and storage technology. Electrochemical water splitting involves two half-cell reactions, the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER). Compared to the HER, the OER is a complex four-electron-transfer reaction which has very sluggish reaction kinetics, thus hindering the overall energy conversion efficiency.^[1-3] To improve the OER performance, good OER catalysts are essential. Cost-effective transition metal oxides attract plenty of research interest because of their competitive OER activity and rich electronic and physical properties.

Decades of research efforts in this field have resulted in the discovery of several valuable descriptors and principles, such as e_g theory,^[4] electron transfer energy,^[5] metal-oxygen bond covalency^[6-7] and covalency competition in spinel oxides,^[8] to

guide the design of efficient OER catalysts. These descriptors and principles are closely related to the adsorption/desorption energy of OER reaction intermediates, which originate from the Sabatier principle. More recently, researchers have begun to realize that some electrochemical reactions are spin-dependent, and that the OER is one of them. Pioneering work has been done by R. Naaman et al, who focused on chiral molecules and proposed the concept of Chiral-Induced Spin Selectivity Effect (CISS) in electrochemical reactions.^[9] Under alkaline conditions, the reactants of OER are $\text{OH}^-/\text{H}_2\text{O}$ which possess singlet spin configuration, however, the product of OER is triplet oxygen gas.^[10-12] The generation of triplet product from singlet reactant leads to slow reaction kinetics.^[3, 13-14] In order to tackle this issue, layered-antiferromagnetic and ferromagnetic catalysts which could promote spin-selective electron transfer process have been developed. Galán-Mascarós, J. R et al have reported that the OER activities of several ferrites were significantly enhanced by applying an external magnetic field.^[15] They proposed that the magnetic field induced OER activity enhancement is related to the catalysts' bulk magnetic properties. However, a detailed mechanism is missing. To facilitate the spin-selective electrons transfer process and boost OER reaction kinetics, I investigated a layered-antiferromagnetic LiCoVO_4 inverse spinel oxide, which stabilizes OER active Co^{2+} ions in the edge-shared octahedral sites ($\text{Co}^{2+}_{\text{Oh}}$).^[16-18] In an octahedral crystal field, the d^7 Co^{2+} ions exhibit high spin configuration $S = 3/2$ ($t_{2g}^5 e_g^2$),^[19] which means each $\text{Co}^{2+}_{\text{Oh}}$ ion has an ideal magnetic moment of 3 μ_B . As a result of the presence of $\text{Co}^{2+}_{\text{Oh}}$ ions in octahedral sites of the spinel structure, these edge-shared octahedral channels are magnetically polarized. These magnetically polarized channels are able to facilitate spin-selective electron transfer during the OER and facilitate triplet oxygen generation.^[3, 10] In comparison, I also investigated

a normal spinel oxide catalyst ZnCo_2O_4 which possesses OER active Co^{3+} ions (Co^{3+} ions possess low spin $S = 0$, $t_{2g}^6 e_g^0$), but the edge-shared Co^{3+} octahedra in this material are not magnetically polarized. The thesis tests this hypothesis in chapter 4, which reveals the significance of spin-polarized channels for water oxidation.

Some researchers tried to use density functional theory (DFT) simulations to find out the root mechanism of those phenomena, such as when Gracia et al. proposed the magnetic moment μB^{eg} of active site's e_g electrons as an OER descriptor for transition-metal perovskite oxides.^[3] These pioneering works provide a much clearer view of the fundamental origin of the magnetic field induced OER activity enhancement. However, these DFT models have their limitations, as most highly active oxide-based OER catalysts are not very stable and undergo surface reconstruction during OER.^[20-21] Reconstructed catalysts are in a core/shell structure, with an OER active oxyhydroxide shell that serves as the real active surface. Here I propose that using bi-magnetic core-shell catalysts which mimic surface reconstructed catalysts could be a better way to explore the origin of the direct magnetic field induced enhancement of OER than the aforementioned bulk catalysts. I prepared several $\text{Fe}_3\text{O}_4@\text{Ni}(\text{OH})_2$ core-shell nanoparticle samples with different Fe_3O_4 core sizes and different shell thicknesses. I proposed that by controlling the Fe_3O_4 core size, I could tune the magnetic domain structure of ferromagnetic (FM) Fe_3O_4 . By controlling the shell thickness of antiferromagnetic (AFM) $\text{Ni}(\text{OH})_2$, I was able to investigate the effect of the interfacial properties. Thus, I am able to link the bulk magnetic properties of the FM core and interfacial properties to the not well-understood magnetic field induced enhancement of

oxygen catalysis. The thesis tests this hypothesis in chapter 5. The result reveals that only multi-domain catalysts exhibit the magnetic field induced OER enhancement, and the interfacial FM-AFM coupling also plays an important role.

In addition, for practical applications, water electrolyzers operate at elevated temperatures (50 to 80 °C) to boost overall efficiency as opposed to the room temperature (25 °C) at which most catalysts are investigated.^[22] The bulk magnetic properties of OER catalysts are closely related to the temperature. The elevated operation temperature of water electrolyzers exceeds the Curie temperature of most FM OER catalysts, thus, the ordered spin alignment of FM OER catalysts would be disrupted by thermal agitation.^[23-24] Therefore there is a need for the development of high Curie temperature FM OER catalysts which could utilize the unique interfacial FM-AFM coupling and spin-selective electron transfer properties of FM OER catalysts for practical applications. Here I proposed a $\text{SmCo}_5@ \text{CoO}_x\text{H}_y$ core-shell catalyst as a suitable candidate for high temperature OER applications. The SmCo_5 core is a strong FM material with a very high Curie temperature (1020 K)^[25] which indicates that its ordered bulk spin alignment and magnetic properties should be preserved even at high operating temperature. The thesis tests this hypothesis in chapter 6. The result reveals that the magnetic field induced OER enhancement is retained at a maximum operating temperature of 60 °C. Moreover, the $\text{SmCo}_5@ \text{CoO}_x\text{H}_y$ exhibits a promising TOF. This finding indicates that the $\text{SmCo}_5@ \text{CoO}_x\text{H}_y$ catalyst has great potential for practical applications.

1.2 Objective and scope

The overall objective of this thesis is to explore the not well-studied spin-related OER mechanism and propose a useful design method of highly efficient OER catalysts. This could help the community to better understand the magnetic field induced enhancement of oxygen electrocatalysis and serve as a guidance for OER catalyst design. It is known that OER is a spin-dependent electrochemical reaction and that the generation of triplet oxygen gas from singlet reactants $\text{OH}^-/\text{H}_2\text{O}$ leads to slow reaction kinetics. To solve this issue, layered AFM inverse spinel oxide LiCoVO_4 was investigated. The edge-shared octahedra with high spin Co^{2+} centers would form spin-polarized channels which promote spin-selective electron transfer and facilitate the triplet oxygen generation. As most highly active oxide-based OER catalysts undergo surface reconstruction during the reaction, previously established relationships between catalysts' bulk magnetic properties and OER activities are limited. To gain a better understanding, I proposed that FM-AFM core-shell catalysts could be a suitable model to mimic the surface reconstructed OER catalysts. $\text{Fe}_3\text{O}_4@\text{Ni}(\text{OH})_2$ core-shell catalysts with different core sizes and shell thicknesses were investigated. By tuning the core size and shell thickness, the catalyst's FM core domain structure and interfacial properties between core and shell region were investigated. This study reveals that the interfacial FM-AFM coupling of $\text{Fe}_3\text{O}_4@\text{Ni}(\text{OH})_2$ core-shell catalysts acts as a spin filter which facilitates selective removal of electrons with spin direction opposing the magnetic moment of FM core during the OER process. Furthermore, the magnetic domain structure of the FM core plays a critical role in the electron transport process. An external magnetic field could align the FM core's magnetic domains in an orderly fashion, which facilitates spin-selective electron transport with minimal scattering.

Lastly, in industrial applications, water electrolyzers are operated at elevated temperatures (50 to 80 °C) to boost overall reaction efficiency. However, most OER catalysts developed in the laboratory are investigated under room temperature conditions. This high operation temperature exceeds the Curie temperature of most FM catalysts which could disrupt the ordered spin alignment of FM catalysts. Thus, the unique magnetic field induced OER activity enhancement of FM OER catalysts cannot hold at elevated temperatures. By designing a $\text{SmCo}_5@ \text{CoO}_x\text{H}_y$ catalyst with a high Curie temperature FM SmCo_5 core, it is possible to preserve the magnetic field induced OER activity enhancement even at a high operating temperature. This catalyst exhibits great potential for practical applications.

1.3 Dissertation Overview

This thesis explores the spin-related reaction mechanism of oxygen electrocatalysis and draws a magnetism/OER activity correlation model that depends on two main parameters: interfacial spin coupling and domain structure. Moreover, this thesis also presents a highly active OER catalyst $\text{SmCo}_5@ \text{CoO}_x\text{H}_y$ which is suitable for high temperature practical applications.

Chapter 1 gives the detailed background of spin-dependent oxygen electrocatalysis and the rationale for the fundamental research on spin-dependent oxygen electrocatalysis. This chapter also highlights the scope and goals of this thesis.

Chapter 2 reviews the previous literature on the recent development of oxide-based OER catalysts and summarizes the important principles and descriptors that have been discovered. This chapter gives an overview of oxygen electrocatalysis for the readers.

Chapter 3 discusses the material synthesis and characterization methods and validates the logic of experimental design in this thesis. It also covers the data analysis methods for electrochemical data which were used in this thesis.

Chapter 4 investigates a layered-antiferromagnetic LiCoVO_4 inverse spinel oxide which possesses magnetic polarized edge-shared octahedra. This chapter reveals that these magnetically polarized channels are able to facilitate spin-selective electron transfer during the OER and facilitate triplet oxygen generation.

Chapter 5 uses bi-magnetic core-shell $\text{Fe}_3\text{O}_4@\text{Ni}(\text{OH})_2$ which mimics surface reconstructed catalysts to explore the origin of the direct magnetic field induced enhancement of OER activity. This chapter reveals both interfacial FM-AFM coupling and the core's magnetic domain structure play an important role in spin-dependent OER. The magnetism/OER activity model revealed in this chapter provides a new design method for OER catalysts.

Chapter 6 applies the new design method proposed in chapter 5 to design a highly OER active catalyst $\text{SmCo}_5@\text{CoO}_x\text{H}_y$. The $\text{SmCo}_5@\text{CoO}_x\text{H}_y$ possesses a high Curie temperature FM SmCo_5 core. It could maintain the magnetic field induced OER activity enhancement at an elevated temperature of 60 °C. This catalyst's unique property grants it huge potential to utilize spin-selective electron transfer, induced by the spin-pinning effect, in high temperature practical and industrial applications.

Chapter 7 draws a conclusion for the thesis and suggests future work.

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Chapter 2

Literature Review

2.1 Background of transition metal oxides in energy conversion and storage technologies

Fossil fuels such as coal, diesel and petroleum are current major energy sources for human society. The usage of these fossil fuels has caused severe environmental impacts, like air pollution and global warming. Thus, it is important to utilize environmentally friendly energy sources to reduce the consumption of fossil fuels. However, most renewable energy sources have intermittent natures, which means effective energy conversion and storage techniques are required. Techniques that depend on oxygen and hydrogen electrocatalysis, such as metal-air batteries, water electrolyzers and PEM fuel cells, attract plenty of research interest. Figure 2.1 gives an overview of the energy conversion and storage cycle based on oxygen and hydrogen gases.^[1] The harvested renewable energy can be stored in chemical bonds by using electrolyzers to split water into oxygen and hydrogen gases. The stored energy can be converted into electricity by PEM fuel cells. It is found that the overall device efficiency of electrolyzers and fuel cells is limited by the slow reaction kinetics of oxygen-related electrochemical reactions, namely oxygen evolution reaction (OER) and oxygen reduction reaction (ORR). Thus, effective catalysts are essential.^[1-2]

Figure 2.1 (a) Schematic illustration of H₂ and O₂ based energy conversion and storage technique. (b) Illustration of the overpotentials of OER, ORR, HER and HOR. (c) Schematic illustration of a water electrolyzer. (d) Schematic illustration of a PEM fuel cell.^[1]

Noble metals and noble metal oxide catalysts, such as IrO₂ and RuO₂ (OER catalysts) and Pt/C (ORR catalyst), exhibit excellent catalytic performance for the OER and ORR. However, they have extremely high prices and limited reserves making them unsuitable for practical applications. Thus, cost-effective transition metal-oxide-based catalysts with competitive catalytic performance are promising alternatives.

2.2 Practices and benchmark system of oxygen catalysis

To accelerate the development of oxygen electrocatalysis, a good benchmark system is essential to promote direct comparison between catalysts' catalytic activity.^[3] Currently, there are three major parameters, (1) specific activity based

on the catalysts' surface area; (2) the overpotential at a fixed current density; (3) the specific mass activity.

The specific/intrinsic catalytic activity of the catalyst is defined as current per unit surface area of the catalyst.^[4] It is important to obtain the accurate surface area in order to precisely evaluate the specific catalytic activity of a catalyst. Commonly, there are two approaches to obtain the catalysts' surface area, (1) the electrochemically active surface area (ECSA) measurement; and (2) Brunauer–Emmett–Teller (BET) surface area measurement. For oxide-based catalysts, in order to determine the ECSA of catalysts, the double-layered capacitance (C_{DL}) needs to be measured first.^[4-5] As shown in Figure 2.2a, by applying scan-rate dependent cyclic voltammograms (CV) measurements at the non-Faradaic region, the non-Faradaic capacitive current (i_c) could be obtained.^[6-7] It is known that the i_c equals the scan rate (ν) multiplied by the double-layer capacitance C_{DL} ($i_c = \nu C_{DL}$). By plotting the capacitive current versus the scan rate and applying a linear fitting, the slope of the fitted line is equal to the C_{DL} (Figure 2.2b).^[4-5] The ECSA of the catalyst could be obtained by normalizing the C_{DL} to the specific capacitance (C_S) of the oxide ($ECSA = C_{DL}/C_S$). The commonly used value of specific capacitance for metal oxides is $40 \mu F/cm^2_{ox}$.^[8] However, the C_S values of different transition metal oxides vary from 22 to $130 \mu F/cm^2_{ox}$ in alkaline conditions, which leads to a significant error in the ECSA measurement.^[4, 9] In addition, it is very challenging to measure the C_S for powder samples experimentally.

Figure 2.2 (a) Illustration of how to obtain the double-layer capacitance of oxide-based catalysts. (b) Non-faradaic capacitive current as a function of scan rate.^[4]

The BET method utilizes the isothermal physisorption of gas molecules on a sample surface to measure the specific surface area of the sample.^[4] It is clear that the BET surface area accurately represents the surface area of powder samples. The major concern is the validity of using BET surface area to evaluate the catalysts' specific activity. The BET surface area is not the actual ECSA of the catalysts, but it is a reasonable reflection of the catalysts' ECSA.^[4] For instance, this validity can be proved by investigating the relationship between the coulombic charge of the characteristic $\text{Co}^{3+}/\text{Co}^{4+}$ redox peak of Co_3O_4 oxides with various particle sizes and their BET surface areas. As shown in Figure 2.3a, Co_3O_4 with a smaller particle size exhibits a larger $\text{Co}^{3+}/\text{Co}^{4+}$ redox peak. The coulombic charges of $\text{Co}^{3+}/\text{Co}^{4+}$ cathodic redox peaks of Co_3O_4 oxides were plotted against their BET surface areas, which shows a linear relationship (Figure 2.3b).^[4] This result indicates that oxides' BET surface area is a reasonable reflection of its ECSA for powder catalysts. The reliability of using BET method to evaluate the catalysts' specific activity is further proved by the observations that the specific OER/ORR activity of oxide catalysts

estimated by the BET method matches well with the activity measured at well-defined epitaxial oxide thin-film surfaces. This indicates that the BET method is highly accurate for evaluating the specific activity of OER catalysts.

Figure 2.3 (a) The CV curves of Co_3O_4 oxides with different particle sizes, which demonstrate the $\text{Co}^{3+}/\text{Co}^{4+}$ redox peak region. (b) the relationship between coulombic charges of $\text{Co}^{3+}/\text{Co}^{4+}$ cathodic peaks of various Co_3O_4 oxides and their BET surface areas.^[4]

Comparing the overpotential (η) at a current density of $10 \text{ mA/cm}^2_{\text{geo}}$ is another widely used method to evaluate the performance of catalysts. However, this $\eta@10 \text{ mA/cm}^2_{\text{geo}}$ is not a reasonable parameter to be used to represent catalysts' intrinsic catalytic activity. Firstly, the $\eta@10 \text{ mA/cm}^2_{\text{geo}}$ is predominantly controlled by the mass loading of catalysts. As shown in Figure 2.4, if the electrode loads more catalyst on a current collector with fixed geometric surface area, it only needs a very small overpotential to achieve $10 \text{ mA/cm}^2_{\text{geo}}$.^[10] This does not accurately represent the intrinsic activity of the catalyst. Secondly, the OER is a surface reaction that means only the active sites on the catalyst surface participate in the reaction. Thus,

the $\eta@10 \text{ mA/cm}^2_{\text{geo}}$ condition is not suitable to describe the intrinsic activity of the catalysts.

To evaluate the mass specific activity, the reaction current is normalized to the total mass loading of the catalyst on the working electrode. From an engineering perspective, this is a good parameter to evaluate the overall device performance, but it does not represent the intrinsic catalytic performance of the catalyst. With the same amount of catalyst, the mass specific activity could be significantly enhanced by nano-sizing the catalyst.

Figure 2.4 (a) Schematic illustration of different catalyst loading within the same working electrode surface. (b) the catalyst loading effect on the $\eta@10 \text{ mA/cm}^2_{\text{geo}}$ ^[10]

2.3 OER mechanisms

2.31 Adsorbate evolution mechanism

The conventional OER adsorbate evolution mechanism (AEM) involves a proton-coupled four-electron transfer process on the oxide surface.^[1, 11] The most commonly used two OER mechanisms are shown in Figure 2.5. The only difference between these two mechanisms is that Figure 2.5a contains a bare catalyst surface

compared to Figure 2.5b. When the transition metal oxide catalyst is immersed in an electrolyte solution, the catalyst surface would adsorb species from the electrolyte. The types of adsorbed species are closely depended on the pH of zero charge (pH_{pzc}) of the catalyst surface.^[12-13] In alkaline conditions, the pH value is most likely higher than the pH_{pzc} of oxide catalysts ($\text{pH}_{\text{pzc}} \sim 7$ to 11 for perovskites^[14] and binary oxides^[15]), thus, the catalyst surface is covered by negatively charged species such as OH^- groups. For this reason, the OER mechanism in Figure 2.5b is more suitable for the OER mechanism discussion under alkaline conditions. The initial active metal center is covered with an OH^* (* denotes surface adsorbed species) and the OER intermediates contain OH^* , O^* , OOH^* and OO^* . Considering the mechanism in Figure 2.5b, the standard free energy (ΔG) required to trigger each step is equal to the free energy difference between its final and initial state.^[16] Thus, $\Delta G_1 = G^0_{\text{O}^*} - G^0_{\text{OH}^*}$, $\Delta G_2 = G^0_{\text{OOH}^*} - G^0_{\text{O}^*}$, $\Delta G_3 = G^0_{\text{OO}^*} - G^0_{\text{OOH}^*}$ and $\Delta G_4 = G^0_{\text{OH}^*} - G^0_{\text{OO}^*}$. The step with maximum ΔG value will be the rate-limiting step for the OER.^[16]

Figure 2.5 (a) OER mechanism proposed by Rossmeisl for oxide surface.^[1, 16] (b)

OER mechanism proposed by Goodenough for perovskite oxides.^[1, 17]

2.32 Lattice oxygen mechanism

Recently, a new lattice oxygen mechanism (LOM) involving a non-concerted proton-electron transfer process in OER was proposed by Alexis and co-workers.^[18]

As shown in Figure 2.6, not only the surface adsorbed oxygen species but also the lattice-oxygen is involved in the OER. Compared to the conventional concert-proton electron transfer mechanism, this new mechanism successfully explains the pH-dependency phenomenon of OER.

Figure 2.6 (a) Possible non-concerted proton-electron transfer OER mechanism that involves $^{34}\text{O}_2$ generation. (b) Possible non-concerted proton-electron transfer OER mechanism that involves $^{36}\text{O}_2$ evolution.^[18]

However, this LOM mechanism is not universal. Here, two perovskite oxides LaCoO_3 and SrCoO_3 are selected to illustrate the requirements for triggering lattice-oxygen oxidation. The bulk electronic band structures of these two oxides are shown in Figure 2.7. According to the illustration below, LaCoO_3 's M-3d band lies above its O-2p band and the Fermi level of LaCoO_3 is far away from its O-2p band. Under OER conditions it is impossible to excite electrons from the O-2p band to the Fermi level.^[18] Thus, the lattice oxygen of LaCoO_3 is not involved in the reaction. Using divalent Sr^{2+} ions to replace trivalent La^{3+} ions, the Fermi level and M-3d orbital are pushed down. The electrons from the partially filled O-2p orbital

of SrCoO_3 could be excited to its Fermi level under OER potentials, thus the lattice-oxygen is involved.^[18] Normally, the transition metal oxides with high metal-oxygen bond covalency are more likely to follow the LOM reaction path.^[18-20]

Figure 2.7 Illustration of the bulk band structures of LaCoO_3 and SrCoO_3 ^[18]

2.4 Design principles of highly effective oxide-based OER catalysts

2.4.1 Revealing the OER active geometric site in spinel oxides

The spinel structure (AB_2O_4) is composed of tetrahedral (Td) and octahedral (Oh) geometric sites (Figure 2.8a). Cations in the tetrahedral site are bonded with four oxygen anions, thus possessing a coordination number of four. In octahedral sites, the cations bond with six oxygen anions, thus possessing a coordination number of six.^[21] It is critical to identify which geometric site dominates the OER catalysts' catalytic activities. A classical method to solve this question is to use the OER inactive d^0 Al^{3+} and Zn^{2+} ions to preferentially occupy the octahedral and tetrahedral sites, respectively.^[21-22] Thus, researchers could fix the same cation in different geometric sites, such as ZnCo_2O_4 and CoAl_2O_4 , to identify the dominant geometric site in spinel oxides for OER. Xu and co-workers did systematic studies on spinel oxides and proposed that the cations in octahedral sites are OER catalytic active

sites.^[21] In addition, the e_g occupancy of active cations in octahedral sites could serve as a promising descriptor for OER and ORR catalyst design. According to their report, an active cation in an octahedral site with e_g filling ~ 0.9 exhibits optimal ORR activity, and such cations with e_g filling ~ 1.1 exhibit optimal OER activity (Figure 2.8b-c). Moreover, spinel oxides tend to have edge-shared octahedra terminated surfaces.^[23] This indicates cations in octahedral geometric sites are dominantly exposed on catalysts' surfaces.

Figure 2.8 Illustration of spinel crystal structure and OER, ORR activity as a function of e_g occupancy of the cation in the octahedral site. (a) illustration of the spinel structure. (b) ORR activity as a function of e_g occupancy@Octahedral. (c) OER activity as a function of e_g occupancy@Octahedral.^[21]

2.4.2 The significance of e_g theory in oxygen electrocatalysis

Under an octahedral crystal field (MO_6), the transition metal ion's d-orbitals will split into e_g (d_{z^2} and $d_{x^2-y^2}$) and t_{2g} (d_{xy} , d_{yz} and d_{xz}) states.^[24] Furthermore, considering the surface region, the active metal sites have a MO_5 instead of perfect MO_6 coordination. Thus, e_g states further split into $d_{x^2-y^2}$, which lies on a higher energy level compared to d_{z^2} , and d_{z^2} (Figure 2.9). The t_{2g} states are also split into two sets: (1) d_{xy} , which has higher energy; (2) d_{xz} and d_{yz} .^[2]

Figure 2.9 (a) Schematic illustration of the oxygen ligands (red) of MO_6 coordination and d-orbitals of metal cation. (b) Illustration of degenerated d-orbitals under perfect MO_6 and MO_5 octahedral crystal field.

The e_g orbitals exhibit stronger spatial overlap with oxygen 2p-orbitals compared to t_{2g} orbitals, thus, the binding strength of reaction intermediates is linked to its e_g orbitals' (shown in Figure 2.10a) occupancy. The e_g occupancy of the active metal cation reflects the binding strength between the reaction intermediates (OH^* , O^* , OOH^* and OO^*) and the active sites. When e_g occupancy value is too small the binding strength to reaction intermediates is too strong, but if the e_g occupancy value is too big the binding strength is too weak.^[2] Examining the OER and ORR

catalytic activities over 13 different perovskites, Shao-horn and co-workers proposed that perovskite-based catalysts with e_g filling ~ 0.9 exhibit optimal ORR activity and those with e_g filling ~ 1.1 exhibits optimal OER activity (Figure 2.10b).^[2, 25] By applying this e_g theory, some outstanding OER catalysts are synthesized, such as $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ with Co octahedra ($\text{Co}^{2.8+}$, $t_{2g}^5 e_g^{1.2}$). The e_g theory is a successful trial of using the coordination chemistry to estimate the binding strength of reaction intermediates, which guides the rational design of oxide-based OER catalysts.^[26-27]

Figure 2.10 (a) Illustration of the interaction between oxygen orbitals and MO_5 metal d-orbitals.^[2] (b) Illustration of the relation between the OER catalytic activity and the occupancy of the e_g electron of the transition metal (B in ABO_3).^[25]

2.4.3 Metal-oxygen bond covalency

In recent decades, the improvement of computing power has enabled researchers to investigate the bulk electronic structure of catalysts. The metal-oxygen (M-O) bond covalency measures the degree of orbital hybridization between metal d-orbitals and oxygen 2p-orbitals,^[28] which is defined by the energy difference between the metal d band center and oxygen p band center.^[29-30] In general, perovskite-based OER catalysts with large M-O bond covalency facilitate the electron transfer

between the oxygen adsorbates and the active metal sites, thus leading to better OER activity.^[29, 31] Besides DFT simulation, the M-O bond covalency could be quantified by the X-ray absorption spectroscopy (XAS) of oxygen K-edge,^[28] and the experimental results also indicate that a larger M-O bond covalency leads to better OER activity.^[25, 32] The M-O bond covalency solves the question raised by the limitations of e_g theory, where some catalysts have the same e_g filling but they exhibit huge differences in OER/ORR catalytic activities. For example, LaCoO_3 , LaNiO_3 and LaMnO_3 have the same e_g filling ($e_g = 1$) but they exhibit different ORR performance.^[32] This phenomenon was explained by M-O bond covalency, as shown in Figure 2.11 where the ORR activity increases as the M-O bond covalency increases.

Figure 2.11 ORR activity of LaMnO_3 , LaCoO_3 and LaNiO_3 as a function of M-O bond covalency^[32]

Xu and co-workers extended this study into spinel oxides and reported a similar trend (shown in Figure 2.12), where the OER catalytic activity was enhanced by enlarging the M-O bond covalency of the octahedral site.^[31] More recently,

researchers found that the OER catalysts exhibiting lattice-oxygen oxidation generally possess a large M-O bond covalency.^[33] It is good to know that a single descriptor is not sufficient to answer all the questions in oxygen electrocatalysis.

Figure 2.12 OER activity (evaluated by the working potential at 25 $\mu\text{A}/\text{cm}^2_{\text{ox}}$) as a function of metal-oxygen bond covalency.^[31]

2.4.4 Surface reconstructed OER catalysts

Previous studies based on catalysts' bulk properties proposed many useful design principles for OER catalysts, such as e_g theory and metal-oxygen bond covalency. However, a fact should be considered that most transition metal-oxide-based catalysts are not stable under OER conditions and undergo a surface reconstruction process.^[34-35] After surface reconstruction the catalysts are in a core-shell structure with an oxyhydroxide surface layer as the real active surface. More research efforts are needed to utilize and modify current descriptors to fill the gap. Also, more advanced descriptors are critical for oxygen catalysis in alkaline conditions.

2.5 Revealing the importance of spin-dependent OER reaction mechanism

2.5.1 The external magnetic field induced OER enhancement phenomenon

Electrochemical reactions generally possess sluggish reaction kinetics if the reactants and products have different spin configurations.^[36-38] OER is one of these reactions, as the reactant $\text{OH}^-/\text{H}_2\text{O}$ possesses singlet spin state and the product is triplet oxygen gas ($^3\text{O}_2$), which leads to slow reaction kinetics.^[36, 39-40] To solve this issue, researchers tried to use ferromagnetic-based catalysts to facilitate the spin-selective transfer during OER, thus enhancing the overall reaction kinetics. Galán-Mascarós, J. R and co-workers reported that magnetic catalysts' OER activities could be enhanced by applying a moderate external magnetic field (smaller than 450 mT).^[39] As shown in Figure 2.13, this magnetic field induced OER activity enhancement is proportional to catalysts' bulk magnetization, where catalysts with higher bulk magnetization exhibit a larger enhancement in OER activity.^[39] Non-magnetic catalysts do not exhibit any enhancement of OER activity under the external magnetic field.

Figure 2.13 (a) The magnetic field induced maximum magnetocurrent of different magnetic catalysts. (b) The magnetocurrent as a function of catalysts' bulk magnetization. The magnetocurrent is defined as the current difference between OER current with and without an external magnetic field.^[39]

Galán-Mascarós, J. R et al. hypothesized that the external magnetic field promotes the parallel electron spin alignment of oxygen radicals during O-O bond formation.^[39] This explanation does not provide a detailed mechanism of the magnetic field induced OER enhancement.

2.5.2 The theoretical studies of spin-dependent OER mechanism

Besides the experimental studies, researchers also tried to obtain a clear understanding of the spin-dependent OER mechanism by employing DFT simulation. By considering the spin term in DFT simulation, Gracia et al. studied several promising perovskite type OER catalysts and discovered the existence of layered antiferromagnetic ordering in those catalysts.^[36] It is known that electrons with opposite spin configuration to the magnetic moment of the magnetically polarized channels experience less scattering when they transport through these channels.^[41-42] As shown in Figure 2.14, these layered antiparallely ordered magnetically polarized channels facilitate the spin-selective electron transfer from

the reaction intermediates and accumulate sufficient magnetic moment for triplet oxygen evolution.^[36]

Figure 2.14 Schematic illustration of triplet oxygen generation at the magnetically polarized channels.

Furthermore, the average magnetic moment (μ_{ave}) of B site cations of each perovskite catalyst in the magnetically polarized channels was calculated. It was found that the OER activities are closely related to the μ_{ave} value (Figure 2.15). Generally, perovskite OER catalysts with higher μ_{ave} values of their magnetically polarized channels possess better OER activity. This study highlights the importance of spin conservation during OER.

Figure 2.15 The specific OER activity as a function of the average spin accumulation (μ_{ave}) in the magnetically polarized channels.^[36]

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Chapter 3

Experimental Methodology

3.1 Material synthesis

Co-based spinel oxides (LiCoVO_4 and ZnCo_2O_4) were synthesized by using the conventional sol-gel method.^[1-2] The schematic flow chart is illustrated in Figure 3.1.

Figure 3.1 Schematic flow chart of the sol-gel process.

Synthesis of ZnCo_2O_4 spinel oxide. ZnCo_2O_4 spinel oxide was prepared by the aforementioned sol-gel method. The synthesis of ZnCo_2O_4 started with dissolving

zinc acetate dihydrate, cobalt (II) acetate tetrahydrate, and citric acid with a molar ratio of 1: 2: 3 in 200 mL DI water, then 3 mL concentrated nitric acid was added. The mixture solution was heated at 90 °C with constant stirring until viscous gel was formed. The viscous gel was heated in a binder oven at 170 °C for 12 hours to remove remaining water. Lastly, the resulting resin was annealed in an airbox furnace at 450 °C for 6 hours to form pure phase ZnCo_2O_4 .

Synthesis of LiCoVO_4 inverse spinel oxide. LiCoVO_4 inverse spinel oxide was prepared by the solid-state synthesis method. Lithium cobalt (III) oxide vanadium oxide (V_2O_5) with a molar ratio of 2: 1 were mixed and ground. The powder mixture was annealed in an airbox furnace at 700 °C for 2 hours. Then the resulted oxide was ground and annealed at 700 °C for 2 hours again to ensure pure phase LiCoVO_4 powder was obtained.

Synthesis of 22 nm Fe_3O_4 nanoparticles (NPs). The 22 nm Fe_3O_4 NPs were prepared by a two-step wet-chemical method.^[3] The first step is to synthesize the iron-oleate complex. The iron-oleate complex was obtained from the reaction of iron pentacarbonyl and oleic acid.

Then the iron-oleate complex was decomposed and acted effectively as a growth source in synthesizing monodisperse nanocrystals with increased particle size. After the reaction was completed, the Fe_3O_4 NPs were collected by centrifugation. The collected Fe_3O_4 NPs were washed with hexane/ethanol and dispersed in hexane for further usage.

Synthesis of 120 nm Fe_3O_4 NPs. The 120 nm Fe_3O_4 NPs were prepared by a wet-chemical method with minor modification.^[4] In a typical synthesis, iron (III) chloride hexahydrate precursor was dissolved in ethylene glycol (EG). Then sodium acetate trihydrate, which was used for electrostatic stabilization, was added in the

mixture to prevent particle agglomeration. Polyethylene glycol 2,000 and polyethyleneimine acted as surfactants to further prevent particle agglomeration. The mixture solution was sealed in an autoclave, then heated to 200 °C and kept at this temperature for 15 hours. After the reaction was finished, the black product was collected by centrifugation. The 120 nm Fe₃O₄ NPs were washed with ethanol and H₂O, then dispersed in ethanol for further usage.

Synthesis of Fe₃O₄@Ni(OH)₂ core-shell catalysts. The 120@7 Fe₃O₄@Ni(OH)₂ core-shell NPs were prepared as follows: 120 nm Fe₃O₄ NPs, nickel (II) acetylacetonate, and hexadecylamine were dissolved in mesitylene. The mixture was sonicated for 20 minutes to form a gel-like solution. The gel-like solution was sealed in a press bottle and kept at 170 °C for 1 hour in the oil bath. Then it was kept at 200 °C for another 75 minutes. After the reaction was completed, the black products were collected by centrifugation and washed with ethanol, then dispersed in ethanol for further usage.

120@15 and 120@43 Fe₃O₄@Ni(OH)₂ core-shell NPs were prepared using the aforementioned procedure, except that the amount of Ni(acac)₂ and HDA were tuned respectively.

22@7 Fe₃O₄@Ni(OH)₂ and bulk@7 Fe₃O₄@Ni(OH)₂ core-shell NPs were obtained using the aforementioned procedure, except that the 120 nm Fe₃O₄ NPs were replaced with 22 nm Fe₃O₄ NPs and commercial Fe₃O₄ NPs. In addition, the amount of Ni(acac)₂ and HDA precursors were also adjusted.

Preparation of SmCo₅ particles. The samarium-cobalt alloy was purchased from Sigma-Aldrich with a disc shape (diameter 10 mm, thickness 6 mm). The SmCo₅ disc was ground into fine powders by using a mortar and pestle.

3.2 Working electrode preparation

The working electrode was prepared by the drop-casting method. In this thesis total of three types of working electrodes were used (shown in Figure 3.2), L-shape working electrode with a 5 mm glassy carbon disk, rotation disk electrode (RDE) with a 5 mm glassy carbon disk, and carbon paper (size: 2 x 2 cm).

Figure 3.2 Illustration of three types of working electrodes.

The electrode preparation method for the Chapter 4 of this thesis describes in the following sentences. The catalysts for electrochemical measurements were prepared by mixing spinel oxide (ZnCo_2O_4 or LiCoVO_4) with Vulcan carbon with a mass ratio of 5:1. The ink was prepared by dispersing 12 mg catalyst (10 mg catalyst oxide and 2 mg Vulcan carbon) into 1.95 mL mixture solution of DI water and isopropyl (volume ratio 4:1). Then 50 μL Nafion perfluorinated resin solution (5 wt% in water) was added as the binder. Then ink was sonicated for 30 minutes to form a homogeneous solution. 10 μL of catalyst ink was drop cast onto a fresh polished glassy carbon working electrode surface and dried under ambient conditions. The resulting oxide loading per disk is 50 μg .

The working electrode preparation method for Chapter 5 of this thesis: 4 mg of catalyst was dispersed in 1 mL of a mixed solvent containing Nafion perfluorinated

resin solution, *i*PrOH, and water ($V_{\text{Nafion}}/V_{i\text{PrOH}}/V_{\text{water}} = 0.125: 1: 4$). The mixture was sonicated for at least 30 minutes to form a homogeneous dispersion of catalyst ink (concentration: $4 \text{ mg}_{\text{ox}} \text{ mL}^{-1}$). Then 180 μL catalyst ink was drop cast onto both sides of a carbon paper electrode ($2 \times 2 \text{ cm}$) to yield a final mass loading of $90 \mu\text{g}_{\text{catalyst}} \text{ cm}^{-2}_{\text{disk}}$.

The electrode preparation method for Chapter 6 of this thesis: The catalyst ink was prepared by dispersing 18 mg catalyst and 12 mg conductive carbon in 3 mL ethanol/Nafion mixture solution (with a volume ratio of 10/1). Then the mixture was sonicated for at least 1 hour to form a homogeneous ink. Next, 10 μL of the catalyst ink was drop cast onto the RDE surface to yield a catalyst loading of $0.510 \text{ mg}_{\text{total}} \text{ cm}^{-2}$ ($0.306 \text{ mg}_{\text{cat}} \text{ cm}^{-2}$).

3.3 Electrochemical characterization

The OER measurements were carried out by using a three-electrode set-up in 1 M KOH alkaline solution (Figure 3.3a).^[5] The counter electrode was a 1.5 cm x 1.5 cm x 0.2 mm Pt plate and the reference electrode was Hg/HgO (1 M KOH inside reference electrode). For pH-dependent measurements the electrolytes are 0.01 M, 0.1 M, and 1 M KOH solution which represent pH values of 12, 13 and 14 respectively. In addition, an SCE (saturated calomel electrode) reference electrode was used for electrochemical measurements under a neutral electrolyte. The potential was controlled between the reference and the working electrode (Figure 3.3b), and the current signal was measured between the counter and the working electrode (Figure 3.3b).^[5] The rotation speed of RDE for OER experiments was 1600 rpm as the OER is not a mass transport limited reaction.^[5]

Figure 3.3 (a) Schematic illustration of a three-electrode setup. (b) The detailed circuit diagram of the typical three-electrode system.^[5]

The oxygen evolution reaction performance was evaluated by cyclic voltammetry (CV) with a scan rate of 10 mV/s. The Chronoamperometry (CA) method was employed to test the stability performance of the catalysts. Under 1 M KOH solution, a high density polyethylene (HDPE) cell was used to avoid corrosion of the quartz cells. A quartz cell was used for electrochemical measurements at lower pH values, such as pH 13 and 12, and the entire measurement was controlled within 1 hour to avoid corrosion. Before OER measurement the electrolyte was bubbled with oxygen gas for around 30 minutes to reach the O_2 saturation condition.^[6] Electrochemical Impedance Spectroscopy (EIS) measurement was conducted at

constant potential with 10 mV perturbations, the perturbation frequency range is from 200 kHz to 1 Hz.^[7] EIS measurements were conducted before OER measurements to obtain the ohmic resistance for the electrochemical system and check the condition of the electrochemical cell setup.^[6]

To mitigate the ohmic loss impact, the applied potentials were corrected by a standard iR-correction method.^[6, 8] The iR-correction equation is given below:

$$E_{iR-correct} = E_{app} - iR$$

The E_{app} is the applied potential, i is the OER reaction current and R is the ohmic resistance.

Calibration of the reference electrode is essential before each electrochemical experiment. In this thesis, the reference electrodes are calibrated with a hydrogen electrode before and after each experiment. The general conversion equation “E (vs. RHE) = E (vs. Hg/HgO) + 0.098 V + 0.059 × pH”. The term E (vs. Hg/HgO) is the measured working potential which refers to Hg/HgO reference electrode.^[6, 9]

3.4 Material characterization

X-ray diffraction (XRD). XRD is used to investigate the crystal structure as-synthesized oxides. As crystals are composed of the regular arrangement of atoms, the crystalline atoms diffract the incident X-ray beam into many specific directions. Incident X-ray waves interact with the regular array of atoms, generate scattered waves. Most of those scattered X-ray waves cancel out each other with destructive interference. Some scattered X-ray waves possess constructive interference in specific directions, which is determined by Bragg’s law:^[10-11]

$$2d \cdot \sin \theta = n \cdot \lambda$$

Here, d is the distance between the diffraction crystal planes. Angle θ is the incident angle, which is the angle between incident X-ray beams and diffraction planes. In this equation λ is the wavelength of the X-ray source, n is any integer number. For waves, when the phase difference between each wave is the integer multiples of the wavelength, constructive interference will occur.^[10] The schematic illustration of a powder XRD with a point detector setup is shown in figure 3.4.

Figure 3.4 Schematic illustration of a powder XRD with a point detector setup.^[10]

A powder X-ray diffractometer is designed to collect the scattered X-ray signals which fulfil Bragg's condition. Different crystal structures generate different diffraction patterns. The collection of signals from all the crystal planes is compared with the patterns in the database to identify the unknown crystal structure. In order to figure out the crystal structure of the sample, a standard PDF card is used to match the characteristic peaks with the obtained XRD patterns. In this thesis chapters 4, 5, and 6, the XRD technique is employed as a useful tool to investigate the crystal structure of spinel oxide catalysts.

Brunauer-Emmett-Teller (BET). BET theory is used to explain the physical adsorption of gas molecules on the solid surface, which was raised by Stephen Brunauer, Paul Hugh Emmett, and Edward Teller in 1938. BET technique is an

important technique that is applied to measure the specific surface area of powder materials. The BET theory applies to systems of multilayer adsorption (Figure 3.5) and usually utilizes probing gases that do not chemically react with material surfaces as adsorbates to quantify specific surface area.^[12] Nitrogen is the commonly used gas adsorbate for BET measurements. During the adsorption and desorption process, the equilibrium and saturation pressure of the adsorbate is measured. With that, the relationship of the amount of adsorbed gas molecules against the relative pressure can be obtained.^[12] This relationship is also called BET adsorption isotherm.

Figure 3.5 Multilayer adsorption model in BET theory.

X-ray photoelectron spectroscopy (XPS). XPS is an important technique for surface chemistry analysis. XPS measurement is normally conducted in a high vacuum condition, a focused X-ray beam irradiates the sample surface. The kinetic energy and the number of electrons escapes from the sample surface region (around tens of nanometers) are measured to form the XPS spectra.^[13] XPS can detect all elements with an atomic number larger than 3, and the detection limits for most elements are parts per thousand (parts per million are possible under strict conditions). According to the photoelectric effect equation, the binding energy (BE)

of the photoelectron equals the incident X-ray energy minus the kinetic energy (KE) of the photoelectron and substrates the work function (Φ_s).^[14]

$$E_{binding} = E_{photon} - (E_{kinetic} + \Phi)$$

The detailed illustration is shown in Figure 3.6.

Figure 3.6 Illustration of the working mechanism of XPS technique.

Transmission electron microscopy (TEM). In this thesis, TEM was employed to investigate the size distributions of nanoparticle catalysts. The elemental mapping function of TEM was applied to investigate the elemental distributions of interested elements.

In TEM, an electron beam has been accelerated by a high applied potential to penetrate the specimen, thus the specimen has to be thin enough (< 100 nm). The image is formed by the transmitted electron beam. The resolution of a microscope is generally controlled by the Rayleigh criterion (Figure 3.7).^[15] The maximum resolution, R , is controlled by the wavelength (λ) of the incident photon and the numerical aperture (NA) of the microscope.^[16] The Abbes Equation is shown below:

$$R = \frac{0.61 \cdot \lambda}{NA}$$

The wavelength of the electron is much smaller than the light, thus TEM has a much higher resolution compared to optical microscopes. According to the Broglie equation, the wavelength of an electron is related to its kinetic energy,^[17] the wavelength of an electron is inversely proportional to its momentum, which means at higher operation voltage the resolution is better.

Figure 3.7 Illustration of resolving two-point sources of light and the Rayleigh criterion .^[15]

X-ray absorption spectroscopy (XAS). The working principle of XAS is using an X-ray beam to penetrate the specimen and measure the intensity of the transmitted X-ray beam (Figure 3.8a). This X-ray intensity attenuation and adsorption coefficient (μ) could be characterized by Beer's law,^[18] the equation is listed below:

$$I_t = I_0 \cdot e^{-\mu(E)t}$$

Here, I_0 represents the incident X-ray intensity, I_t represents the transmitted X-ray intensity, t represents the specimen thickness and $\mu(E)$ is the adsorption coefficient. The adsorption coefficient $\mu(E)$ depends on the photon energy of the X-ray beam.^{[18-}

^{19]} XAS measures the energy-depend adsorption coefficient, μ , and presents it as a function of the X-ray energy (Figure 3.8b). If the incident X-ray beam energy is too

low, it cannot excite the sample's electrons to the unoccupied energy states or the vacuum level, which leads to a flat plateau (Figure 3.8b).^[18] However, a pre-edge peak may exhibit in some transition metals caused by 1s to 3d transition.^[19-20]

Figure 3.8 (a) Schematic illustration of XAS measurement, I_0 is incident beam intensity, t is sample thickness and I_t is the transmitted beam intensity. (b) adsorption coefficient μ as a function of photon energy, with indications of the pre-edge peak, XANES, EXAFS regions.^[18]

A significant X-ray adsorption peak occurs, when the incident beam energy is strong enough to excite the core electrons to the unoccupied energy states. This shows as X-ray absorption near edge structure (XANES) in the XAS spectrum (Figure 3.8b). The binding energy of core-electron varies when element possesses different valence states, thus, the XANES region could be used to analyses the oxidation state and electronic structure of the measuring element.^[18-20] As shown in Figure 3.8b and 3.9a, if the X-ray beam energy is significantly high, the core-electrons could be kicked out electrons as photoelectrons (continuum state). These photoelectrons act like waves, which interact with the neighboring atoms (Figure 3.9b) to form outgoing and scattering waves. The interaction between those waves triggers the oscillation of the adsorption coefficient signal, which represents in the extended X-ray absorption fine structure (EXAFS) region (Figure 3.8b). This

EXAFS signal reflects the short-range scattering which could be used to analyze the local crystal structure such as coordination number and bond length.^[18, 21-22]

Figure 3.9 (a) Schematic illustration of the electron excitation process, electrons represent by black circles. (b) Schematic illustration of an interference pattern which forms by the outgoing (solid black lines) and reflected (dashed blue lines) photoelectron waves between absorbing atom (gray) and its neighboring atoms (purple).^[18]

Vibrating-sample magnetometer (VSM). VSM is a device that is used to measure the magnetic properties of the specimens, such as bulk magnetization and hysteresis curve. The schematic diagram of the VSM setup is shown in Figure 3.10. In VSM a constant magnetic field is applied, which induces a magnetization in the specimen. After that, the specimen is vibrated. The vibrating specimen induces perturbations to the external field, which are recorded by a set of coils or sensors. The measured electromotive force (emf) signal depends on three parameters; (1) the frequency and amplitude of the vibration; (2) the applied external magnetic field and (3) the magnetization of the specimen.^[23] In this thesis, VSM was employed to investigate the magnetic properties of oxide catalysts, such as the coercivity (H_C), hysteresis curve, and saturated magnetization (M_S).

Figure 3.10 Schematic illustration of a VSM set-up.^[23]

Density functional theory (DFT). The entire DFT builds on two fundamental mathematical theorems proved by Kohn and Hohenberg. The derivation of a set of equations was done by Kohn and Sham in the mid-1960s. Kohn and Hohenberg proved that the ground-state energy of the wave function (Schrodinger equation) is a unique function of electron density. The electron density that reduces the overall energy of the system is the true electron density corresponding to the full solution of the Schrodinger equation.^[24] The fundamental algorithm is the Kohn-Sham equation, which is shown below:^[25]

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}) + V_H(\mathbf{r}) + V_{XC}(\mathbf{r}) \right] \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r}).$$

The left-hand side of the equation contains three potential V_r , V_H , and V_{XC} . The first term V_r can be obtained from the Schrodinger equation, which determines the

interaction between electrons and nuclei. The second term V_H is named Hartree potential, which determines the coulomb interaction between electrons. V_{XC} is the exchange-correlation energy, which defines the exchange energy and contributes to the single-electron equation.^[26] The formula of Hartree potential and exchange-correlation energy is listed below.^[25]

$$V_H(\mathbf{r}) = e^2 \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3 r'. \quad V_{XC}(\mathbf{r}) = \frac{\delta E_{XC}(\mathbf{r})}{\delta n(\mathbf{r})}.$$

Here, $n(\mathbf{r})$ is the electron density, $\mathbf{r}$ is the space vector. To solve this Kohn-Sham equation, the Hartree potential V_H and exchange-correlation energy V_{XC} are needed. To solve this problem, an iterative method is applied (flow chart is shown in figure 11):

1. An initial or trial electron density $n(\mathbf{r})$ is given.
2. Using the given electron density $n(\mathbf{r})$ to solve the Kohn-Sham equation, and figure out the single-electron function $\psi_{i(\mathbf{r})}$
3. With the single-electron function $\psi_{i(\mathbf{r})}$, a calculated electron density $n(KS)$ can be obtained as: $n(KS) = 2 \sum \Psi^* i(r) \Psi i(r)$
4. Comparing the obtained electron density $n(KS)$ with the electron density in step 2. If these two electron densities are the same, this is the ground-state electron density. Otherwise, the calculated electron density $n(KS)$ will be used in step 2, then the following calculation will be processed again until the requirement is met.

Figure 3.11 Illustration of the Kohn-Sham algorithm flow chart.^[27]

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Chapter 4

Revealing the importance of spin-polarized channels for water oxidation

4.1 Introduction

Transition metal oxides have attracted attention in recent years, as they are cost-effective, earth-abundant, and have competitive OER catalytic activity. Earth-abundant cobalt oxides like spinel Co_3O_4 , layered LiCoO_2 , and perovskite $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\sigma}$ (BSCF), and $\text{CaCu}_3\text{Fe}_4\text{O}_{12}$ (CCFO) are some of the most efficient transition-metal-based OER catalysts.^[1-3] In order to design effective Co-based catalysts, the research community has proposed several descriptors. One such descriptor was proposed by Shao-Horn and co-workers, who reported the e_g theory which links the M-O binding energy to the active transition metal ion's e_g value to guide the design of perovskite OER catalysts.^[1] According to this design guideline, BSCF with an average e_g filling of 1.1 for B-site cations was discovered to exhibit the highest OER activity.^[1] As for spinel oxide OER catalysts, cations in octahedral sites are reported to be the OER active sites.^[4] Thus, e_g theory is also a valid design guideline for spinel oxide catalysts. However, e_g theory has some limitations. It is very difficult to accurately estimate the e_g value, and it is challenging to identify the active sites for a complex oxide system. Recently, the different spin configurations

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between OER reactants and product have attracted attention. According to previous studies, the reaction is slow if the reactants and products have different a spin polarization.^[5-6] With that, a comprehensive theoretical study of spin transportation and conservation in OER catalysis was conducted by Gracia et al.^[7] He proposed that the contribution of active sites' e_g electron to their magnetic moment, μ_B^{eg} , as an OER descriptor for perovskites.^[7] Besides having the optimal μ_B^{eg} value, the most active perovskite OER catalysts exhibit spin-selective conduction channels at electronic ground states.^[6-7] According to previous reports, most of the octahedral cobalt ions (CoO_6) that exist in perovskite and spinel structures have a valence state of +3. Co^{3+} ions in an octahedral crystal field are low spin ($t_{2g}^6 e_g^0$) and the fully paired d electrons lead to a net magnetic moment of zero.^[8-9] However, if d^7 Co^{2+} ions can be stabilized under active octahedral sites, they are expected to possess a high spin state $S=3/2$ ($t_{2g}^5 e_g^2$).^[10] With a high spin configuration, each Co^{2+} ion has an ideal magnetic moment of $3 \mu_B$, the edge-shared Co^{2+} octahedra in spinel could be magnetically polarized.^[11]

In this chapter, LiCoVO_4 was investigated, which possessed an inverse spinel structure with the unique property of Co^{2+} presented in octahedral sites ($\text{Co}^{2+}_{\text{Oh}}$).^[12-14] In comparison, normal spinel ZnCo_2O_4 with Co^{3+} in octahedral sites ($\text{Co}^{3+}_{\text{Oh}}$) was also studied. LiCoVO_4 was found to exhibit a high OER activity compared to ZnCo_2O_4 . It appears that the high spin Co^{2+} ($S=3/2$) in bulk octahedron promotes OER activity through spin-polarized channels for better electron transfer. Density functional theory (DFT) calculation shows that the layered antiferromagnetic LiCoVO_4 inverse spinel oxide contains magnetically polarized channels. The average magnetic moment (μ_{ave}) per transition-metal atom in the spin conduction channel is around $2.66 \mu_B$. Such channels are able to enhance the selective removal

of spin-oriented electrons from the reactants during OER, which facilitates the accumulation of appropriate magnetic moments for triplet oxygen molecule evolution.^[6-7] In addition, the LiCoVO_4 reported has been identified as a new oxide catalyst with excellent OER activity.

4.2 Experimental details

4.2.1 Materials synthesis

The spinel oxides are synthesized through a typical sol-gel method and solid-state synthesis method.^[15-16] For ZnCo_2O_4 , one portion of acetate mixture (Zn and Co with a molar ratio of 1: 2) and two portions of citric acid were mixed and dissolved in 200 mL DI water, then 3 mL concentrated nitric acid was added. The resulting solution was heated at 90 °C with constant stirring until a viscous gel was formed. Then the viscous gel was put into an oven and heated at 170 °C for 12 hours to remove the remaining water. Lastly, the resulting resin was ground then annealed in an airbox furnace at 450 °C (ramp rate 5 °C/min) for 6 hours to obtain pure phase ZnCo_2O_4 . For LiCoVO_4 , LiCoO_2 and V_2O_5 (molar ratio 2: 1) were mixed and ground. The resulting mixture was annealed at 700 °C (ramp rate 5 °C/min) for 2 hours. Then the resulting oxide was ground and annealed at 700 °C for 2 hours to ensure pure phase LiCoVO_4 powder was obtained.

4.2.2 Electrochemical measurements

The catalysts for electrochemical measurements were prepared by mixing spinel oxide (ZnCo_2O_4 or LiCoVO_4) with Vulcan carbon with a mass ratio of 5: 1. The catalyst ink was prepared by dispersing 12 mg catalyst (10 mg catalyst oxide and 2 mg Vulcan carbon) into 1.95 mL mixture solution of DI water and isopropyl

(volume ratio 4: 1). Then 50 μL Nafion perfluorinated resin solution (5 wt% in water) was added as the binder.^[16] The ink was sonicated for at least 30 minutes to form a homogeneous solution. 10 μL catalyst ink was drop cast onto a fresh polished glassy carbon working electrode (5 mm diameter GC) and dried under ambient conditions. The oxide loading for each working electrode is 50 μg per disk.

The electrochemical measurements were conducted in 1 M KOH with a three-electrode setup. A Hg/HgO reference electrode (1 M KOH inside reference electrode) and a Pt-plate counter electrode were employed. The oxygen evolution reaction performance was evaluated by cyclic voltammetry (CV). The potential range for each CV scan is between 0.9 to 1.6 V (vs RHE) with a scan rate of 10 mV/s. The conversion between working potentials versus Hg/HgO and RHE is: $E(\text{vs RHE}) = E(\text{vs Hg/HgO}) + E_{\text{Hg/HgO}}(\text{vs SHE}) + 0.059 \times \text{pH}$. And $E_{\text{Hg/HgO}}(\text{vs SHE}) = 0.098 \text{ V}$ at 25 °C. The ohmic resistance of electrolyte and wiring was measured by the impedance measurement. The effect of an external magnetic field on catalysts' OER performance was also investigated. Chronoamperometry (CA) technique was employed, a 600 s CA measurement was conducted for each sample. A 250 mT uniform magnetic field was applied at 300 s onwards.

4.2.3 DFT simulation

All the density functional theory (DFT) calculations were performed by the Vienna Ab initio Simulation Package,^[17] employing the projected augmented wave (PAW) model. The exchange and correlation effect was described using Perdew-Burke-Ernzerhof (PBE) functional,^[18] within the generalized gradient approximation (GGA) approach. The GGA + U calculations are performed using the model proposed by Dudarev et al.^[19], with the U_{eff} ($U_{\text{eff}} = \text{Coulomb } U - \text{exchange } J$) values of 3.5 eV, 3.3 eV, and 4.7 eV for V, Co, and Zn, respectively. The cutoff energy

was set to be 450 eV for all the calculations. For bulk geometry optimization, the Monkhorst–Pack^[20] k-point mesh of $6 \times 6 \times 6$ was employed; for computing the electronic structure, a $9 \times 9 \times 9$ k-point mesh was adopted. For all calculations, the Brillouin zone was integrated using the tetrahedron method with Blöch corrections. The force and energy convergence tolerance was set to be 0.05 eV Å⁻¹ and 10⁻⁵ eV, respectively.

4.3 Results and discussion

XRD patterns of LiCoVO₄ and ZnCo₂O₄ are shown in Figure 4.1a and 4.1b, which indicate that LiCoVO₄ and ZnCo₂O₄ possess the cubic-spinel structure with Fd $\bar{3}$ m space group. LiCoVO₄ XRD pattern (Figure 4.1a) exhibits a weak (111) peak at 18.59 ° and a relatively strong (022) peak at 30.53 °, which indirectly indicates that the LiCoVO₄ oxide has an inverse spinel structure.^[14, 21-22] Previous reports have shown that vanadium ions occupying tetrahedral sites would lead to an increase in (022) peak intensity at the expense of (111) peak intensity, explaining these results.^[21-23] According to the previous reports, the as-synthesized ZnCo₂O₄ spinel oxide possesses Co³⁺_{Oh} and Zn²⁺ ions are in tetrahedral sites.^[24-25]

Figure 4.1 (a) XRD pattern of LiCoVO_4 with reference LiCoVO_4 pattern (PDF # 96-153-7582). (b) XRD pattern of ZnCo_2O_4 with reference ZnCo_2O_4 pattern (PDF # 96-591-0137).

The size distributions of as-synthesized LiCoVO_4 and ZnCo_2O_4 were investigated by scanning electron microscope (SEM). As shown in Figure 4.2, the particle size of LiCoVO_4 is at the micrometer level which is larger compared to ZnCo_2O_4 (around 100 nm). The surface area was investigated by BET technique, the specific surface area of ZnCo_2O_4 and LiCoVO_4 is $40.79 \text{ m}^2/\text{g}$ and $0.1 \text{ m}^2/\text{g}$ respectively (Figure 4.2a and 4.2b), which matches well with SEM results.

Figure 4.2 SEM images and isothermal adsorption-desorption curves of LiCoVO₄ and ZnCo₂O₄. (a) The isothermal adsorption-desorption curve of LiCoVO₄. (b) The isothermal adsorption-desorption curve of ZnCo₂O₄. (c) SEM image of LiCoVO₄. (d) SEM image of ZnCo₂O₄.

The X-ray absorption near edge structure (XANES) measurements were conducted to reveal the valence states of cobalt ions and vanadium ions. The position of the XANES absorption edge provides information on the metal cation's valence state.^[25-26] As shown in Figure 4.3a, the Co K-edge energy of LiCoVO₄ is the same as CoO K-edge energy, which confirms Co²⁺ ions are presented in LiCoVO₄. The K-edge energy of ZnCo₂O₄ is higher than Co₃O₄ which indicates Co³⁺ ions are presented in ZnCo₂O₄. The valence state of the vanadium ion is 5+ (Figure 4.3b), and it is double confirmed by XPS. Figure 4.3c shows the V 2p XPS spectra, the

binding energy difference between V 2p_{3/2} and V 2p_{1/2} peak is 7.33 eV which firmly indicates vanadium ions are 5+. [27-28]

Figure 4.3 (a) Normalized Co K-edge XANES spectra of LiCoVO₄ and ZnCo₂O₄. (b) Normalized V K-edge XANES spectra of LiCoVO₄. (c) V_{2p} XPS spectra of LiCoVO₄. (d) FTIR spectra of LiCoVO₄, 700-850 cm⁻¹ region is attributed by VO₄ tetrahedron stretching vibration.

The coordination environment and structural position of V⁵⁺, Co²⁺ ions were revealed by extended X-ray absorption fine structure (EXAFS). As shown in Figure 4.4a, the Co-O bond length is 1.61 Å (peak 1) which is longer compared to the Co-O bond length in previous reports (approximate 1.5 Å^[16, 25, 29]). This is due to cobalt ions having a low valence state of 2+ in LiCoVO₄, which leads to a longer Co-O bond length compared to commonly reported (Co ions have valence state of 3+) Co-O bond length. Peak 2 located at 2.75 Å represents Co-Co_{Oh}, indicating that

Co^{2+} ions mainly occupy octahedral sites.^[28, 30] The vanadium EXAFS of LiCoVO_4 is shown in Figure 4.4b, the Peak 1 located at 1.36 Å, which associates with the scattering path from V^{5+} ion to its nearest neighbor oxygen ions, represents the V-O bond length. Peak 2 located at around 3.03 Å represents the scattering path from the metal ions to their nearest metal ions in tetrahedral geometric sites.^[28, 30] Furthermore, Fourier-transform infrared (FTIR) measurement was conducted to double confirm the vanadium ions' coordination environment. As shown in Figure 4.3d, a vibration peak at 700-850 cm^{-1} was observed, which mainly contributes to VO_4 tetrahedron stretching vibration.^[23, 28] This result confirms V^{5+} ions of LiCoVO_4 are located in tetrahedral geometric sites.

Figure 4.4 (a) Co K-edge EXAFS spectra of LiCoVO_4 . (b) V K-edge EXAFS of LiCoVO_4 . (c) Co K-edge EXAFS spectra of ZnCo_2O_4 . (d) Zn K-edge EXAFS of ZnCo_2O_4 .

The OER performance was evaluated by cyclic voltammetry (CV) technique under 1 M KOH alkaline conditions with a three-electrode setup. The potential range is from 0.9 to 1.6 V (vs RHE) with a scan rate of 10 mV/s. In this work, all OER current densities are normalized by BET surface area to present the intrinsic catalytic activity.^[31] And the iR correction was applied to compensate for the potential loss on the electrolyte. The cobalt ions are the active sites for both ZnCo_2O_4 and LiCoVO_4 , as other cation ions are OER inert d^0 metal cations.^[25] LiCoVO_4 exhibits much better OER catalytic performance compared to ZnCo_2O_4 (Figure 4.5a). This indicates that Co^{2+} octahedron is more active compare to Co^{3+} octahedron. The redox peak at 1.1 V (Figure 4.5a) is a standard $\text{Co}^{2+}/\text{Co}^{3+}$ redox peak,^[25] which also indicates the existence of Co^{2+} ions in LiCoVO_4 . The charges associated with $\text{Co}^{2+}/\text{Co}^{3+}$ oxidation and reduction peaks are calculated and presented in Figure 4.5a. The $\text{Co}^{2+}/\text{Co}^{3+}$ redox pair exhibits a negligible charge difference of $0.37\text{E-}5$ C, which indicates this redox pair is highly reversible.

Figure 4.5 (a) Representative CV curves (2nd cycle) of LiCoVO_4 , ZnCo_2O_4 , and IrO_2 . (b) The Tafel plot comparison included benchmark IrO_2 ^[1] and BSCF^[32].

Co ions' valence state in bulk pristine LiCoVO_4 and cycle LiCoVO_4 was investigated by XAS. As shown in Figure 4.6c, the Co K-edge energy of pristine

and cycled LiCoVO_4 does not shift which indicates the Co ions remain $2+$ valence state after CV cycling. Co $2p_{3/2}$ XPS spectra of pristine and cycled LiCoVO_4 are shown in Figure 4.6a. The satellite peak at 786 eV is strong evidence for Co^{2+} ions.^[33-35] The $\text{Co}^{2+}/(\text{Co}^{2+} + \text{Co}^{3+})$ peak area ratios (Figure 4.6b) of pristine (57.6 %) and cycled LiCoVO_4 (56.3 %) are almost the same. This again proves the Co^{3+} ions are fully reduced to Co^{2+} ions during the cathodic CV sweep.

Figure 4.6 (a) Co $2p_{3/2}$ XPS spectra of pristine and cycled LiCoVO_4 . (b) XPS peak area ratios. (c) XAS Co K-edge spectra of pristine and cycled LiCoVO_4 .

Furthermore, TEM images (Figure 4.7) of pristine and cycled LiCoVO_4 indicate that there is no remarkable surface reconstruction during OER. The Tafel plot (Figure 4.5b) shows that LiCoVO_4 has better OER activity than IrO_2 and its OER activity is competitive to the most active oxide-based catalyst $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\sigma}$ (BSCF).

Figure 4.7 TEM images of pristine and cycled LiCoVO_4 .

In order to understand the fundamentals of the tested OER active spinel oxides, the magnetic property and electronic structure of these oxides were investigated. The magnetic properties of ZnCo_2O_4 and LiCoVO_4 were investigated by vibrating-sample magnetometer (VSM). As shown in Figure 4.8a and 4.8c, linear hysteresis loops of ZnCo_2O_4 and LiCoVO_4 with very small slopes are observed. The magnetic susceptibility of ZnCo_2O_4 and LiCoVO_4 are $6.6\text{E-}6$ and $6.1\text{E-}5$ emu/gOe, respectively. As shown in Figure 4.8b and 4.8d, the reciprocal of magnetic susceptibility is plotted against temperature and linear fitting was conducted. The interception of $1/\chi$ of both ZnCo_2O_4 (-146.7 K) and LiCoVO_4 (-14.9 K) are found to be negative. The small magnetic susceptibility and negative interception of $1/\chi$ indicate that ZnCo_2O_4 and LiCoVO_4 are antiferromagnetic.^[36-37]

Figure 4.8 (a) Hysteresis curves of LiCoVO₄. (b) Field-cooled and zero-field-cooled susceptibility plotted versus temperature for LiCoVO₄, insert is the Curie-Weiss plot of LiCoVO₄. (c) Hysteresis curves of ZnCo₂O₄. (d) Field-cooled and zero-field-cooled susceptibility plotted versus temperature for ZnCo₂O₄, insert is the Curie-Weiss plot of ZnCo₂O₄.

As mentioned above, the LiCoVO₄ and ZnCo₂O₄ are antiferromagnetic. DFT simulation with antiferromagnetic ground states was carried out to investigate the electronic structure of LiCoVO₄ and ZnCo₂O₄. The computed partial density of states (pDOS) of LiCoVO₄ and ZnCo₂O₄ are shown in Figure 4.9. The ZnCo₂O₄ exhibits a symmetric pDOS (Figure 4.9a) with a band gap of 1.7 eV, which is consistent with the previous reports.^[38-39] In ZnCo₂O₄ the Co³⁺ ions locate under

octahedral field with all paired valence electrons lead to a net zero spin value. The LiCoVO_4 also shows a symmetric pDOS (Figure 4.9b) with a smaller band gap of 1.36 eV. Thus, the electrons in LiCoVO_4 are easier to be excited into the conduction band and transfer away. And significant overlapping between O-2p orbital and Co-3d orbitals of LiCoVO_4 at near Fermi region could be observed. However, ZnCo_2O_4 does not exhibit such strong Co-3d and O-2p orbital overlapping. This indicates that LiCoVO_4 has stronger Co-O bond covalency that leads to better OER performance, which is also consistent with previous reports.^[38, 40-41]

Figure 4.9 Bulk electronic structure of ZnCo_2O_4 and LiCoVO_4 (a) pDOS of ZnCo_2O_4 . (b) pDOS of LiCoVO_4 .

The enhancement of OER catalytic activity by magnetic field was recently reported by José Ramón Galán-Mascarós et al.^[42] The founding shows that the magnetic enhancement of catalysts' OER activity has certain correlation to the catalysts' bulk magnetization. Under a moderate magnetic field, materials with higher bulk magnetization exhibit larger enhancement of their OER activities.^[42] Therefore, we investigated the effect of an external magnetic field on LiCoVO_4 and ZnCo_2O_4 by applying a 250 mT magnetic field during chronoamperometry (CA) measurement.

The results (Figure 4.10) indicate that the external magnetic field does not enhance their OER activity. Because both LiCoVO_4 and ZnCo_2O_4 are antiferromagnetic materials with very low magnetic susceptibility, an external magnetic field is not expected to enhance their OER activity, which is consistent with the previous report.^[42]

Figure 4.10 (a) LiCoVO_4 CA at 1.6 V, a 250 mT magnetic field is applied at 300 s; (b) ZnCo_2O_4 CA at 1.6 V, a 250 mT magnetic field is applied at 300 s.

The planar view along the [001] direction of the spinel and the (001) plane spin distribution map of ZnCo_2O_4 are shown in Figure 4.11. This material contains edge-shared Co^{3+} ions with symmetric spin-up and spin-down electrons (paired electrons), which results in zero magnetization for Co^{3+} ions. Thus, the edge-shared octahedron channels in ZnCo_2O_4 have zero net magnetism.

Figure 4.11 The planar view along [001] direction of typical spinel structure and the spin distribution map of ZnCo₂O₄ (001) plane, red indicates spin up, blue indicates spin down.

In LiCoVO₄, Co²⁺ and Li⁺ ions are located in edge-shared octahedral sites. The OER active Co²⁺ ions here possess a high spin configuration ($t_{2g}^5 e_g^2$). Each Co²⁺ ion has a magnetic moment of $\pm 2.66 \mu_B$ (Figure 4.12) with positive and negative moments alternating with layer. As shown in Figure 4.12a, the oxygen ions bound to them also have a small magnetic moment ($\pm 0.016 \mu_B$), which is caused by the spin donation from the Co²⁺ ion through Co_{3d}-O_{2p} orbital overlapping.^[6] Compared to ZnCo₂O₄, these edge-shared octahedron channels in LiCoVO₄ are magnetically polarized. According to previous studies, electrons with opposite spin directions have weaker scattering effects when such electrons transfer through the magnetic lattice.^[6, 43-44] Thus, the magnetic polarised channels in LiCoVO₄ (Figure 4.12c) could act as spin-selective conduction channels with smaller electron transfer barrier for the electrons with the opposite spin. In the oxygen evolution reaction, the reactants have singlet configuration but the final product is a triplet molecule. The differing spin configuration between reactants and products leads to a slower

reaction as the spin is not conserved.^[6] Therefore, extra energy or stimulus for spin coupling is needed to trigger this reaction.^[5-6] In the LiCoVO_4 system, the Co-O bonds along the magnetically polarized channels have a certain spin character which is caused by spill-over of Co^{2+} magnetic polarization through $\text{Co}_{3d}\text{-O}_{2p}$ overlapping. According to Gracia's recently proposed mechanism,^[6-7] under an applied working potential, the active sites on the magnetically polarized channels could extract spin-oriented electrons from reactants and transfer them through the aforementioned channels. This process would break the electron pairs on the adsorbates and promote the accumulation of appropriate magnetic moments on the active sites. This facilitates the formation of triplet oxygen molecules. Thus, LiCoVO_4 exhibits excellent OER performance.

Figure 4.12 (a) The spin value magnitudes of Co and O ions of LiCoVO_4 and ZnCo_2O_4 along the spin channels. (b) Crystal structure of LiCoVO_4 with spin

isosurface, ions with yellow color isosurface indicate net up spin, ions with blue color isosurface indicates net down spin, ions without isosurface indicates net spin is zero. (c) Spin distribution map of spin-up and spin-down layers in LiCoVO_4 along [001] direction.

4.4 Summary and conclusion

In summary, the as-synthesized LiCoVO_4 inverse spinel oxide exhibits Co^{2+} ions in octahedral sites. Compared to ZnCo_2O_4 , the $\mu_{\text{B}}^{\text{eg}}$ value of OER active sites in LiCoVO_4 is optimized. At the same time, LiCoVO_4 shows stronger Co-O bond covalency than ZnCo_2O_4 , which further promotes its OER performance. Besides that, layered antiferromagnetic LiCoVO_4 contains magnetically polarized channels. Under applied potential, active sites in those channels may facilitate the extraction of certain spin-oriented electrons from the singlet reactants. This leads to the accumulation of magnetic moments at the intermediate/catalyst interface, boosting triplet oxygen evolution. The LiCoVO_4 oxide appears to allow for spin conservation throughout the reaction, which also leads to good OER performance.

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Chapter 5

Ferromagnetic–Antiferromagnetic coupling core–shell catalyst for water oxidation

5.1 Introduction

Electrochemical water splitting involves two half-cell reactions, namely the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER). The HER has very fast reaction kinetics at a relatively low overpotential compared to OER. The OER is a complex four-electron-transfer anodic reaction that has sluggish reaction kinetics which limits the energy conversion efficiency of water electrolysis.^[1-2] In order to improve the efficiency of the OER, researchers put plenty of effort into the development of OER catalysts. Several principles, such as the e_g occupancy,^[2] the metal-oxygen bond covalency^[3] and electron transfer energy,^[4] have been proposed for the design of highly efficient transition metal oxide-based OER catalysts. These principles are generally built based on their relation to the adsorption energy of reaction intermediates. Recently, researchers have looked beyond of this paradigm and noticed the importance of spin conservation for OER.^[5-7] For OER the initial reactant OH^- possesses a singlet spin ground state, however, the final product is triplet oxygen. Reactions with different spin states between reactants and products generally possess slow reaction

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kinetics.^[8-9] In order to solve this issue, ferromagnetic OER catalysts, which promote spin-selective electron transfer process, have begun to attract research interest in the electrocatalysis community. Galán-Mascarós, J. R et al have reported that the OER catalytic activity of highly magnetic ferrites exhibits significant enhancement by directly applying a magnetic field.^[10] However, the OER activity of antiferromagnetic catalysts is not enhanced by applying an external magnetic field.^[5, 11] Some researchers have made attempts to figure out the fundamental mechanism of these phenomena using density functional theory (DFT) simulation.^[5, 12] For example, Gracia et al. proposed the contribution of active sites' e_g electron to their magnetic moment, μB^{eg} ,^[8] as an OER descriptor for perovskites. On the experimental side, a fact should be considered that most catalysts are not stable under OER conditions and in fact, they are in a core-shell structure with an oxyhydroxide surface layer as the real active surface after surface reconstruction.^[13] In this work, bi-magnetic core-shell nanoparticles (NPs) with different core sizes and shell thicknesses were prepared that mimic surface reconstructed catalysts, to investigate the effect of magnetic domain structure on direct magnetic field induced OER catalytic activity enhancement. According to previous findings, most highly active transition metal-oxide based OER catalysts exhibit surface reconstruction or surface amorphization.^[14-15] By controlling the thickness of the active surface region, a link between catalysts' bulk magnetic properties and surface catalytic activities is established. These nanoparticles are composed of a ferromagnetic (FM) Fe_3O_4 core and an antiferromagnetic (AFM) $Ni(OH)_2$ shell. Three different core sizes and three different shell thicknesses were prepared. We found that the magnetic coercivity of the FM/AFM core-shell system was enhanced compared to the FM core alone. This is because the interface coupling energy is larger than the

antiferromagnetic anisotropy energy.^[16] Using a 120 nm core, we tested different shell thicknesses' OER activity by cyclic voltammetry (CV) under alkaline conditions, with and without external magnetic fields. The results showed that the enhancement of samples' OER catalytic activities by an external magnetic field increases as the shell thickness decreases. Furthermore, we investigated the OER activity of $\text{Fe}_3\text{O}_4@\text{Ni}(\text{OH})_2$ with different core sizes covered by a 7 nm shell. The samples with 120 nm and bulk cores (300 nm) show similar increases in OER activity when an external magnetic field is applied. However, the OER activity of $\text{Fe}_3\text{O}_4@\text{Ni}(\text{OH})_2$ with a 22 nm core was not affected by the external magnetic field.

5.2 Experimental details

5.2.1 Material synthesis

Synthesis of 22 nm Fe_3O_4 nanoparticles (NPs). The 22 nm Fe_3O_4 NPs were prepared by a two-step wet-chemical method.^[17] The first step is the synthesis of the iron-oleate complex. In a typical synthesis, 1.35 g (5 mmol) of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 4.5 g (15 mmol) sodium oleate were dissolved in a mixed solvent composed of 10 mL ethanol, 18 mL hexane, and 8 mL H_2O . Then, the mixture was heated to 70 °C and kept at this temperature for 4 hours. After the reaction finished, the upper organic layer which contains the iron-oleate complex was washed three times with H_2O (5 mL $\times$ 3) in a separator funnel. The obtained organic layers were washed with brine, dried over anhydrous Na_2SO_4 , filtered and evaporated off the hexane. The synthesized iron-oleate complex was in a waxy solid form. Second step is the synthesis of Fe_3O_4 NPs. The iron-oleate complex and 3.7 g (13 mmol) of oleic acid were dissolved in 50 g of trioctylamine at room temperature. The mixture was slowly heated to 320 °C with a ramping rate of 3 °C/min and kept at this temperature

for 30 minutes. During this process, the initial transparent solution turned brownish-black. After the reaction finished, the solution was cooled down to room temperature. Then 100 mL of ethanol was added to precipitate the Fe_3O_4 NPs. After a centrifugation step (12,000 rpm for 10 minutes) the precipitate, i.e., Fe_3O_4 NPs, was washed five times with hexane/ethanol ($v/v = 1/10$) and dispersed in hexane for further usage.

Synthesis of 120 nm Fe_3O_4 NPs. The 120 nm Fe_3O_4 NPs were prepared by a wet-chemical method with slight modification.^[18] Firstly, 1.08 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ were dissolved in 8.25 mL of EG, then 400 mg of PEG 2000 and 10 mg of PEI were added. The mixture solution was sonicated for 20 minutes to form a homogenous brown color solution. Then 2 g of NaAc was dissolved in 5 mL of EG to form a mixture solution. Then this mixture solution was slowly added into the brown color solution. This solution was stirred for 5 minutes then it was sealed in a Teflon-lined stainless-steel autoclave (23 mL). The autoclave was heated to 200 °C within 30 minutes and kept at that temperature for 15 hours. After it was cooled down to 25 °C, the black product was collected by centrifugation. The product was washed five times with ethanol and H_2O , then it was dispersed in ethanol for further usage.

Synthesis of $\text{Fe}_3\text{O}_4@\text{Ni}(\text{OH})_2$ core-shell catalysts. The 120@7 $\text{Fe}_3\text{O}_4@\text{Ni}(\text{OH})_2$ core-shell NPs were prepared as follow: 5 mg of $\text{Ni}(\text{acac})_2$ and 30 mg of HDA were dissolved in 4 mL of mesitylene, then 0.1 mmol of 120 nm Fe_3O_4 NPs (pre-dispersed in EtOH, 2.2 M) was added. The mixture was sonicated for 20 minutes to form a gel-like solution. Then it was sealed in a 15 mL press bottle (Synthware, P160001) and kept at 170 °C for 60 minutes in the oil bath with constant stirring. Then it was kept at 200 °C for 75 minutes to let the reaction finish. After it was cooled down to 25 °C, the black precipitates were collected by centrifugation. The

product was washed five times with ethanol and H₂O, then it was dispersed in ethanol for further usage.

120@15 and 120@43 Fe₃O₄@Ni(OH)₂ core-shell NPs were prepared using the aforementioned procedure, except that 5 mg of Ni(acac)₂ were increased to 10 mg and 25 mg, respectively, and 30 mg of HDA were increased to 60 mg and 150 mg, respectively.

22@7 Fe₃O₄@Ni(OH)₂ core-shell NPs were prepared using the aforementioned procedure, except that 0.1 mmol of 120 nm Fe₃O₄ NPs were replaced with 22 nm Fe₃O₄ NPs. In addition, 5 mg of Ni(acac)₂ and 30 mg of HDA were increased to 20 mg and 120 mg, respectively.

Synthesis of bulk@7 Fe₃O₄@Ni(OH)₂ core-shell sample: 8 mg of Ni(acac)₂ and 80 mg of HDA were dissolved in 10 mL of mesitylene, then 16 mg of commercial Fe₃O₄ NPs was added. Then the mixture was sonicated for 20 minutes to form a gel-like solution. The mixture was sealed in a 50 mL Synthware press bottle and kept at 170 °C for 60 minutes in the oil bath under stirring. Then increased the oil bath temperature to 200 °C and kept it for another 75 minutes. After the reaction finished, the solution was cooled down to 25 °C and the black product was collected by centrifugation. The product was washed five times with ethanol and H₂O, then it was dispersed in ethanol for further usage.

5.22 Electrochemical measurements

The oxygen evolution reactions (OER) were carried out by using a three-electrode setup under 1.0 M KOH electrolyte. The catalyst was loaded onto a carbon paper (2 × 2 × 2 cm²) working electrode. A Pt counter electrode and a Hg/HgO reference electrode were employed. The catalyst ink was prepared by dispersing 4 mg of catalyst into 1 mL of a mixed solvent containing Nafion perfluorinated resin

solution (5 wt% in water), *i*PrOH and water ($V_{\text{Nafion}}/V_{i\text{PrOH}}/V_{\text{water}} = 0.125: 1: 4$). The ink was sonicated for at least 30 minutes to form a homogenized dispersion of catalysts (concentration: $4 \text{ mg}_{\text{ox}} \text{ mL}^{-1}$). Then 180 μL catalyst ink was drop cast onto both sides of the carbon paper electrode which yields a final mass loading of $90 \mu\text{g}_{\text{catalyst}} \text{ cm}^{-2}_{\text{disk}}$. The electrochemical measurements were performed by using Biologic SP 150 potentiostat. Cyclic voltammetry (CV) measurements with a scan rate of 20 mV s^{-1} were conducted and the potential range is from 1.10 to 1.75 V (vs. RHE). The measured potentials were converted to RHE with the conversion equation: $E (\text{vs. RHE}) = E (\text{vs. Hg/HgO}) + 0.098 \text{ V} + 0.059 \times \text{pH}$, then the *i*R correction was performed. The term $E (\text{vs. Hg/HgO})$ is the measured working potential which refers to Hg/HgO reference electrode. The reference electrode was calibrated with a hydrogen electrode before each measurement. The obtained current density (*j*) was normalized with the carbon paper geometric surface area (8 cm^2).

After the working electrode reached its steady-state, i.e., about 50th cycles, the cell was fixed on the electromagnet instrument. The magnetic field was generated by a commercial induction set-up operated at +3.0 A to generate a 0.3 T magnetic field. After the working electrode was magnetized for 15 min, an additional CV cycle was recorded under the magnetic field.

5.23 Structural characterization.

Transmission electron microscopy (TEM), aberration-corrected high-resolution TEM (HRTEM), dark-field scanning TEM (DF-STEM), and elemental mapping images were recorded by a JEOL JEM-2100F microscope operated at 200 keV acceleration voltage. The samples for TEM experiments were prepared by dropping

as-prepared NPs suspensions onto carbon-coated copper grids and drying them completely at room temperature.

X-ray diffraction (XRD) patterns were recorded with a Shimadzu XRD-6000 powder XRD, using Cu K α radiation ($\lambda=1.5406$ Å). The XRD samples were prepared by dropping the as-prepared NPs suspensions onto a glass slide.

The electronic states of as-synthesized catalysts were examined by X-ray photoelectron spectroscopy (XPS) on a Shimadzu Kratos Axis Supra instrument with a monochromatic Al K α X-ray source. The measured binding energies were calibrated with adventitious C 1s peak. The XPS samples were prepared by dropping the as-prepared NPs suspensions onto silicon substrates.

Magnetic properties of samples were measured with a Superconducting Quantum Design (SQUID) magnetometer (MPMS-XL). The SQUID measures the magnetization of samples as a function of the magnetic field, the signals were recorded at 300 K with applied fields between -5 T to +5 T. To substantially prove the existence of the AFM–FM coupling at the sample interface, the magnetism of the pristine and after CV cycling 120@7 Fe₃O₄@Ni(OH)₂ NPs was measured under both field-cooled (FC) mode and zero-field-cooled (ZFC) mode.

5.3 Results and discussion

The core–shell nanoparticles are prepared by a two-step wet-chemical method. The nanoparticles with a 120 nm Fe₃O₄ core and different shell thicknesses, 43, 15, and 7 nm, are denoted as 120@43, 120@15, and 120@7, respectively. The crystal structures and morphologies of these core–shell nanoparticles were first investigated by X-ray diffraction (XRD) and transmission electron microscopy (TEM). The statistical core size distribution is shown in Figure 5.1a, the average size of Fe₃O₄ core was measured to be 120 ± 22 nm. The XRD patterns in Figure

5.1b only exhibit the diffraction patterns of Fe_3O_4 , which indicates that the core-shell particles are composed of a crystal Fe_3O_4 core and an amorphous shell.

Figure 5.1 (a) TEM image of 120 nm Fe_3O_4 core, inset is sized distribution map.

(b) XRD patterns of samples with 120 nm Fe_3O_4 core and shell thickness of 43, 15, and 7 nm.

TEM images in Figure 5.2 reveal that the Fe_3O_4 core has clear lattice fringes, which confirmed its crystallinity. For example, the lattice spacings in 120@15 and 120@7 were measured to be $2.51 \text{ \AA}$ and $2.97 \text{ \AA}$, which match the (311) and (220) crystal planes of cubic Fe_3O_4 , respectively. This is corroborated by the sharp peaks of (311) at 30.12° and (220) at 35.47° shown in the XRD patterns (Figure 5.1b). In the shell region (Figure 5.2), the atoms are arranged without obvious long-range order, indicating the shell has an amorphous structure. Furthermore, the elemental mappings in Figure 5.2 a–c show the representative core-shell structures, in which the cores are composed of Fe element and the shells composed of Ni element. In addition, the estimated shell thickness from the elemental mapping of Ni and Fe is a good match with the layer thicknesses visible in the bright field TEM images.

Figure 5.2 TEM images, DF-STEM images and the corresponding STEM-EDS element mappings of (a) 120@43 nm, (b) 120@15 nm, and (c) 120@7 nm Fe_3O_4 @ $\text{Ni}(\text{OH})_2$ NPs, respectively.

The X-ray photoelectron spectroscopy (XPS) results of pristine samples' Ni 2p_{3/2} spectra are shown in Figures 5.3. All core-shell samples exhibited a typical Ni²⁺ peak of Ni(OH)₂ peak at 854.7 eV, which is a good match of previous reports.^[19-20]

Figure 5.3 Ni 2p_{3/2} XPS spectra of pristine 120@7, 120@15 and 120@43

The OER activities of these core-shell nanoparticles were investigated by cyclic voltammetry (CV) under 1 M KOH alkaline condition with a three-electrode setup. Whenever the working electrode being tested reached its steady-state (after about 50 CV cycles, Figure 5.4), an external magnetic field was applied for 15 minutes, then another CV cycle was recorded under the field.

Figure 5.4 Pre-cycling to achieve steady state performance of samples with a 120 nm core and different shell thicknesses. (a) 120 nm Fe_3O_4 , (b) 120@7, (c) 120@15 and (d) 120@43.

During the pre-cycling process, all samples' CV curves exhibited the typical $\text{Ni}^{2+}/\text{Ni}^{3+}$ redox peaks at 1.43 V (Figure 5.4) which indicated that the $\text{Ni}(\text{OH})_2$ was reconstructed into OER active NiOOH during the cycling step. To further verify this, XPS spectra of cycled samples (after the catalyst reached a steady-state, around 50 CV cycles) were obtained. As shown in Figure 5.5, the $\text{Ni } 2p_{3/2}$ XPS spectra of cycled samples exhibit both Ni^{2+} and Ni^{3+} peaks at 854.7 eV and 856.4 eV respectively.^[19-20] These results indicate Ni^{3+} NiOOH was formed during the cycling process. As CV cycles are composed of an anodic scan and a cathodic scan,

thus some NiOOH could be reduced into Ni(OH)₂. This is the reason Ni²⁺ signal was observed in cycled sample' Ni 2p_{3/2} XPS spectra.

Figure 5.5 Ni 2p_{3/2} XPS spectra of cycled 120@7, 120@15 and 120@43.

In order to confirm the catalyst remained its core-shell structure after it reached steady-state, the high-resolution TEM (HRTEM) images and EDX mapping of cycled samples are taken. As shown in Figure 5.6, these catalysts remained their core-shell morphology when they reached the steady-state and the shell thickness of each sample did not exhibit any change. The core region of cycled samples remained unchanged, which exhibited clear lattice fringes and the d-spacing matches well with the cubic Fe₃O₄ crystal structure.

Figure 5.6 TEM images of cycled (50 cycles) core-shell nanoparticles (a) 120@43, (b) 120@15 and (c) 120@7.

To further confirm the elemental composition of the cycled samples the EDX mapping of cycled samples was taken. EDX mappings of cycled samples (Figure 5.7) also confirm that samples' core-shell structure has well remained. The Ni is

uniformly distributed in the shell region and the Fe is uniformly distributed in the core region.

Figure 5.7 EDX mappings of cyclized (50 cycles) core-shell nanoparticles (a) 120@43, (b) 120@15 and (c) 120@7

The electrochemical data are presented in Figure 5.8. As shown in Figure 5.8a, the 120 nm Fe_3O_4 has a much higher overpotential (505 mV) at j of $5 \text{ mA/cm}^2_{\text{disk}}$ compared to the rest of core-shell samples. The OER catalytic activity of all samples exhibits some degree of enhancement under a 0.3 T (3000 Oe) external magnetic field (Figure 5.8a and 5.8b). Furthermore, the enhancement of samples' OER catalytic activities by an external magnetic field increases as the shell thickness decreases. Notably, the 120@7 exhibits the largest (43.8 %) increment of the OER current density (Figure 5.8b) compared to other samples. The Tafel slope of 120@7 is reduced from 78.4 to 64.3 mV/dec by the external magnetic field, which is the greatest reduction among all samples (Figure 5.8c). The turnover frequency (TOF) of the 120@7 also exhibits the largest increment from 0.263 to 0.346 molecules per second (Table 4.1), which matches well with the Tafel results.

Figure 5.8 Electrochemical results (a) OER activities of 120@43, 120@15, 120@7, and 120 nm Fe₃O₄ NPs, and OER activities under an external magnetic field of 120@43_B, 120@15_B, 120@7_B, and Fe₃O₄_B NPs. (b) Percentage of j increment at 1.55 V vs RHE under the external magnetic field. (c) Tafel plots of 120@43, 120@43_B, 120@15, 120@15_B, 120@7, 120@7_B and 120 nm Fe₃O₄ and 120 nm Fe₃O₄_B.

Table 4.1 TOFs with and without an external magnetic field of Fe₃O₄@Ni(OH)₂ catalysts with different shell thicknesses, all TOFs are calculated at an overpotential of 320 mV.

	120@43	120@15	120@7
TOF (s ⁻¹)	0.173	0.318	0.263
TOF under magnetic field (s ⁻¹)	0.195	0.369	0.346
TOF enhancement (%)	12.4	16.2	31.3

According to previous reports, the magnetic field induced OER activity enhancement is related to the catalysts' magnetism.^[10, 21] A catalyst with very high net magnetism would exhibit a larger enhancement of OER activity under the magnetic field.^[8, 10] However, Fe_3O_4 is FM with a relatively small net magnetism. As shown in Figure 5.9a, the 120 nm Fe_3O_4 nanoparticle could reach its saturated magnetism (70.1 emu/g) under a 2200 Oe magnetic field. Thus, other factors may lead to the significant enhancement of the OER activity under a moderate 3000 Oe magnetic field. Figure 5.9a and 5.9b show that the $\text{Fe}_3\text{O}_4@\text{Ni}(\text{OH})_2$ samples have higher magnetic coercivity compared to the pristine Fe_3O_4 , which indicates the existence of FM–AFM coupling (Figure 5.9d) at the core–shell structure interface.^[16] And the magnetic coercivity of core-shell nanoparticles increases as the shell thickness increases. The hysteresis curves of cycled samples (50 cycles to reach steady-state) were also measured. As shown in Figure 5.9c, the H_C values of cycled samples exhibited the same trend as pristine samples, which indicated the FM-AFM coupling remains after CV cycling.

Figure 5.9 Magnetic properties of core-shell catalysts. (a) Hysteresis loops of pristine 120@43, 120@15, 120@7, and 120 nm Fe_3O_4 NPs, inset is the enlarged H_c region taken from the grey dot square. (b) H_c values of pristine 120@43, 120@15, 120@7, and 120 nm Fe_3O_4 NPs. (c) Hysteresis loops of cycled 120@43, 120@15, 120@7, and 120 nm Fe_3O_4 NPs, inset is the enlarged H_c region taken from the grey dot square. (d) Illustration of FM-AFM coupling effect.

When the interface coupling energy is larger than the antiferromagnetic anisotropy energy, a strong FM–AFM coupling is expected at the interface which facilitates the effective magnetic anisotropy, thus enhancing coercivity.^[16] In order to further prove the existence of the FM–AFM coupling at the sample interface, we conducted VSM measurements for 120@7 under 15 and 300 K, respectively. When the

temperature was reduced to 15 K, which is well below the Neel temperature of $\text{Ni}(\text{OH})_2$,^[22] we found that the H_C of 120@7 (270.1 Oe) at 15 K is much larger than the H_C of 120@7 (65.3 Oe) at 300 K (Figure 5.10). Furthermore, the saturated magnetization (M_S) also increased when the temperature was at 15 K. When the temperature was reduced below the Neel temperature (22 K) of the AFM $\text{Ni}(\text{OH})_2$ shell,^[22] the spin at interface coupled with the spin arrangement of the Fe_3O_4 core (Figure 5.9d),^[16, 23] and thus the H_C and M_S would be larger compared to H_C and M_S at 300 K. These results firmly support the existence of FM–AFM coupling at the interface of the core–shell samples.

Figure 5.10 Hysteresis loops of 120@7 at 300 K and 15 K.

The interfacial FM–AFM coupling of core–shell samples acts as a “spin filter” which facilitates selective removal of electrons with spin direction opposing the magnetic moment of FM core during OER reaction. As shown in Figure 5.11, at the Fermi region the partially filled conduction band of Fe_3O_4 is dominated by a minority spin state, which opposes the net magnetic moment of Fe_3O_4 .^[24–25]

Considering the critical step of OER, the reaction intermediate Ni-OOH^* reacts with OH^- and loses one electron to form Ni-OO^* . According to angular momentum conservation, the electron with the spin configuration of minority spin would be selectively removed.^[5] Taking consideration of the need for wavefunction symmetry,^[26-27] the Ni-OO^* reacts with OH^- would selectively remove one electron to generate triplet oxygen. This spin-selective electron transfer process during OER accumulates sufficient magnetic moment at the active sites which facilitates triplet oxygen evolution. As OER is a surface reaction, the shell thickness of core-shell nanoparticles plays a critical role. If the shell is too thick, the reaction intermediates at the surface are far from the FM–AFM interface, which means the “spin filter” cannot play its role effectively. Thus, we find the OER activity enhancement decreases as the shell thickness increases (Figure 5.8). With a relatively thin shell, the reaction intermediates could interact with the FM–AFM effectively, which is why 120@7 exhibits the highest enhancement among other samples.

Figure 5.11 Spin-selective electron transfer mechanism in core-shell nanoparticles.

Previous studies have proposed that paramagnetic/ferromagnetic catalysts' magnetic domains could be aligned under an external magnetic field, which facilitates spin selective electron removal during OER, thus promoting triplet oxygen generation.^[10, 28-29] This suggests that single domain magnetic catalysts could utilize spin selective electron transfer during OER even without an external magnetic field.^[30] The samples with a 7 nm Ni(OH)_2 shell and different Fe_3O_4 core sizes, bulk (300 nm), 120 nm, and 22 nm were synthesized and denoted as bulk@7, 120@7, and 22@7 respectively. The crystal structure of the as-synthesized samples was investigated by the XRD technique. As shown in Figure 5.12, the XRD patterns indicate all core-shell samples have a crystallized Fe_3O_4 core and an amorphous

Ni(OH)₂ shell. The 22@7 exhibits broader XRD peaks compared to bulk@7 and 120@7, which also indicates 22@7 has the smallest particle size.

Figure 5.12 XRD pattern of bulk@7, 120@7, and 22@7 samples.

We further utilized the TEM to investigate these samples at the atomic scale. As shown in Figure 5.13a–5.13f, the Fe₃O₄ core have has fully covered by the thin Ni(OH)₂ shell and the average shell thicknesses of all samples were measured to be about 7 nm. Employing the HRTEM technique (Figure 5.13d–5.13f), we observed the particles are composed of the crystalline core and the amorphous shell. In the representative crystalline core regions, the lattice spacings in 22@7, 120@7 and bulk@7 were measured to be 2.41 Å, 2.97 Å, and 2.49 Å, corresponding to the (222), (220), and (311) crystal plane of cubic Fe₃O₄, respectively. According to the elemental mapping results (shown in Figure 5.13g-5.13i), the Ni element uniformly distributes around the nanoparticle and Fe element uniformly distributes at the core region.

Figure 5.13 Structural characterization of $\text{Fe}_3\text{O}_4@\text{Ni}(\text{OH})_2$ core-shell catalysts with different core sizes. TEM images of (a) 22@7, (b) 120@7, and (c) bulk@7, respectively. HRTEM images of (d) 22@7, (e) 120@7, and (f) bulk@7, respectively. DF-STEM images and the corresponding STEM-EDX element mappings of (g) 22@7, (h) 120@7, and (i) bulk@7, respectively.

Furthermore, the XPS technique was used to analyse the surface property of the core-shell nanoparticles. As shown in Figure 5.14a, the XPS results of pristine samples' Ni $2p_{3/2}$ spectra exhibit a typical Ni^{2+} peak of $\text{Ni}(\text{OH})_2$ at 854.7 eV, which is a good match of previous reports.^[19-20] Together with the XRD and TEM results, the core-shell nanoparticles are confirmed to possess a crystalline Fe_3O_4 core and a 7 nm amorphous $\text{Ni}(\text{OH})_2$ shell.

Figure 5.14 Ni 2p_{3/2} XPS spectra of (a) pristine 22@7, 120@7 and bulk@7. (b) cycled 22@7, 120@7 and bulk@7.

All catalysts were cycled around 50 CV cycles to reach the steady-state before we record the catalytic performance. Another batch of HRTEM characterization was conducted to investigate their morphology after CV cycling. The bright-field TEM images (Figure 5.15a-5.15c) confirm the samples' shell thickness remains as 7 nm after the cycling process. In addition, the elemental mappings (Figure 5.15d-5.15f) indicate that the samples remain the core-shell structures, in which the cores compose of Fe element and the shells compose of Ni element. According to the XPS results (Figure 5.14b), the Ni(OH)₂ shell was reconstructed into NiOOH during the cycling process. The CV cycling ends with a negative scan, thus, Figure 5.14b exhibits a weak Ni²⁺ signal in Ni 2p_{3/2} spectra.

Figure 5.15 Electron microscopy characterization of $\text{Fe}_3\text{O}_4@\text{Ni}(\text{OH})_2$ core-shell samples with different shell thicknesses after CV cycling. (a) XRD patterns of samples with 7 nm $\text{Ni}(\text{OH})_2$ shell and core sizes of bulk, 120, and 22 nm. (a–c) HRTEM images and (d–f) DF–STEM images and the corresponding STEM–EDS element mappings of bulk@7 nm, 120@7 nm, and 22@7 nm samples, respectively. The magnetic properties of these samples were investigated by VSM. Figure 5.16 shows that the 22@7, 120@7, and bulk@7 samples reach the M_s under an external magnetic field of 540, 1642, and 2574 Oe, respectively. Thus, the magnetic domains in 120@7 and bulk@7 core–shell nanoparticles could be fully aligned under the applied external magnetic field (3000 Oe).

Figure 5.16 Hysteresis loops of different core-shell NPs, 22@7, 120@7, bulk@7, and Ni(OH)₂.

According to the CV results in Figure 5.17a, the external magnetic field has no effect on the OER performance of the 22@7 sample. However, the 120@7 and bulk@7 samples exhibit significant enhancement of OER performance under the external magnetic field. As shown in Figure 5.17b, under the external magnetic field, the OER current densities of bulk@7 and 120@7 increased by 39.4 % and 32.8 %, respectively, but the current density of 22@7 shows a negligible increment (3 %). As shown in Table 4.2, the TOFs of bulk@7 and 120@7 (Figure 5.17c and 5.17d) increased from 0.271 and 0.263 s⁻¹ to 0.376 and 0.346 s⁻¹ under an external magnetic field, respectively. The TOFs increment of bulk@7 (38.9 %) and 120@7 (31.3 %) matches well with the current density increment. The Tafel plot is shown in Figure 5.17d, which also exhibits a similar trend. The TOF of 22@7 (0.443 s⁻¹) is among the best of all catalysts, however, there is negligible change on the Tafel slope and TOF under the external magnetic field. All the results firmly indicate the external magnetic field does not have any effect on the 22@7 sample. All the results firmly indicate the external magnetic field does not have any effect on the 22@7 sample.

Figure 5.17 OER enhancement by domain alignment structure. (a) CV curves of bulk@7, 120@7, and 22@7 core-shell NPs. (b) Percentage of j increment at 1.6 V vs RHE under the external magnetic field. (c) TOF values and (d) Tafel plots of 22@7, 22@7_B, 120@7, 120@7_B, bulk@7, and bulk@7_B.

Table 4.2 TOFs with and without an external magnetic field of Fe₃O₄@Ni(OH)₂ catalysts with different core sizes, all TOFs are calculated at an overpotential of 320 mV.

	120@7	22@7	bulk@7
TOF (s ⁻¹)	0.263	0.437	0.271
TOF under magnetic field (s ⁻¹)	0.346	0.443	0.376
TOF enhancement (%)	31.3	1.3	38.9

It is well known that domain size is a material property. Previous studies reported that the critical diameter of a Fe_3O_4 single domain nanoparticle is around 26–40 nm.^[31-32] Based on that we assume the 22@7 core-shell nanoparticle has a single domain magnetic core, which allows it to utilize spin-selective electron transfer and promotes triplet oxygen formation. Figure 5.16 shows that the 22@7, 120@7, and bulk@7 samples reach the M_s under an external magnetic field of 540, 1642, and 2574 Oe, respectively. Thus, the magnetic domains in 120@7 and bulk@7 core-shell nanoparticles would be fully aligned under the applied external magnetic field (3000 Oe). The electrons with opposite spin configuration to the magnetic moment of the core have much less resistance could be selectively removed, which facilitates the triplet oxygen evolution.^[8-9] This is the reason that an enhancement of OER performance of 120@7 and bulk@7 samples was observed in Figure 5.17a. As shown in Figure 5.16, the bulk@7 core-shell sample has a higher M_s (93.5 emu/g) compared with the 120@7 sample (57.5 emu/g) which also exhibits a more significant enhancement of OER performance. This result is in good agreement with previous reports,^[5, 10, 30] as a catalyst with a higher net magnetism will exhibit greater improvement of OER performance under an external magnetic field.

The experimental results illustrate that the size of Fe_3O_4 controls the magnetic domain structure of the core region. If the size is larger than 40 nm, the core is a multi-domain core, which is composed of different magnetic domains. With the multi-domain core, each domain has a different magnetic configuration, leading to a disordered state in the entire system. Although each domain has a spin filter at their region, the spin-selectively removed electrons still have to move through the whole system in order to be transported to the external circuit, and large amounts of scattering is expected (Figure 5.18).

Figure 5.18 Schematic illustration of spin-selective electron transport OER mechanism (note that all electrodes are carbon support free).

When an external field is applied, sufficient to reach the saturation magnetism, the domains inside a multi-domain core are fully aligned. The spin-selectively removed electrons at each region would have the same spin configuration and the scattering in the electron transport process is minimized,^[33] which leads to significant enhancement in OER activity (120@7 and bulk@7). However, if the core (22 nm) with a single domain, the spin selectively removed electrons can be transported to the external circuit with minimal scattering. These findings explained why no obvious enhancement of OER activity is observed for 22@7.

5.4 Summary and conclusion

In summary, we have synthesized $\text{Fe}_3\text{O}_4@\text{Ni}(\text{OH})_2$ core-shell nanoparticles that possess interfacial FM-AFM coupling. The interfacial FM-AFM coupling of core-shell samples acts as a spin filter which facilitates selective removal of electrons with spin direction opposing the magnetic moment of FM core during the OER process. Utilizing the FM-AFM coupling effect could be a way to improve reaction kinetics of other chemical reactions which reactants and products possess different spin states. Furthermore, the magnetic domain structure of the FM core plays a critical role in the electron transport process. The single domain FM core with ordered magnetic dipoles facilitates spin-selective electron transport with minimal

scattering even without an external magnetic field. Thus, no enhancement of OER performance under the magnetic field was observed for single domain core-shell catalyst. With a multiple domain core, the applied magnetic field aligns the magnetic domains which optimize the electron transport process. Thus, a significant enhancement of OER performance was observed for the multiple domain core catalysts. The magnetism/OER activity model revealed in this work provides a new design principle for OER catalysts.

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Chapter 6

Investigation of ferromagnetic OER catalyst for high temperature practical application

6.1 Introduction

With the increasing demand for hydrogen fuel, the technologies for sustainable hydrogen production are essential. Water electrolyzers that consume harvested renewable energy to produce hydrogen gas are attracting much attention. One of the obstacles to the large-scale deployment of water electrolyzers is the development of highly efficient and cost-effective catalysts for the water evolution reaction (OER). In order to overcome this challenge, significant research effort has been focused on transition-metal and transition metal-oxide-based catalysts.^[1-3] These efforts have discovered valuable design principles, such as d-band theory^[4], e_g theory^[1, 5-6] and metal-oxygen bond covalency^[7-8] for OER catalysts. More recently, researchers have begun to notice that OER is a spin-dependent electrochemical reaction.^[9-10] The generation of the triplet product, oxygen gas, from the singlet reactant, OH⁻/H₂O, leads to slow reaction kinetics.^[9-11] Galán-Mascarós et al. reported that by applying an external magnetic field the OER activity of ferromagnetic (FM)/paramagnetic (PM) catalysts could be significantly enhanced.^[12-13] They claimed that the magnetic field induced OER activity enhancement is related to the catalysts' bulk magnetic properties. However, during the OER process, most active catalysts undergo surface reconstruction to form OER

active metal oxyhydroxides.^[14] Our group's previous studies revealed that surface reconstructed FM catalysts exhibited FM/antiferromagnetic (AFM) coupling at the interface.^[13, 15] The aligned spins at the FM/AFM interface act as spin filters, which facilitate the spin-selective transfer of electrons and promote triplet oxygen generation. However, in practical applications water electrolyzers are operated at elevated temperatures (50 to 80 °C) to boost the overall reaction efficiency as opposed to the room temperature that most catalysts are studied at.^[16] These operation temperatures exceed the Curie temperature of the majority of FM catalysts. In this way, the aligned spins and magnetic domains are disturbed by thermal agitation. To utilize the spin-selective electron transfer property of FM OER catalysts in practical applications, high Curie temperature FM OER catalysts are desired.

In this chapter, I designed a core/shell structured $\text{SmCo}_5/\text{CoO}_x\text{H}_y$, which has a FM core with extremely high Curie temperature (1020 K),^[17] to utilize the spin-selective electron transfer induced by the FM/AFM coupling effect for high-temperature practical applications. The hysteresis loop of reconstructed $\text{SmCo}_5/\text{CoO}_x\text{H}_y$ under FC mode exhibits an exchange bias (H_{EB}) of 127.5 Oe. However, only negligible exchange-bias (0.25 Oe) could be observed in the hysteresis loops of pristine SmCo_5 . This confirms that the uncompensated spins are pinned at the interface by FM/AFM coupling.^[18-19] When the $\text{SmCo}_5/\text{CoO}_x\text{H}_y$ catalyst was magnetized under a 1.25 T magnetic field, the OER activity at 1.65 V of magnetized $\text{SmCo}_5/\text{CoO}_x\text{H}_y$ increased by 109.6 %. The turnover frequency (TOF) of magnetized $\text{SmCo}_5/\text{CoO}_x\text{H}_y$ is 1.55 s^{-1} which is comparable to those of the most active OER catalysts reported. As mentioned previously, OER catalysts need to operate at elevated temperatures, 50~80 °C. This leads to the concern that these highly reactive OER catalysts' spin-

related properties, such as spin-polarization of the bulk material and FM/AFM coupling effect at the interface, would be disrupted. In this chapter, the operation temperature was elevated to 50, 60, 70 and 80 °C to mimic water electrolyzers' practical operation conditions. Surprisingly, the OER activity enhancement remains for the magnetized $\text{SmCo}_5/\text{CoO}_x\text{H}_y$, indicating that the interfacial FM/AFM coupling for $\text{SmCo}_5/\text{CoO}_x\text{H}_y$ core/shell catalyst is preserved, up to 60 °C. The highly active $\text{SmCo}_5/\text{CoO}_x\text{H}_y$ which is also resilient to high temperature conditions exhibits great potential for practical applications.

6.2 experimental details

6.2.1 Material preparation

The SmCo_5 was purchased from Sigma-Aldrich with a disc shape (diameter 10 mm, thickness 6 mm). The SmCo_5 disc was ground into fine powders by using a mortar and pestle. The core-shell $\text{SmCo}_5/\text{CoO}_x\text{H}_y$ was prepared by an electrochemical pre-treatment process. Firstly, the pristine SmCo_5 catalyst underwent a pre-treatment which composed 20 cyclic voltammetry (CV) scans in 0.1 M KCl neutral solution. The potential range is from 0.6 to 1.2 V vs Ag/AgCl with a scan rate of 100 mVs^{-1} . Then the working electrode was rinsed by DI-water several times (at least 3 times) to remove the residual electrolyte. After that, the $\text{SmCo}_5/\text{CoO}_x\text{H}_y$ electrode is ready for use.

6.2.2 Material characterization

The X-ray diffraction pattern was collected by using the Bruker D8 Advance instrument which operated at 40 kV with Cu $K\alpha$ radiation ($\lambda = 1.54059 \text{ \AA}$). XRD patterns were collected with a 2θ range of 30 to 75 ° with a step interval of 0.02 °. The STEM and line scan were performed on a JEOL 2010 transmission electron microscope at 200 kV. The sample was prepared by dropping SmCo_5 suspension

(in ethanol) onto a carbon-coated Cu TEM grid. The concentration of leached Sm and Co cations in the neutral electrolyte was determined by ICP-ms. The magnetic hysteresis loops of the SmCo_5 and $\text{SmCo}_5/\text{CoO}_x\text{H}_y$ samples were measured by a vibrating sample magnetometer (VSM). The specific surface area of the catalyst was investigated by Brunauer, Emmett, and Teller (BET) area measurements. N_2 adsorption-desorption isotherms of the catalyst were measured at -196°C using ASAP Tristar II 3020. Soft XAS was carried out at the Singapore Synchrotron Light Source facility for catalysis research (XAFCA) beamline. The Co-L XAS spectrum was taken in the total electron yield mode. *In-situ* Raman tests were performed by Raman spectrometer (Horiba LabRAM HR Evolution) using a 532 nm laser with a 50 $\times$ objective lens. The Raman spectra were recorded *in-situ* at OCV and under different applied potentials spanning from 1.4 to 1.75 V vs RHE in the neutral solution and 1.2 to 1.70 V vs RHE in the alkaline solution.

6.2.3 Electrochemical measurement

Working electrode preparation. The working electrode preparation method in this chapter is composed of two parts: 1) ink preparation and 2) drop-casting. The ink was prepared by mixing 18 mg catalyst and 12 mg carbon in 3 mL mixed ethanol/Nafion mixture solution (with a volume ratio of 10: 1). Then the ink mixture was sonicated for at least 1 hour to obtain a homogeneous ink solution. 10 μL catalyst ink was drop cast onto a fresh polished RDE (5 mm diameter GC) and dried under ambient conditions, which yields an approximate catalyst loading of 0.510 $\text{mg}_{\text{total}} \text{cm}^{-2}$ (0.306 $\text{mg}_{\text{cat}} \text{cm}^{-2}$).

OER measurements. Room temperature OER measurements were performed by using a three-electrode system. A glassy carbon RDE (PINE, 5 mm diameter, 0.196 cm^2) and a Pt plate (10 x 10 x 0.1 mm) were served as the working and counter

electrode respectively. Ag/AgCl (saturated KCl solution) and Hg/HgO (1 M KOH solution) reference electrodes were used in neutral and alkaline electrolytes, respectively. The electrochemical data was recorded by a BioLogic SP-150 electrochemical station.

The SmCo₅ working electrode was pretreated in neutral 0.1 M KCl electrolyte to form the SmCo₅/CoO_xH_y core-shell catalyst. After the pre-treatment, the working electrode was rinsed with DI-water several times (at least 3 times) to remove the residual electrolyte. Then, the OER performance was evaluated in an O₂-saturated 0.1 M KOH (99.99% metal purity) solution. The as-prepared SmCo₅/CoO_xH_y working electrode was cycled 20 CV cycles with a scan rate of 100 mV s⁻¹ and a potential range of 0.3 to 1.0 V (vs. Hg/HgO) to reach the steady-state. Then the CV scan rate was changed to 10 mV s⁻¹ to measure the OER activity. The second CV curve was used to represent the OER activity. An electromagnet was used to provide desired magnetic fields to magnetize the SmCo₅/CoO_xH_y working electrode. Before the magnetization process, the electrode was gently swung to remove the surface electrolyte. Then the SmCo₅/CoO_xH_y working electrode was magnetized under a 0.55, 0.70, 0.85, 1.10, or 1.25 T magnetic field for 15 minutes. After that, the OER performance of the magnetized sample was recorded by applying the same OER measurement procedures.

All OER results were iR-corrected, which was calculated by the following equation:

$E_{iR\text{-corrected}} = E - iR$, where i is the measured current and R is the ohmic resistance (~45 Ω) of the O₂-saturated 0.1 M KOH electrolyte.

A two-electrode setup, where SmCo₅/CoO_xH_y and Pt plate (1 cm × 1 cm) were acted as anode and cathode, was used to evaluate the full-cell water splitting performance

under elevated temperatures. The $\text{SmCo}_5/\text{CoO}_x\text{H}_y$ was loaded on a $1\text{ cm} \times 1\text{ cm}$ Ni foam with a mass loading of $1\text{ mg}_{\text{cat}}\text{ cm}^{-2}$.

Turnover frequency (TOF) calculations. The TOF was calculated according to the equation:

$$T = \frac{j \times A}{4Fn}$$

where F is the Faraday constant (96485 C mol^{-1}); j is the current density ($\text{mA cm}^{-2}_{\text{ox}}$) obtained at overpotential (η) = 420 mV vs. RHE; A is the catalyst's BET surface area and n is the number of Co atoms. In this chapter, all Co atoms from reconstructed surface regions were taken into account. Based on the TEM images, the estimated thickness of the surface reconstructed region is 5 nm.

6.3 Results and discussion

The XRD technique was employed to examine the crystal structure of the pristine SmCo_5 catalyst. As shown in Figure 6.1a, the XRD pattern of SmCo_5 indicates that the pristine SmCo_5 catalyst possesses a hexagonal unit cell with a space group of $P6/mmm$.^[20] The high-resolution transmission electron microscopy (HRTEM) image of the pristine SmCo_5 sample is shown in Figure 6.1b, the clear lattice fringe indicates the SmCo_5 has good crystallinity. The d spacing value was measured to be 0.302 nm, which represents the (101) crystal plane of hexagonal SmCo_5 .

Figure 6.1 The crystal structure of pristine SmCo_5 (a) XRD pattern of SmCo_5 , (b) the HRTEM image of pristine SmCo_5 .

$\text{SmCo}_5/\text{CoO}_x\text{H}_y$ core/shell catalyst was synthesized by a pre-treatment process in the neutral solution (Figure 6.2). According to the Pourbaix diagram, under an oxidation potential of 1.75 V vs RHE, the Sm atoms on pristine SmCo_5 surface were oxidized into soluble Sm^{3+} ions and leached into the neutral electrolyte. The surface region of SmCo_5 nanoparticles was reconstructed into OER active $\text{SmCo}_5/\text{CoO}_x\text{H}_y$.

Figure 6.2 Schematic illustration of the pre-treatment process to synthesis $\text{SmCo}_5/\text{CoO}_x\text{H}_y$ core-shell catalyst.

To investigate the Sm leaching inductively coupled plasma mass spectrometry (ICP-ms) measurements, transmission electron microscopy (TEM) bright-field images and TEM line scan measurements were conducted. A significant amount of Sm ions, 15.7 ppb, compared to Co ions, 2.87 ppb, were detected in the neutral electrolyte after the pre-treatment, which indicates the Sm leaching. In the HRTEM image (Figure 6.3a) a 5 nm amorphous CoO_xH_y shell could be observed. Clear lattice fringe could be observed at the core region, which indicates SmCo_5 core remains its crystallinity. The d-spacing was measured to be 0.302 nm which matches the (101) crystal plane of hexagonal SmCo_5 . TEM line scan was employed to investigate the elemental distribution at the interface region. At the surface region of the $\text{SmCo}_5/\text{CoO}_x\text{H}_y$ the Sm signal is negligible (Figure 6.3b), which also confirms the Sm leaching during the pre-treatment process. As shown in Figure 6.3b, at a distance around 5 nm from the catalyst surface the Sm signal began to rise. The Co and O element signal was observed at out most of the catalyst surface. This result suggests that the 5 nm thick amorphous layer is most likely to be CoO_xH_y .

Figure 6.3 The structure of $\text{SmCo}_5/\text{CoO}_x\text{H}_y$ core-shell catalyst (a) the HRTEM of $\text{SmCo}_5/\text{CoO}_x\text{H}_y$, (b) TEM line scan of $\text{SmCo}_5/\text{CoO}_x\text{H}_y$ at the interface region.

In order to confirm that the amorphous shell is CoO_xH_y , *in-situ* Raman spectroscopy was employed to investigate the structural change during the surface reconstruction process. As shown in Figure 6.4a, the Raman spectrum of the pristine SmCo_5 does not exhibit any vibration peak under the open-circuit voltage (OCV) condition. When the anodic potential was applied on the working electrode, two Raman vibration peaks at 517 and 436 cm^{-1} were observed, which corresponds to the A_{1g} and E_g vibrational modes of Co-O and Co-O-Co in CoO_xH_y , respectively.^[21-22] Furthermore, soft X-ray adsorption spectroscopy (sXAS) measurements were employed to identify the surface (less than 5 nm) valence state and spin state of Co ions in the $\text{SmCo}_5/\text{CoO}_x\text{H}_y$. CoO with the high spin Co^{2+} and LiCoO_2 with the low spin Co^{3+} were used as reference samples. In Figure 6.4b, the Co L-edge sXAS spectrum of $\text{SmCo}_5/\text{CoO}_x\text{H}_y$ exhibits a Co- L_3 peak at 780.9 eV with a shoulder at 782.8 eV, which indicates the Co ions at the surface reconstructed CoO_xH_y shell possesses a valence of 3+ and low spin state. This result is consistent with the above *in-situ* Raman results that pristine SmCo_5 was reconstructed into $\text{SmCo}_5/\text{CoO}_x\text{H}_y$ core/shell catalyst after pre-treatment. The TEM image in Figure 6.3a shows that the CoO_xH_y shell thickness is around 5 nm.

Figure 6.4 Surface structure characterization (a) *in-situ* Raman spectrum of SmCo₅ during the pre-treatment process. (b) The Co L-edge sXAS spectra of the SmCo₅/CoO_xH_y, reference CoO and reference LiCoO₂.

To study the magnetic property of the samples, magnetic hysteresis loops under conditions of field-cooled (FC), zero-field-cooled (ZFC), and 300 K (close to the operating temperature of OER tests) were collected for the SmCo₅/CoO_xH_y catalyst. As shown in Figure 6.5a, under the FC mode SmCo₅/CoO_xH_y's magnetic hysteresis loop exhibits an obvious negative shift compared to that tested in the ZFC condition, which indicates the existence of the exchange bias.^[23] Also, a larger saturation magnetic moment can be obtained under the FC mode. The hysteresis loop of reconstructed SmCo₅/CoO_xH_y under FC mode (Figure 6.5a) exhibits an exchange bias (H_{EB}) of 127.5 Oe. In comparison, only negligible exchange-bias (0.25 Oe) could be observed in the hysteresis loops of pristine SmCo₅ (Figure 6.5b). These results confirm a strong exchange bias between the SmCo₅ core and the CoO_xH_y shell, which enables the pinning of spins at the interface and is generally defined as

the “pinning effect”.^[18] This feature provides an opportunity for investigating the spin-related OER performances of the as-prepared core/shell structured catalyst even without an operando external MF as the pinning effect can maintain the spin alignment in the interfacial CoO_xH_y .

Figure 6.5 The ZFC and FC mode magnetic hysteresis loops: (a) ZFC and FC mode hysteresis loop of $\text{SmCo}_5/\text{CoO}_x\text{H}_y$. (b) ZFC and FC mode hysteresis loop of SmCo_5 .

By applying an external magnetic field with field strength larger than the coercivity of the magnetic materials can effectively tune its spin alignment. The magnetic remanence of $\text{SmCo}_5/\text{CoO}_x\text{H}_y$ was investigated by applying a varied magnetic field. At room temperature the coercivity of $\text{SmCo}_5/\text{CoO}_x\text{H}_y$ is around 0.5 T, thus, the studies under 0.55, 0.70, 0.85, 1.10, and 1.25 T magnetic fields were carried out. Figure 6.6a shows the magnetic hysteresis loops of the $\text{SmCo}_5/\text{CoO}_x\text{H}_y$ under various magnetic fields. The remanence of $\text{SmCo}_5/\text{CoO}_x\text{H}_y$ increases as the field strength increases (Figure 6.6). It reaches a saturation value around 36 emu/g when the applied magnetic field reaches 1.10 T, further increment of the field strength has a negligible effect on the remanence (Figure 6.6b).

Figure 6.6 Remanence study (a) The hysteresis loops of $\text{SmCo}_5/\text{CoO}_x\text{H}_y$ under a various magnetic field, 300 K. (b) The remanence of $\text{SmCo}_5/\text{CoO}_x\text{H}_y$ at each applied magnetic field.

The effect of spin polarization of the bulk $\text{SmCo}_5/\text{CoO}_x\text{H}_y$ catalyst on its OER behavior was investigated at room temperature. The electrochemical performance was investigated by using a standard three-electrode setup in 0.1 M KOH solution. Polarization curves of the $\text{SmCo}_5/\text{CoO}_x\text{H}_y$ catalyst before and after magnetization were collected. The magnetization time was set as 15 minutes, and all the obtained currents were normalized to the BET surface area ($0.1759 \text{ m}^2/\text{g}$, Figure 6.7) of the electrode materials to get the intrinsic activity.

Figure 6.7 The Brunauer-Emmett-Teller (BET) surface area study.

The two polarization curves of the $\text{SmCo}_5/\text{CoO}_x\text{H}_y$ catalyst tested without magnetic field nearly overlapped (Figure 6.8a), which excludes the other factors that may influence the performance. As shown in Figure 6.8, a significant enhancement of OER performance was observed for magnetized samples compared to non-magnetized samples. When the working electrode was magnetized under a stronger magnetic field (1.25 T), the enhancement of OER activity was larger compared to when it was magnetized under a weaker magnetic field (0.55 T). This result matches well with previous finding that the OER enhancement increases as with the magnetism of the bulk catalysts.^[12] In this work, the $\text{SmCo}_5/\text{CoO}_x\text{H}_y$ was magnetized under different magnetic fields, which led to different magnetic remanences. As shown in Figure 6.6b, $\text{SmCo}_5/\text{CoO}_x\text{H}_y$ possesses a larger magnetic remanence (38.8 emu/g) when it was magnetized under a 1.25 T magnetic field compared to a 0.55 T magnetic field (19.8 emu/g).

Figure 6.8 OER polarization curves of $\text{SmCo}_5/\text{CoO}_x\text{H}_y$ before and after magnetization under different magnetic field: (a) 0 T, (b) 0.55 T, (c) 0.7 T, (d) 0.85 T, (e) 1.1 T and (f) 1.25 T.

Furthermore, the increments of j (at 1.65 V) after magnetization under different magnetic fields were plotted in Figure 6.9. The increment of j increases as the magnetic field strength increases and it would reach a saturation value (107.8 %) when the field strength reaches 1.10 T and above. This matches the trend of the catalyst's remanence (Figure 6.6), as the catalyst reaches its saturated remanence after an applied field larger than 1.10 T. The magnetic remanence value represents the magnetic polarization of the SmCo_5 core, a higher remanence indicates magnetic domains are more orderly aligned in the SmCo_5 core region. According to previous studies, electrons with opposite spin direction have weaker scattering effects when such electrons transfer through the magnetic lattice.^[9, 24] Electrons with spin configuration opposed to the SmCo_5 majority spin would have less scattering when it passes through SmCo_5 to the current collector. This would

facilitate a spin-selective removal of electrons from reaction intermediates which facilitates triplet oxygen generation as pointed out early by Gracia et al.^[9, 25-26]

Figure 6.9 The j increment (at 1.65 V) of $\text{SmCo}_5/\text{CoO}_x\text{H}_y$ under different magnetic fields and the $\text{SmCo}_5/\text{CoO}_x\text{H}_y$ remanence values under different magnetic fields.

The Tafel slopes were derived from polarization curves to investigate the activity and kinetic parameters of the catalysts. As shown in Figure 6.10a, at an overpotential of 350 mV the 1.25 T magnetized $\text{SmCo}_5/\text{CoO}_x\text{H}_y$ exhibits a prominent OER current density of 3.3 mA cm^{-2} , which is almost two orders of magnitude of the spinel-typed Co_3O_4 catalyst,^[27] 30-times higher than that of noble-metal-based IrO_2 ,^[26] and it's comparable to the benchmark perovskite-based catalyst BSCF.^[11] The Tafel slope of the $\text{SmCo}_5/\text{CoO}_x\text{H}_y$ is reduced from 79.49 to $63.32 \text{ mV dec}^{-1}$ when the $\text{SmCo}_5/\text{CoO}_x\text{H}_y$ is magnetized under a 1.25 T magnetic field. Figure 6.10b shows the chronopotentiometry (CP) results for the as-prepared unmagnetized $\text{SmCo}_5/\text{CoO}_x\text{H}_y$ and 1.1 T magnetized $\text{SmCo}_5/\text{CoO}_x\text{H}_y$ under a fixed current density of 7.8 mA cm^{-2} . The potential of the unmagnetized $\text{SmCo}_5/\text{CoO}_x\text{H}_y$ sample remained nearly unchanged within a period of 32000 s, which indicates $\text{SmCo}_5/\text{CoO}_x\text{H}_y$ catalyst is stable. However, the potential of the 1.1 T magnetized $\text{SmCo}_5/\text{CoO}_x\text{H}_y$ was gradually increasing until it approached the potential value of

unmagnetized $\text{SmCo}_5/\text{CoO}_x\text{H}_y$. This degradation of OER activity most probably arises from the interfacial spin relaxation during the long-term test.

Figure 6.10 Tafel plot and stability results: (a) Tafel plot of magnetized and unmagnetized $\text{SmCo}_5/\text{CoO}_x\text{H}_y$, (b) chronopotentiometry (CP) test at a fixed current density of 7.8 mA/cm^2

In practical applications water electrolyzers are operated at elevated temperatures, $50\sim 80^\circ\text{C}$, to boost the overall reaction efficiency.^[16] These elevated operation temperatures exceed the Curie temperatures of the majority of FM catalysts. In this way, the orderly aligned spins and magnetic domains are disrupted by the thermal agitation.^[28-30] To fill the gap, core/shell structured $\text{SmCo}_5/\text{CoO}_x\text{H}_y$ was hypothesized, which possesses a FM core with extremely high Curie temperature (1020 K), to utilise the spin-selective electron transfer induced by the FM/AFM coupling effect for high temperature practical applications. To verify this hypothesis, OER measurements were conducted at elevated temperatures (50 to 80°C). In order to avoid damaging the reference electrode under the high operation temperatures, a two-electrode setup with $\text{SmCo}_5/\text{CoO}_x\text{H}_y$ anode and Pt cathode was adopted to evaluate the water-splitting activity at elevated temperatures. As shown in Figure 6.11, the OER activity of unmagnetized $\text{SmCo}_5/\text{CoO}_x\text{H}_y$ increases with the operation temperature. The OER increment of 1.1 T magnetized

SmCo₅/CoO_xH_y could be observed up to 60 °C. When the operating temperature is higher than 60 °C the magnetized SmCo₅/CoO_xH_y does not exhibit increment in its OER performance compared to unmagnetized SmCo₅/CoO_xH_y. In Figure 6.11f the *j* increment of magnetized SmCo₅/CoO_xH_y (at 1.65 V vs RHE) is plotted against the operating temperature. The result shows the *j* increment of magnetized SmCo₅/CoO_xH_y decreases as the operating temperature increases.

Figure 6.11 OER performance of unmagnetized and 1.1 T magnetized SmCo₅/CoO_xH_y at elevated operating temperatures: (a) 25 °C, (b) 50 °C, (c) 60 °C, (d) 70 °C, (e) 80 °C and (f) the *j* increment at 1.65 V (vs RHE) as a function of operation temperature.

The operating temperature (50 to 80 °C) is lower than the Curie temperature (1020 K) of the SmCo₅ core, thus, the magnetic domain orientation of the SmCo₅ core does not change much. In this case, the temperature induced thermal agitation most likely affects the interfacial spin alignment. As shown in Figure 6.12, before the

magnetization process the magnetic domains in FM SmCo_5 core are partially aligned, and the spin at the core/shell interface is disordered. When the $\text{SmCo}_5/\text{CoO}_x\text{H}_y$ is magnetized under a 1.1 T magnetic field, firstly, the magnetic domains in the core region become more polarized. This is proved by the magnetic remanence improvement of magnetized $\text{SmCo}_5/\text{CoO}_x\text{H}_y$ (Figure 6.6). Secondly, the interfacial spin in the CoO_xH_y could also be polarized and its spin orientation follows the SmCo_5 core's magnetic domains' spin orientation. That is why an obvious exchange-bias was observed in $\text{SmCo}_5/\text{CoO}_x\text{H}_y$ (Figure 6.5). These interfacial polarized spins could serve as a spin filter, which facilitates selective removal of electrons with spin direction opposing the magnetic moment of FM core during OER reaction. This spin-selective electron transfer process during OER accumulates sufficient magnetic moment at the active sites which facilitates triplet oxygen evolution.^[9, 25] Thus, the OER increment was observed for the magnetized $\text{SmCo}_5/\text{CoO}_x\text{H}_y$. When the operating temperature is higher than 60 °C, the SmCo_5 core's magnetic domain structure does not change much, however, the interfacial polarized spin becomes disorder again (Figure 6.12). Thus, no OER increment would be observed at higher temperatures (Figure 6.11). The $\text{SmCo}_5/\text{CoO}_x\text{H}_y$ core-shell catalyst could maintain the interfacial spin polarization up to 60 °C, which exhibits a huge potential for high temperature practical applications.

Figure 6.12 The schematic diagram of how the spin alignment of $\text{SmCo}_5/\text{CoO}_x\text{H}_y$ affects by operating temperature.

6.4 Conclusion

In summary, we have synthesized $\text{SmCo}_5/\text{CoO}_x\text{H}_y$ core-shell catalyst which possesses an interfacial spin-pinning effect. The interfacial polarized spin of core-shell sample acts as a spin filter which facilitates selective removal of electrons with spin direction opposing the magnetic moment of FM core during the OER process. Utilizing the spin-pinning effect could be a way to improve the reaction kinetics of other chemical reactions in which reactants and products possess different spin states. Furthermore, the SmCo_5 core has uniquely high Curie temperature and strong FM property, which preserves its interfacially polarized spin and bulk magnetic domain structure even at an elevated operating temperature of 60 °C. This catalyst's unique property grants its huge potential to utilize spin-selective electron transfer, induced by the spin-pinning effect, in high temperature practical applications. Future work on this topic would aim to further increase the temperature while preserving the spin-pinning effect. A possible way is to modify the magnetic property of the oxyhydroxide layer by introducing other cations to form a $(\text{Co}_x\text{M}_{1-x})\text{O}_x\text{H}_y$ top layer, thus generating a FM/AFM interface which possesses a stronger spin-pinning effect.

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Chapter 7

Summary and Future Work

7.1 Summary

This thesis presents in-depth studies to explore spin-dependent OER mechanisms for transition metal oxide catalysts and proposes a new rational design for highly efficient OER catalysts.

We began with utilizing the unique edge-shared octahedra in spinel oxide to create magnetically polarized channels to facilitate spin-selective electron transfer. In order to achieve this, a layered antiferromagnetic inverse spinel oxide LiCoVO_4 , which possesses edge-shared Co^{2+} octahedra, was chosen. In an octahedral crystal field, the Co^{2+} ion possesses a high spin configuration $S = 3/2$ ($t_{2g}^5 e_g^2$) which has a net magnetic moment of $3 \mu_B$, which indicates the Co^{2+} edge-shared octahedra is spin/magnetically polarized. Furthermore, the Li^+ and V^{5+} ions possess d^0 configurations that are OER inert. In comparison, we synthesized ZnCo_2O_4 , with non-polarized Co^{3+} edge-shared octahedra. In an octahedral site, Co^{3+} ion possesses a low spin configuration ($t_{2g}^6 e_g^0$) with a net magnetic moment of $0 \mu_B$, which indicates the Co^{3+} edge-shared octahedral is non-magnetically polarized. The OER performance of LiCoVO_4 is much higher compared to ZnCo_2O_4 which indicates that spin-polarized channels are critical in OER. These spin-polarized channels facilitate spin-selective electron transfer during OER and promote triplet oxygen generation.

Besides that, we noticed that most transition metal-oxide-based catalysts are not stable under OER conditions and they are in fact in a core-shell structure with an oxyhydroxide surface layer as the real active surface after surface reconstruction. We designed bi-magnetic core-shell nanoparticles (NPs) with different core sizes and shell thicknesses that mimic such catalysts, to investigate the effect of magnetic domain structure on direct magnetic field induced OER catalytic activity enhancement phenomena. $\text{Fe}_3\text{O}_4@\text{Ni}(\text{OH})_2$ catalysts composed of a ferromagnetic (FM) Fe_3O_4 core and an antiferromagnetic (AFM) $\text{Ni}(\text{OH})_2$ shell were prepared. In these studies, we found that the interfacial FM-AFM coupling of these core-shell catalysts facilitates selective removal of electrons with spin direction opposing the magnetic moment of FM core, improving OER kinetics. The shell thickness is found to be critical in generating the coupling effect for OER enhancement. The magnetic domain structure of the FM core also plays a critical role. With a multiple domain core, the applied magnetic field aligns the magnetic domains, enhancing the electron transport process. A significant enhancement of OER activity is observed for the multiple domain core catalysts. We, therefore, proposed a magnetism/OER activity model that depends on two main parameters: interfacial spin coupling and domain structure.

Furthermore, this thesis applies the findings from these studies to design a good OER catalyst for high temperature practical applications. In practical applications, water electrolyzers operate in elevated temperatures, 50 to 80 °C, which exceed the Curie temperature of most FM OER catalysts, which may disrupt the ordered spin alignment of FM catalysts. Thus, the unique magnetic field induced OER activity enhancement of FM OER catalysts cannot hold at elevated temperatures. We design a $\text{SmCo}_5@\text{CoO}_x\text{H}_y$ core-shell catalyst with a high Curie temperature strong FM

SmCo₅ core. It maintained the magnetic field induced OER activity enhancement even at an elevated temperature of 60 °C. This catalyst's unique property grants it huge potential to utilize spin-selective electron transfer, induced by the spin-pinning effect, in high temperature practical applications.

7.2 Future work

(1) In this thesis I focus on spinel oxide-based FM-AFM core-shell OER catalysts and propose that the interfacial spin pinning of these core-shell catalysts facilitates spin-selective removal of electrons, improving OER kinetics. Ferromagnetism also occurs in some transition metals and transition metal alloys, such as Ni, Co, and permalloy (Ni₈₀Fe₂₀). In alkaline conditions, most transition metal-based OER catalysts are oxidized and form an oxyhydroxide (MOOH) surface under the OER potentials,^[1-2] thus, the interfacial spin pinning is also expected to occur in such materials. In this manner, our findings from oxide-based OER catalysts may be extendable to FM metallic OER catalysts.

Previous studies have shown that a trace amount of Fe additive in Co and Ni oxide-based OER catalysts can significantly boost the catalysts' OER activity. Xu and co-workers reported that the OER performance of CoAl₂O₄ is significantly enhanced when some Al ions are replaced by Fe ions (Figure 7.1).^[3] For the Ni-based OER catalyst Ni_{1-x}Fe_xOOH, Shannon and co-workers also reported a similar phenomenon where this catalyst's OER performance was enhanced significantly upon replacing 25 % of Ni ions with Fe ions.^[4]

Figure 7.1 OER performance of $\text{CoFe}_x\text{Al}_{2-x}\text{O}_4$, $x=0, 0.1, 0.25, 0.5, 1, 1.5$ and 2 .

I would propose that FM $\text{Ni}_{80}\text{Fe}_{20}$ alloy is a potential candidate for highly effective OER catalysts. After a simple pre-treatment process (around 50 CV cycles in alkaline conditions) a core-shell $\text{Ni}_{80}\text{Fe}_{20}\text{-Ni}_x\text{Fe}_y\text{OOH}$ could be obtained from this alloy. The interfacial spin pinning effect is expected to be present in this core-shell catalyst and an increment in OER activity is also expected when an external magnetic field is applied. Furthermore, metallic-based FM cores are much more conductive compared to oxide-based FM cores, making this type of catalyst likely to have better OER performance.

(2) In this thesis, the OER performance of each catalyst is investigated using an electrochemical cell. However, better catalysts for working electrodes, as in an electrochemical cell, do not necessarily translate into better water electrolyzer performance. Thus, lab-scale evaluation of the OER performance of the catalysts can only serve as a performance indicator for water electrolyzers.^[5]

For this reason, I would like to recommend evaluating the OER performance of as-synthesized catalysts in a membrane electrode assembly (MEA) water

electrolyzer.^[5] Furthermore, instead of using a potentiostat to power the MEA water electrolyzer, it could be powered by solar panels. Recently, Thomas and co-workers reported a photovoltaic-electrolysis system comprising two MEA electrolyzers and one InGaP/GaAs/GaInNAsSb triple-junction solar panel (Figure 7.2), which achieved a 30 % solar to hydrogen efficiency.^[6] I would also propose integrating the MEA water electrolyzer (with $\text{SmCo}_5/\text{CoO}_x\text{H}_y$ catalyst) with a commercial solar panel to investigate its solar to hydrogen efficiency.

Figure 7.2 Schematic illustration of the photovoltaic-electrolysis system.

(3) In this thesis I focused more on the physical and electronic properties of the catalysts and I did not pay much attention to the electrolyte. In oxygen electrocatalysis, H_2O has two roles; H_2O serves as 1) solvent of the electrolyte and

2) reactant of the OER. It would be interesting to separate these two roles of H_2O in oxygen electrocatalysis. To this end, researchers have tried to confine water nanodomains inside a stable organic matrix to isolate H_2O 's role as the reactant.^[7-8] By tuning the size of the H_2O nanodomain, the effect of H_2O 's nanostructure on electrochemical reactions can be investigated. Recently, Dr Alexis and co-workers reported that by increasing the concentration of H_2O in an acetonitrile electrolyte, the HER onset potential of the Pt electrode shifted towards less negative values at higher water content.^[7] This result indicates that the size of water domains in the electrolytes is likely to influence the HER activity of a Pt electrode.

Figure 7.3 HER performance of a Pt electrode in acetonitrile electrolyte with different water content (1, 2.5, 5, 7.5, and 10 % in mass from light to dark blue) (a) acetonitrile electrolyte with supporting salt of 100 mM of TBAClO₄. (b) acetonitrile electrolyte with supporting salt of 100 mM of NaClO₄.

While the aforementioned study is focused on the HER, it could potentially be extended to the OER. I would therefore propose investigating how the size of water domains affects the OER performance of different OER catalysts.

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