Investigation of transition metal oxides as electrocatalysts for water oxidation

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**INVESTIGATION OF TRANSITION METAL OXIDES AS
ELECTROCATALYSTS FOR WATER OXIDATION**

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

2021

INVESTIGATION OF TRANSITION METAL OXIDES AS ELECTROCATALYSTS FOR WATER OXIDATION

LI HAIYAN

SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

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

2021

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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Supervisor Declaration Statement

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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Authorship Attribution Statement

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

Chapter 4 is published as H. Li, Y. Chen, S. Xi, J. Wang, S. Sun, Y. Sun, Y. Du, Z. J. Xu. Degree of Geometric Tilting Determines the Activity of FeO₆ Octahedra for Water Oxidation. *Chemistry of Materials* **30**, 4313-4320 (2018). DOI: 10.1021/acs.chemmater.8b01321.

The contributions of the co-authors are as follows:

- Assoc. Prof. Z. J. Xu supervised the project.
- I wrote the manuscript draft. Assoc. Prof. Z. J. Xu revised the manuscript.
- Dr. Y. Chen and I performed the material synthesis and electrochemical characterization.
- Dr. Y. Chen collected the X-ray diffraction data and conducted the Rietveld analysis.
- I conducted the density functional theory calculation. Dr. Y. Sun helped interpret the density of state data.
- Dr. Y. Du and Dr. S. Xi collected the X-ray absorption spectroscopy data in Singapore Synchrotron Light Source.
- Dr. J. Wang and Dr. S. Sun collected the scanning electron microscopy images in the Facility for Analysis, Characterization, Testing and Simulation.

Chapter 5 is published as H. Li, S. Sun, S. Xi, Y. Chen, T. Wang, Y. Du, M. Sherburne, J. W. Ager, A. C. Fisher, Z. J. Xu. Metal–Oxygen Hybridization Determined Activity in Spinel-Based Oxygen Evolution Catalysts: A Case Study of ZnFe_{2-x}Cr_xO₄. *Chemistry of Materials* **30**, 6839-6848 (2018). DOI: 10.1021/acs.chemmater.8b02871.

The contributions of the co-authors are as follows:

- Assoc. Prof. Z. J. Xu supervised the project.

- I wrote the manuscript draft. Assoc. Prof. Z. J. Xu, Prof. A. C. Fisher, Dr. M. Sherburne, and Dr. J. W. Ager revised the manuscript and provided valuable advice.
- I performed the material synthesis, collected the X-ray diffraction patterns and electrochemical data, conducted the density functional theory calculation, and analyzed the related data.
- Dr. Y. Chen performed the Rietveld refinement of the X-ray diffraction data.
- Dr. Y. Du and Dr. S. Xi collected the X-ray absorption spectroscopy data in Singapore Synchrotron Light Source. Dr. S. Xi. helped interpret the extended X-ray absorption fine structure data and carried out the spectral fitting.
- Dr. S. Sun collected the scanning electron microscope images in the Facility for Analysis, Characterization, Testing and Simulation.

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- I performed the material synthesis, collected the X-ray diffraction patterns, performed the electrochemical measurements, and analyzed the related data.
- Dr. Y. Chen performed the Rietveld refinement of the X-ray diffraction data, the fitting of the X-ray photoelectron spectroscopy data, and the analysis of the inductively coupled plasma mass spectroscopy data.
- Dr. J. Ge conducted the transmission electron microscopy and the energy-dispersive X-ray spectroscopy in the Facility for Analysis, Characterization, Testing and Simulation.

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Abstract

Scalable hydrogen production by water splitting has been given high expectations to satisfy the ever-growing demands for renewable clean energy and cut greenhouse gas emissions. In the past decades, massive research efforts have been made globally to develop highly efficient oxygen evolution electrocatalysts, because of the significant energy loss caused by the slow oxygen evolution reaction (OER) during water electrolysis. Earth-abundant transition metal (TM) oxides emerge as the potential candidates due to their inexpensiveness and promising activity. For science-based catalyst design, gaining fundamental understandings of the oxygen evolution catalysis on transition metal oxides is essential. This thesis first addresses the role of geometric tilting in influencing the catalytic efficiency of FeO_6 octahedra. By setting FeO_6 octahedra into crystalline environments, including AFeO_3 ($\text{A} = \text{Y}, \text{Gd}, \text{Pr}, \text{and La}$) perovskites, ZnFe_2O_4 spinel, and $\beta\text{-FeOOH}$, a negative correlation is identified between the catalytic performance and the tilting degree of FeO_6 octahedra. It is elucidated that FeO_6 octahedral tilting changes the Fe-O covalency and therefore varies the catalytic performance of ferrites. Secondly, by a case study of $\text{ZnFe}_{2-x}\text{Cr}_x\text{O}_4$ ($x = 0 - 2$), the influential electronic parameter of the octahedrally-coordinated transition metals in spinel-type oxide catalysts is explored. The specific OER activity of $\text{ZnFe}_{2-x}\text{Cr}_x\text{O}_4$ is found to have a volcano-shaped dependence on the Cr content. It is identified that the metal-oxygen hybridization at active sites (defined as the percentage of O 2p states that hybridize with TM 3d states), which also follows a volcano-shaped trend with the Cr content, governs the OER activity of $\text{ZnFe}_{2-x}\text{Cr}_x\text{O}_4$. To rationalize the correlations identified between the bulk electronic parameters and the catalytic performance of metal oxides, a deep understanding of how the oxide surfaces catalyse OER is critical. Recently, growing studies have revealed the surface restructuring of some metal oxides under OER conditions. To identify the real active phase for perovskites undergoing surface reconstruction upon water oxidation, cubic $\text{SrCoO}_{3-\delta}$ perovskites respectively modified by bulk Fe dopant and Fe ions incorporated from the electrolyte are investigated as OER catalysts. It is found that the activity of $\text{SrCoO}_{3-\delta}$ oxide electrode is sensitive to the electrolyte environment and the two Fe-modified $\text{SrCoO}_{3-\delta}$ catalysts, with similar surface amorphous layers but different remaining bulk phases, exhibit roughly equal activities.

Accordingly, the reconstructed surface, instead of the remaining bulk, is identified to be directly responsible for the measured catalytic performance.

Lay Summary

Electrochemical water splitting provides a way to efficiently store the intermittent electricity generated by renewable energy sources, such as wind, tide, and sunlight, into environmentally friendly hydrogen fuel. In the water-splitting process, the energy loss mainly comes from the sluggish oxygen evolution reaction (OER) at the anode. Hence, an efficient electrocatalyst is required to accelerate the rate of water oxidation, i.e., OER. After decades of exploration, oxides based on earth-abundant transition metal elements including nickel, cobalt, and iron emerge to be potential OER electrocatalysts in alkaline media, because of their moderate price and good catalytic performance. For science-based catalyst design, the exploration of structure-functionality relationships is a common approach. To be specific, the physicochemical properties of transition metal oxides can be finely tuned by changing the elemental composition and/or the geometric structure, and thus correlations can be built between the altered catalyst properties and the resulting catalytic performance, from which the factors critical to the OER catalysis may be revealed. By this means, this thesis contributes to gaining the fundamental understandings of the oxygen evolution catalysis on transition metal oxides. The first project addresses how the geometric effect, for example, the variation in Fe-O-Fe bond angles, influences the catalytic efficiency of pure iron-based oxides. The second project deals with the electronic parameter governing the catalytic performance of spinel oxides, one type of the widely concerned OER catalyst materials. For some transition metal oxides, the initially crystalline surface structures are changed into amorphous forms during the OER process. Hence, the third project attempts to resolve the confusion as to whether the observed catalytic performance is solely governed by the *in situ* formed surface species or also subjected to the strong influence of the underlying bulk oxide.

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Figure 7.4 Cyclic voltammograms of BaNiO₃ perovskite in 0.1 M KOH electrolyte.

Figure 7.5 Tafel plots of BaNiO₃ perovskite in Fe-free and Fe³⁺-spiked KOH solutions.

Abbreviations

BET	Brunauer-Emmett-Teller
CV	Cyclic voltammetry
DFT	Density Functional Theory
DOS	Density of State
EDS	Energy Dispersive X-ray Spectroscopy
EXAFS	Extended X-ray Absorption Fine Structure
FESEM	Field Emission Scanning Electron Microscopy
GCE	Glassy Carbon Electrode
HRTEM	High Resolution Transmission Electron Microscopy
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
OER	Oxygen Evolution Reaction
XANES	X-ray Absorption Near Edge Structure
XAS	X-ray Absorption Spectroscopy
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray Diffraction
SEM	Scanning Electron Microscopy
TEM	Transmission Electron Microscopy

Chapter 1

Introduction

A massive effort has been made globally to develop highly efficient oxygen evolution electrocatalysts for scalable water electrolysis. Earth-abundant transition metal oxides are promising candidates. This chapter first presents hypotheses regarding the geometric effect on the catalytic performance of FeO_6 octahedra, the single influence of the octahedral units on the specific activity of spinel oxides, and the active phase responsible for the measured activity of self-reconstructed perovskites. According to the above hypotheses, the objectives and scope of this thesis are elaborated. Next, the dissertation overview is briefly described. At last, the major research findings in this thesis are summarized.

1.1 Hypothesis

Water electrolysis has excellent potential for large-scale production of clean energy, which hence is an effective means to alleviate the energy crisis and reduce greenhouse gas emissions. However, its efficiency is seriously impeded by the sluggish oxygen evolution reaction (OER) at the anode.^[1] Therefore, extensive attention has been drawn to develop advanced catalysts to boost the OER reaction rate. After years of exploration, oxides based on earth-abundant transition metal (TM) elements, especially nickel (Ni), cobalt (Co), and iron (Fe), emerge to be highly promising OER catalysts because of their moderate price and promising performance in alkaline media. Both the efficient catalyst screening and the rational catalyst design are inseparable from understanding intrinsic factors influential in the oxygen evolution catalysis on earth-abundant transition metal oxides (TMOs).^[1]

Fe has been found as an interesting species in promoting Co and Ni oxides/(oxy)hydroxides' OER activity,^[2-8] although itself was ever believed not very active in the form of oxides and (oxy)hydroxides. However, Fe is more earth-abundant than Co and Ni, and recently growing studies have indicated Fe being capable of efficiently catalyzing OER.^[9] To help the development of highly active iron-based OER electrocatalysts, a better knowledge of the local chemical environment of the highly efficient Fe sites is essential. As FeO_6 octahedra network can be set into specially selected crystalline phases and thus are adjustable, the geometric effect of FeO_6 octahedron on the OER catalysis of Fe oxides and (oxy)hydroxides can be explored. The variation in the geometric structure may change the electronic properties critical to determining the catalytic performance. Chapter 4 tests the hypothesis that the OER catalytic performance of FeO_6 octahedra can be improved by modulating the geometric tilting degree due to the increase in Fe-O covalency.

Perovskite and spinel are two widely focused oxide families for developing OER catalysts, owing to their tunability in physicochemical properties. Unlike an ABO_3 -type perovskite where only B-site TM is considered to have a critical compositional effect on the OER catalysis, a spinel oxide (AB_2O_4) provides two geometrical sites, T_d and O_h , for transition metal A and B to occupy. As the T_d coordination yields a lower degree of metal-oxygen covalency than the O_h coordination, T_d -site TM is regarded to be inferior to the same element in O_h site for water oxidation, which is supported by experimental results.^[10-11]

However, the superexchange interaction between catalytically active T_d - and O_h -site cations, which is generally stronger than that between O_h -site cations,^[12] have an undetermined influence on the activity of O_h -site cations. Nevertheless, few previous studies on spinel-type OER catalysts designedly exclude the possible impact from T_d - O_h superexchange interaction and analyze the single effect of O_h -site transition metal (TM_{O_h}) on OER catalysis. Without interference from T_d -site active cations, Chapter 5 tests the hypothesis that the OER catalytic performance of spinel oxides is governed by the electronic structure of TM_{O_h} cations.

The transition of surface crystalline structures into amorphous states during OER has been observed on some perovskite oxide electrocatalysts, especially those with a bulk O p band centre near the Fermi level.^[13-16] This challenges the previous design principle that the measured OER activity can be directly related to as-synthesized perovskites' electronic properties. Experimentally, it is almost impossible to separate the *in situ* derived surface species and the underlying bulk phase. Therefore, it is elusive whether the observed catalytic performance is exclusively dominated by the restructured surface or also strongly influenced by the remaining bulk. Chapter 6 tests the hypothesis that for perovskite oxides self-reconstructed upon water oxidation, the reconstruction-derived surface species principally account for the measured OER catalytic performance.

1.2 Objectives and Scope

Given the above hypotheses, the objective of this thesis is to gain essential understandings of the oxygen evolution catalysis on earth-abundant transition metal oxides. Iron-based materials are hopeful candidates for highly cost-efficient OER electrocatalysts. To elucidate the influence of geometric tilting on catalyzing OER, FeO_6 octahedra are set into specially selected crystalline ordered environments, including perovskite, spinel, and oxyhydroxide. With the aid of theoretical calculation, the physical origin of the correlation identified between the FeO_6 octahedral tilting degree and the catalytic efficiency is disclosed. To reveal the electronic structures of TM_{O_h} cations critical to the activity of spinel oxides, $ZnFe_{2-x}Cr_xO_4$ ($x = 0 - 2$) are studied as OER electrocatalysts. With the assistance of X-ray absorption spectroscopy technique and theoretical computation, a

catalytic-critical electronic parameter that determines the OER activity of $\text{ZnFe}_{2-x}\text{Cr}_x\text{O}_4$ is identified. To differentiate the OER activities contributed by the reconstructed surface and the remaining bulk, the catalytic behaviors of cubic $\text{SrCoO}_{3-\delta}$ (SC) perovskite and Fe-modified SC in alkaline solution are investigated. Two approaches are used to incorporate Fe into SC, i.e., bulk Fe doping ($\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$, SCF02) and surface absorbing Fe ions from Fe^{3+} -spiked electrolyte ($\text{SC} + \text{Fe}^{3+}$). The activity comparison among SC, SCF02, and $\text{SC} + \text{Fe}^{3+}$ evidences the dominant role of the reconstruction-derived surface structures in catalyzing OER.

1.3 Dissertation Overview

This thesis addresses the structure-activity relationship of earth-abundant transition metal oxide electrocatalysts for water oxidation and the fundamental origin of the identified structure-activity relationship.

Chapter 1 provides a rationale for the investigation of earth-abundant transition metal oxides as OER electrocatalysts and outlines the goals and scope.

Chapter 2 reviews the literature regarding the evaluation of catalytic activity for metal oxides, the exploration of the structure-functionality relationship in metal oxide OER electrocatalysts, and recent research about developing earth-abundant transition metal oxides as OER electrocatalysts.

Chapter 3 discusses the principles underlying the synthesis methods, characterization techniques, and theoretical calculations.

Chapter 4 elaborates the role of the geometrical tilting of FeO_6 octahedra in influencing the activity of Fe-based catalysts for water oxidation.

Chapter 5 elaborates the role of the electronic structure of O_h -site TM cations in the OER catalysis on $\text{ZnFe}_{2-x}\text{Cr}_x\text{O}_4$ ($x = 0-2$) spinel oxides and identify metal-oxygen hybridization

as the catalytic-critical parameter.

Chapter 6 elaborates the roles of the amorphized surface and the remaining bulk in the OER catalysis on $\text{SrCoO}_{3-\delta}$ perovskite oxide.

Chapter 7 summarizes the whole thesis and presents reconnaissance studies that require further investigation.

1.4 Findings and Outcomes

This research led to several novel outcomes by:

1. Correlating the OER catalytic performance with the geometric tilting degree of FeO_6 octahedra in crystalline ferrites.
2. Elucidating the physical origin of the correlation between the intrinsic OER activity and the geometric titling degree of FeO_6 octahedra.
3. The OER catalytic performance of spinel oxides can be promoted by varying the compositional ratio of O_h -site TM cations.
4. Identifying $\text{TM}_{\text{O}_h}\text{-O}$ hybridization degree as a critical parameter for the OER catalysis on $\text{ZnFe}_{2-x}\text{Cr}_x\text{O}_4$ ($x = 0\text{-}2$) spinel oxides.
5. Demonstrating Fe ions present in the alkaline electrolyte can enhance the catalytic efficiency of $\text{SrCoO}_{3-\delta}$ perovskite oxide.
6. Evidencing the *in situ* formed surface layer, rather than the remaining bulk phase, is principally responsible for the measured catalytic activity of perovskite oxides undergoing self-reconstruction during OER.

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Chapter 2

Literature Review

To accelerate the oxygen evolution reaction (OER) rate, considerable research effort has been devoted to developing highly efficient electrocatalysts in the latest decades. Earth-abundant transition metal (TM) oxides are promising candidates for OER electrocatalysts under alkaline conditions. This chapter first introduces basic knowledge about OER. Following that, the common approach used to evaluate the specific activity of metal oxide powders is presented. Then, the exploration of the structure-activity relationship for a science-based catalyst design is discussed. Finally, recent studies concerning the development of earth-abundant TM-based oxide electrocatalysts are reviewed.

2.1 Oxygen Evolution Reaction

Growing concerns on energy security and environmental protection stimulate the demand for a sustainable energy system. The discovery of a sustainable energy carrier to replace conventional fuels is central to that system. Hydrogen emerges as the best candidate, because of its high energy density and environmental friendliness. Massively producing hydrogen gases by splitting water with electricity generated by renewable but intermittent energy sources (e.g., sunlight, wind, and tide) allows a future powered by sustainable carbon-free fuels.^[1] The electrochemical reaction to derive hydrogen from water, namely water electrolysis, consists of two half-reactions. At the negatively charged cathode, the hydrogen reduction reaction occurs and is referred to as the hydrogen evolution reaction (HER):

At the positively charged anode, the oxygen oxidation reaction happens and is mentioned as the oxygen evolution reaction (OER):

In contrast with HER, in which only the transfer of two electrons is engaged, OER is involved with a more complicated transfer of electrons as well as protons and hence consumes the major energy required to split water.^[2] The sluggish kinetics of OER not only lowers the energy efficiency of the overall water splitting reaction but also impedes the commercialization of this hydrogen production technology. To resolve this problem, a wealth of research has been performed over the past decades on developing efficient, robust, cost-effective, and environmentally friendly catalysts for OER. The harsh conditions of water oxidation in acidic environments limit the candidates for OER catalysts to iridium-based materials, because of their promising activity and relatively high stability at low pH.^[3] However, considering the scarcity and the costliness of noble metals, the large-scale application of iridium-based catalysts is greatly hindered. Therefore, extensive attention has been drawn to exploring more cost-efficient OER catalysts, especially those based on earth-abundant transition metal elements. As a consequence, a lot of highly active complex

transition metal oxides with different structure-types, including perovskite $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF),^[4] spinel $\text{ZnFe}_{0.4}\text{Co}_{1.6}\text{O}_4$,^[5] and layered $\text{LiCo}_{0.8}\text{Fe}_{0.2}\text{O}_2$,^[6] have been developed.

2.2 Catalytic Activity Evaluation

Due to the electrode kinetic barrier, an applied potential (E) higher than the equilibria potential (E_{eq}) is always required to activate the reaction. Overpotential (η) is defined as the potential difference between E and E_{eq} ,

$$\eta = E - E_{eq}$$

The correlation between E and the current density (i) can be expressed by the Butler–Volmer equation,

$$i = i_0 \left[\exp\left(\frac{\alpha_a n F E}{RT}\right) + \exp\left(\frac{\alpha_c n F E}{RT}\right) \right]$$

where i_0 is the exchange current density, F the Faraday's constant, n the number of electrons involving transfer, R the universal gas constant, T the thermodynamic temperature, and α_a and α_c , typically assumed to be 0.5, are the transfer coefficient of anodic reaction and cathodic reaction, respectively.^[7] When the anodic overpotential is sufficiently high, the cathodic current is negligible, and thus the Butler–Volmer equation can be simplified as follow, i.e. the Tafel equation,

$$i \approx i_0 \left[\exp\left(\frac{\alpha_a n F E}{RT}\right) \right]$$

which is equivalent to its logarithm form, and the Tafel slope can be derived from the latter equation. The expression for calculating the Tafel slope (b) is written as follow,

$$b = \frac{\partial \eta}{\partial \log(i)} = \frac{2.303RT}{\alpha F}$$

Besides indicating the rate of the current density (i) increasing with the overpotential (η), Tafel slope (b) can provide insightful information on the electrochemical reaction mechanism. For a reaction involving multiple-electron transfer, the transfer coefficient can be derived from the following equation,

$$\alpha_a = \frac{n_b}{v} + n_r \beta$$

where n_b is the electrons involving transfer prior to the rate-determining step (RDS), v the amount of RDSs that have gone through in the overall reaction, n_r the number of electrons engaged in the RDS, and β the transfer coefficient of the RDS.^[7] This equation is potent for identifying the RDS in an electrochemical reaction. However, it is insufficient to describe the kinetic behaviors of OER because different reaction pathways may have the same value of Tafel slope. Besides, the same reaction process under different overpotentials may have different Tafel slope due to the variation of the surface coverage degree. Therefore, other tools besides Tafel analysis, for example, ab initio modelling, are required to obtain a full understanding of the OER mechanism.

As a critical parameter for evaluating metal oxides' inherent catalytic performance, specific activity denotes the OER kinetic current (at certain overpotential) normalized to the real surface area of a catalyst. For electrocatalysis studies, the knowledge of the real surface area is always essential. Because only the surface atoms can be involved in the electrocatalysis, it is unreasonable to directly compare the geometric-surface-area-based activities from different experimental situations. In contrast, the normalization of the overall activity to the real surface area makes the experimental results universally comparable. As summarized by Trasatti and Petrii, there are at least eleven *in situ* methods and four *ex situ* methods to measure the real surface area of electrodes.^[8] Because each method is established on some specific assumptions and responds in a particular way to its specific probes, the as-obtained real surface area values may vary with different measurement methods and experimental conditions.^[9] For noble metals and their alloys, there are some well-established approaches to evaluate the electrochemically active surface area (ECSA), such as hydrogen underpotential deposition, surface oxide reduction, CO stripping, and underpotential deposition.^[9] However, these *in situ* methods are inapplicable to metal oxide electrocatalysts. Some studies adopt the double-layer-capacitance approach to *in situ* quantify the ECSAs of metal oxides.^[10-11] Nevertheless, except for the weakness that it is hard to obtain the real double-layer capacitance without the interference from faradic currents or electrolyte ions adsorption, the greatest limit to this approach is the accurate determination of area-specific double-layer capacitance, which varies significantly among materials.^[1, 10] Regarding *ex situ* techniques, microscopy study and Brunauer-Emmet-Teller (BET) analysis are the two most common approaches. For porous

metal oxides, microscopy methods are unfavorable, because the inner microstructure information cannot be detected by the observation from the top of the sample material. Besides, the fine out-of-flatness on the surface may be neglected because it is beyond the resolution of microscopy. Moreover, the reliability of the surface area calculated by the microscopy method depends on the accurate approximation of surface morphology. For metal oxides with irregular external morphology,^[12] it is hard to make an appropriate approximation. As for BET analysis, its validness for determining the surface area of metal oxide powders has been scrutinized by several studies,^[13-14] and hence it has been commonly used to extract the specific activity of metal oxide electrocatalysts.

2.3 Exploration of the Structure-Functionality Relationship

Figure 2.1 Classification of 14 descriptors ever reported for the OER activity into five descriptor families, among which electron occupancy and covalency are identified to be the most influential parameters. The radial component reflects the contribution of a descriptor to the factor concerned.^[15]

To expedite the development of advanced electrocatalysts, a good understanding of the factors critical to the OER catalysis on transition metal oxides (TMOs) is vital.^[1] A

prevailing opinion on OER catalysts with high efficiency is based on the Sabatier principle, that is, an optimal catalyst surface cannot bind with reaction intermediates too closely nor too loosely.^[1, 4, 16] Consequently, the surface reactivity is expected to follow a volcano-shaped trend with the binding strength of crucial intermediates, and the highest activity relies on the optimal binding strength. The diversity in the electronic properties of catalyst surfaces is a critical reason for the variety of their binding abilities and hence the difference in reactivities.^[17] Since it is hard to directly observe and measure the adsorption/desorption behavior of OER intermediates on the oxide surface, activity descriptors associated with the electronic structures of TMOs have been proposed (Figure 2.1).^[15] To uncover the physical origin of these identified descriptors, a good knowledge of the OER mechanism and the identification of the real active surface components are essential.

Figure 2.2 Classical OER mechanism on TMO in acid (blue line and marks) and basic (red line and marks) media. M represents surface metal sites. For one of the possible routes (black line), the generation of M–OOH intermediate is a necessary step for oxygen evolution. And for another possible route (green line), oxygen molecules are formed via the direct combination of two neighboring M–O intermediates.^[2]

In the classical OER mechanism proposed for TMO catalysts, the electron-proton transfer is concerted and occurs at surface transition-metal reactive centres.^[18-19] As shown in Figure 2.2, there are two possible pathways to form molecular oxygen on surface metal sites.^[7] One approach, the black route in Figure 2.2, consists of four steps of coupled proton-electron transfer, and the release of molecular oxygen involves the formation of hydroperoxide intermediate M–OOH. In the other pathway, i.e., the green route in Figure

2.2, two M–O species directly combine, and subsequently molecular oxygen is released. For perovskite-type TMOs, Suntivich et al. reported that transition-metal e_g occupancy, in conjunction with covalency, can well explain the observed OER activity trend on the basis of the four-step classical OER mechanism.^[4] The octahedrally-coordinated TM cations in perovskite oxides are regarded as the catalytically active sites and their interaction with OER intermediates largely relies on the coupling between their e_g states and the O 2p states of oxygenated adsorbates.^[4] Hence, the binding strength between the active sites of a perovskite oxide and the OER intermediates is closely related to the e_g occupancy of TM cations. And a moderate level of e_g occupation, which is around unity, represents the optimal binding strength and therefore the maximal intrinsic activity. Besides, augmenting the metal-oxygen covalency can further enhance the OER catalytic performance, which is ascribed to that increased TM-O covalency quickens the charge transfer rate between TM sites and intermediates and hence promotes the reaction kinetics.^[4]

Figure 2.3 One possible lattice-oxygen participation mechanism, in which two lattice oxygens are directly paired to produce molecular oxygen.^[20]

In the conventional OER mechanism, only the redox chemistry of transition metal cations is considered and the generated O_2 molecules are solely derived from water. However, experimental results have demonstrated that the molecular oxygen evolved on some perovskite-type TMOs can come from lattice oxygen.^[21] And a few recent studies propose OER mechanisms involving lattice-oxygen oxidation, i.e., lattice-oxygen participation mechanism (LOM), in which the redox activity of surface lattice oxygen is taken into

consideration.^[21-22] Figure 2.3 displays one possible LOM, which involves decoupled electron-proton transfer steps.^[20] It is found that the increased TM-O covalency of perovskite oxides can trigger the non-concerted LOM and hence the OER mechanism on TMOs relies on the bulk electronic structure.^[21] The possible participation of lattice oxygen oxidation during OER improves the mechanistic understanding, which brings about new strategies for catalyst design.^[23]

During the OER, TMOs suffer high anodic potentials, possibly resulting in the dynamic evolution of electronic properties with the variation of applied potential.^[24-28] This challenges previous views that the measured activity can be directly linked to the optimized electronic structure of as-prepared TMOs and makes it necessary to cast new insights into the structure-functionality relationship previously identified by experimental and theoretical investigations. Although growing studies have demonstrated that many TMO surface structures under OER conditions will be inevitably evolved into certain oxyhydroxide, the real catalytically active phase,^[29-32] distinct difference exists in the OER activities of the same metal oxyhydroxides.^[33] Hence, it can be expected that different catalytic performance can be observed for oxyhydroxides *in situ* derived from different precatalysts.^[34] Therefore, the design of TMOs as precatalysts for the *in situ* formation of surface species with unique electronic structures are also beneficial for the development of desirable OER catalysts.

2.4 Earth-Abundant Transition Metal Oxide Electrocatalysts

2.4.1 Perovskite Oxides

Perovskite oxide (ABO_3) is an extensively studied oxide family for OER catalysis, because of their great flexibility in composition as well as structure and hence the extraordinary adjustability in their physicochemical properties.^[35] As shown in Figure 2.4a, an ideal perovskite oxide is in a highly symmetric cubic structure, in which corner-shared BO_6 octahedra construct a three-dimensional (3D) network and A-site cations reside in the voids of these octahedra. Typically, A site is occupied by relatively larger and more electropositive cations, such as rare earth, alkaline, and alkaline earth metal cations,

whereas B site by transition metal cations, which are smaller in radius and more electronegative. Furthermore, by partially replacing A- and/or B-site elements, a greater amount of perovskite compounds ($A_{1-x}A'_xB_{1-y}B'_yO_3$) can be created, as shown in Figure 2.4b.^[36] Given the principle of electrical neutrality and the possible oxidation states of A-/B-site cations, several situations of charge distribution can be formed, such as $A^IB^VO_3$, $A^{II}B^{IV}O_3$, and $A^{III}B^{III}O_3$. Nevertheless, the charge discrepancy between overall cations and oxygen anions (six) will cause oxygen nonstoichiometry, i.e. oxygen deficiency or oxygen excess, leading to a more general formula $A_{1-x}A'_xB_{1-y}B'_yO_{3\pm\delta}$.^[36] While the B-site TM cations are usually treated as the OER active sites, cations in the A sites are regarded as ineffective in determining electrocatalytic activities. However, the size and valence state of A-site cations can impact the crystal structure symmetry, the B-site cation valency, and the oxygen nonstoichiometry degree. Therefore the variation of A-site cations also can affect the electrochemical reactivity of perovskites.^[36]

Figure 2.4 (a) Crystal structure of ideal perovskite oxides (ABO_3).^[2] (b) Doping strategies for perovskite oxides.^[36]

Massive efforts have been devoted to utilizing perovskite-type oxides as templates to develop highly efficient and robust OER catalysts. As mentioned earlier, Suntivich et al. proposed e_g filling, together with metal-oxygen covalency, as a good activity descriptor for perovskite oxides (Figure 2.5), and successfully predicted BSCF with e_g occupancy close to unity as a highly efficient OER electrocatalyst.^[4] The effectiveness of e_g filling as an activity descriptor has been evidenced by later studies. For example, Lee et al.^[37] suggested that the hexagonal perovskite $BaNiO_3$ is transformed into $BaNi_{0.83}O_{2.5}$ after extensive

potential cycling, and hence the e_g filling of Ni is changed from zero to close to unity, which is responsible for the significantly increased OER activity. Yagi et al.^[38] reported that perovskites containing high-spin Fe^{4+} cations (with $t_{2g}^3 e_g^1$ configuration) in B sites, i.e. SrFeO_3 , CaFeO_3 and $\text{CaCu}_3\text{Fe}_4\text{O}_{12}$, show catalytic activity comparable to that of BSCF.

Figure 2.5 (a) Potential at $50 \mu\text{A cm}^{-2}$ as a function of the e_g occupancy of B-site transition metal in perovskite oxides. (b) Potential at $50 \mu\text{A cm}^{-2}$ as a function of the B-O covalency, under the condition of e_g occupancy = 1.^[4]

Figure 2.6 (a) Drastic surface amorphization of BSCF perovskite within five CV cycles.^[28] (b) Potential at $0.5 \text{ mA cm}^{-2}_{\text{oxide}}$ as a function of the bulk O p band centre (vs. E_F) of Co-based perovskites.^[39]

More recently, the surface structural transformation of perovskite oxides under OER conditions have been intensively reported, irrespective of the pH value of the electrolyte, stimulating further interest in the origin of perovskites' OER catalytic performance. For instance, it was reported by Shao-Horn's group that the initially crystalline structures in the

surface region of BSCF quickly transformed into amorphous layers during catalysis process in basic media, along with the loss of A-site metal cations, i.e., Ba^{2+} and Sr^{2+} , as well as the increment of pseudocapacitance and OER activity (Figure 2.6a).^[28] It was proposed that the surface growth of an amorphous layer allows more active sites of BSCF accessible to the electrolyte, as evidenced by the rise of pseudocapacitive current, and thus leads to the increased OER current. It was also observed that the occurrence of quick surface amorphization under OER conditions was associated with the starting materials. For perovskites as highly active as BSCF, for example, $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.4}\text{Fe}_{0.6}\text{O}_{3-\delta}$, the rapid change in surface atomic structures during oxygen evolution was also observed. On the contrary, for perovskites less catalytically active than BSCF yet under the same electrochemical conditions, such as $\text{La}_{0.4}\text{Sr}_{0.6}\text{CoO}_{3-\delta}$, LaCoO_3 , and LaMnO_3 , no surface amorphous region was detected. The different surface evolution behaviors of these investigated materials under OER conditions was attributed to the difference in their electronic properties, e.g., the O p band centre versus the Fermi level (E_F). As illustrated in Figure 2.6b, the rapid surface amorphization at OER potentials was proposed to take place on perovskites with O p band centre as high as that of BSCF.^[39]

Figure 2.7 Mechanistic picture for the self-reconstruction of BSCF perovskite upon water oxidation.^[29]

With the help of *operando* techniques, Schmidt's group provided direct insights into the local electronic and structural changes of BSCF with the applied potentials and offered a mechanistic picture for the OER/LOER on highly active perovskites with flexible

structures such as BSCF.^[29] Nanometer-sized BSCF, $\text{La}_{0.2}\text{Sr}_{0.8}\text{CoO}_{3-\delta}$, and CoO particles were prepared by flame spray (FS) method rather than the conventionally used sol-gel method. Among the investigated Co-based catalysts, the topmost activity of BSCF was accompanied by the greatest variation in Co valency and the generation of a Co/Fe oxy(hydroxide) layer on the surface. Accordingly, the high OER activities of metal oxides were proposed to result from their ‘instability’ during OER. According to the thermodynamic deduction from the same group, any metal oxide under OER conditions is thermodynamically unstable owing to the oxidation of lattice oxygen anion, i.e., lattice oxygen evolution reaction (LOER).^[40] Hence, the self-reconstruction behavior observed on the surface of BSCF upon water oxidation was expected to be driven by its LOER. Given the close relationship found between the self-reconstruction extent and the OER activity, the ability to undergo LOER was also expected to be the cause of high activity. Thereby, metal oxides with high structural flexibility, such as BSCF, were proposed to be the ideal precatalyst, for which significant ‘instability’ induced by LOER brought about surface reconstruction during OER and thus the formation of an active surface layer. Moreover, structural flexibility was related to the bulk property of metal oxides, i.e., oxygen vacancy content, since the oxygen vacancy concentration of the investigated catalysts varied in the same order as the catalytic performance and the degree of self-reconstruction: $\text{BSCF} > \text{LSC28} > \text{CoO}$. Thus, metal oxides rich in oxygen vacancies were speculated to undergo surface rearrangements under OER conditions, which yielded the formation of metal oxy(hydroxide) layer active for OER. As illustrated in Figure 2.7, the mechanism of dynamic self-reconstruction triggered by LOER was proposed for highly active perovskites, e.g. BSCF. Two processes of oxygen evolution on perovskites were considered, i.e., OER ($2\text{OH}_{\text{aq}}^- \leftrightarrow \frac{1}{2}\text{O}_2 + \text{H}_2\text{O} + 2e^-$) and LOER ($\text{ABO}_{3-\delta} + \text{OH}^- \leftrightarrow \text{BO}(\text{OH}) + \text{A}_{\text{aq}}^{2+} + \frac{2-\delta}{2}\text{O}_2 + 3e^-$), and the latter caused the dissolution of metal cations. While dissolved metal cations with high solubility, such as Ba^{2+} and Sr^{2+} , could diffuse away from the electrode, the dissolved metal cations with extremely low solubility, such as Fe and Co ions, could be redeposited on the surface of oxides by the recombination with OH^- ions from the electrolyte, resulting in the growth of a hydrous amorphous layer rich in Fe and Co cations. Molecular oxygen is simultaneously evolved from the electrolyte and

the Co/Fe oxy(hydroxide) layer, and the lattice oxygen vacancies left by the release of O₂ are continuously replenished by OH⁻ from the electrolyte.

It is noteworthy that the reconstruction of perovskite oxides under electrochemical conditions is not always beneficial for the OER catalysis. Besides BSCF, double perovskite Pr_{0.5}Ba_{0.5}CoO_{3-δ} (PBCO), in which A-site Pr and Ba cations are orderly arranged, was also reported to be a highly active OER catalyst in alkaline media.^[39] By combining DFT-calculated Pourbaix diagrams and in situ XAS, Schmidt's group compared the electrochemical behaviors of PBCO and BSCF nanoperovskites under OER conditions.^[41] Both PBCO and BSCF initially exhibited high activity towards OER. However, PBCO demonstrated a decreasing trend of OER activity during the stability test whereas BSCF displayed an increasing one, which was attributed to their difference in thermodynamic natures under oxidative conditions. BSCF was recognized to be thermodynamically metastable at OER potentials with the pH value of 13. Despite Ba²⁺ and Sr²⁺ leaching during OER, the original perovskite structure of BSCF could be preserved, accompanied by the growth of Co/FeO(OH). In contrast, PBCO was predicted to be thermodynamically unstable under OER conditions due to the dissolution of not only A-site but also B-site cations. However, the disintegration of PBCO was found to be not transient, because the OER activity of PBCO was retained after the stability test. Thus, it was proposed that the formation of Pr hydroxyl phase near the surface slowed down the dissolution of catalytically active Co sites.

2.4.2 Spinel Oxides

Spinel oxide, with the general formula AB₂O₄, is another widely concerned family for the development of OER electrocatalysts. The geometric situation in spinels is more complicated than that in ABO₃-type perovskites. As shown in Figure 2.8a, there are two geometric sites in spinel oxides for transition metal A²⁺ and B³⁺, i.e. tetrahedral (T_d) and octahedral (O_h) sites coordinated by four and six oxygen anions, respectively. Considering that both T_d and O_h sites can be occupied by the mixed population of A²⁺ and B³⁺, a more general formula for spinel-type oxides can be expressed as (A²⁺_{1-λ}B³⁺_λ)_{Td}[A²⁺_λB³⁺_{2-λ}]_{Oh}O₄ (0 ≤ λ ≤ 1), where λ indicates the inversion degree of a spinel.^[42] λ = 0 denotes a normal

spinel with overall A^{2+} in T_d sites, while $\lambda = 1$ represents an inverse spinel with the whole A^{2+} in O_h sites.^[43] If λ is between 0 and 1, the spinel oxide is partially inverse, with A^{2+} present in T_d as well as O_h sites.^[43] The diversity of transition-metal cation distribution and the changeability of cation valency bring about the tunable physicochemical properties of spinel oxides, which may affect their catalytic activity. Therefore, numerous efforts have been devoted to revealing the physicochemical origins governing the electrocatalytic behaviors of spinel-type OER catalysts.

Figure 2.8 (a) Structural model of spinel oxides (AB_2O_4).^[2] (b) Evolution of potential at $25 \mu A/cm^2_{ox}$ with the e_g filling of the octahedrally-coordinated active element in various spinel.^[44]

Given the success of e_g filling on predicting OER activity of perovskites, attempts have been made to utilize it to spinel oxides. Wei et al. investigated the catalytic activity of various spinel oxides to explore the role played by the e_g occupancy of cations and concluded that e_g filling of the active cations in O_h sites has the predictive power for the oxygen electrocatalytic performance of spinel oxides (Figure 2.8b).^[44] Later, Zhou et al. studied $ZnFe_xCo_{2-x}O_4$ ($x = 0 - 2$) as OER electrocatalysts and found that enlarging Co-O covalency by substituting Co with Fe can improve the specific activity.^[45] In addition, Sun et al. proposed that the catalytic performance of cobalt spinel oxides can be promoted by shifting oxygen charge towards O_h -site TM cations.^[46] Furthermore, Chen et al. identified antiferromagnetic inverse spinel oxide $LiCoVO_4$ as a highly efficient OER electrocatalyst. The superior activity of $LiCoVO_4$ was ascribed to the electronic configuration of high spin Co^{2+} in O_h sites, which was regarded to enhance triplet state oxygen molecule evolution.^[47]

Recently, Sun et al. found that the OER activity of spinel oxides are governed by the covalency competition between T_d and O_h sites via influencing the exposure of catalytically active sites and successfully predicted an efficient spinel catalyst through screening the covalency completion of over 300 spinel oxides by a machine-learning assisted mathematical approach.^[45]

Figure 2.9 Reversible surface structural transformation of crystalline Co_3O_4 during OER.^[48]

In recent years, the structural and compositional changes of spinel oxides at oxidative potentials have been increasingly focused on and frequently reported. For example, with the assistance of *operando* X-ray techniques, Bergmann et al. detected that a sub-nanometer thickness of the crystalline Co_3O_4 surface could be reversibly converted into amorphous $\text{CoO}_x(\text{OH})_y$ at OER potentials in 0.1 M KPi electrolyte.^[48] Co_3O_4 possesses a normal spinel structure, with divalent cobalt atoms in T_d sites ($\text{Co}^{2+}_{T_d}$) and trivalent ones in O_h sites ($\text{Co}^{3+}_{O_h}$). Based on experimental observations, it was speculated that the near-surface region of crystalline Co_3O_4 transformed into catalytically active $\text{CoO}_x(\text{OH})_y$ upon water oxidation, via the oxidation of surface divalent Co_{T_d} and the migration/conversion of oxidized Co_{T_d} into unoccupied O_h sites in the reaction zone, which could be reversed by re-crystallization upon reverting to the noncatalytic state (Figure 2.9). The origin of surface amorphization was attributed to the involvement of lattice oxygen in OER, during which the generation of transitory oxygen vacancies led up structural relaxation and thus the variation in Co coordination.

Later on, the reversibility of surface structural changes on Co_3O_4 also has been detected by

operando studies using ambient-pressure XPS and surface XRD.^[49-50] Nevertheless, a recent investigation combining *in situ* electrochemical TEM (*in situ* EC-TEM) with *ex situ* HRTEM revealed that the surface amorphization of Co_3O_4 during oxygen evolution was an irreversible process and the degree of amorphization was dependent on the pH, the electrolyte counterions, and the electrochemical testing method.^[51] Through HRTEM, an amorphous layer within 5 nm thickness was found on Co_3O_4 nanoparticles subjected to 100 CV cycles in neutral KPi electrolyte, which was less marked than those tested under alkaline conditions (0.1 M KOH) or 2 hours of CP at $10 \text{ mA cm}^{-2}_{\text{geo}}$. For many characterization techniques, including *operando* XAS, the signal is often dominated by the underlying bulk crystalline phase. Hence, it is necessary to use techniques as multiple as possible to detect the surface structural and compositional changes of metal oxides after OER.

More recently, Duan et al. demonstrated that the position difference between O p and M_{Oh} (O_{h} -site TM cations) d band centres could indicate the thermodynamical structural stability and the OER mechanism of $\text{ZnCo}_{2-x}\text{Ni}_x\text{O}_4$ ($x = 0 - 2$) spinel oxides.^[30] According to the DFT calculation results, too much Ni substitution into ZnCo_2O_4 resulted in an unstable phase and hence the nonexistence of $\text{ZnCo}_{2-x}\text{Ni}_x\text{O}_4$ ($x > 0.8$) spinel structure. For the spinel oxides predicted to be metastable, i.e., $\text{ZnCo}_{2-x}\text{Ni}_x\text{O}_4$ ($x = 0.6, 0.8$), continuous surface reconstruction into Ni-enriched oxyhydroxide during OER in alkaline media was observed, which was supposed to result in enhanced activity and result from the participation of lattice oxygen in producing O_2 . In contrast, for the spinel oxides predicted to be stable, i.e., $\text{ZnCo}_{2-x}\text{Ni}_x\text{O}_4$ ($x \leq 0.4$), their insignificant variation in OER activity during prolonged electrochemical testing and pH-independent OER performance of the cycled catalysts were attributed to their adoption of conventional adsorbate evolving mechanism for OER catalysis. Later, Wu et al. reported that Fe substitution could facilitate the surface reconstruction of CoAl_2O_4 into active Co oxyhydroxides during OER, due to the activation of the pre-oxidation of Co cations as well as the optimization of the O 2p level. Moreover, it was proposed that Al leaching, which takes place simultaneously with the occurrence of reconstruction, shifts O 2p level down and ends further surface transformation, thus providing a stable surface chemistry.^[31]

2.4.3 Other Transition Metal Oxides

Metal Hydroxide and Oxyhydroxide. Both metal hydroxide ($M(OH)_2$; M denotes transition metals) and metal oxyhydroxide ($MOOH$) are constructed by stacked layers of edge-sharing MO_6 octahedra (Figure 2.10a).^[52] The inter-layer distance can be modulated by intercalating different species. Replacement of partial divalent M^{2+} ions in $M(OH)_2$ by trivalent M^{3+} yields layered double hydroxides (LDHs). For charge balance, anions and water molecules are intercalated between metal layers, thus enlarging inter-layer spacing (Figure 2.10b).

Figure 2.10 (a) Layered hydroxides. (b) Layered double hydroxides with anions and water molecules intercalated between MO_6 layers. Inter-layer distance $d_2 > d_1$. Hydrogen atoms are omitted.^[52]

During water oxidation in alkaline media, the surfaces (or even overall phases) of transition-metal hydroxides (including LDHs) can be electrochemically oxidized to oxyhydroxides. The transformation behaviors of $Ni(OH)_2/NiOOH$ under electrochemical conditions have been extensively discussed, due to the remarkable catalytic activity observed for Ni-based catalysts especially in the presence of Fe. In the model put forward by Bode et al. in the 1970s (Figure 2.11a), four phases of nickel oxides are taken into consideration, i.e. α - $Ni(OH)_2$, β - $Ni(OH)_2$, γ - $NiOOH$, and β - $NiOOH$.^[53] Over a long time, β - $Ni(OH)_2/\beta$ - $NiOOH$ has ever been regarded to be more catalytically active than α - $Ni(OH)_2/\gamma$ - $NiOOH$, because of observations that the transition from α - $Ni(OH)_2$ to β -phase after aging in alkaline media was accompanied by the increment in OER activity.^[54-56] On

the other hand, Gao et al. reported that α -Ni(OH)₂ nanocrystals exhibited excellent activity in alkaline solution, outperforming β -Ni(OH)₂,^[57] which agrees with the finding of Nocera and coworkers that γ -NiOOH was intrinsically more active than β -NiOOH.^[58] Despite the above efforts made to explore the structure-function correlations of Ni(OH)₂/NiOOH, the potential influence of trace Fe electrolyte impurities may be ignored.

Figure 2.11 (a) Ni(OH)₂/NiOOH redox transformation scheme proposed by Bode et al.^[59] (b) OER cyclic voltammetry curves of Ni_{1-x}Fe_xOOH containing different amount of Fe and those of NiOOH measured in purified and unpurified electrolytes.^[60]

Corrigan ever in the 1980s reported that Fe impurities (1 ppm) in reagent grade KOH solution could greatly improve the catalytic activity of nickel oxide thin films.^[61] And recent studies have increasingly evidenced that the increased OER activity of aged Ni(OH)₂/NiOOH results from the incorporation of Fe impurities in KOH electrolyte rather than phase transformation. For example, Boettcher and coworkers removed trace Fe from KOH electrolyte, using high-purity Ni(OH)₂ precipitate as an iron-absorbent.^[60] Consequently, they found that rigorously Fe-free NiOOH, either β - or γ -phase, was slow at catalyzing OER (Figure 2.11b) and that long-term cycling or aging in Fe-free KOH electrolyte led to no activity enhancement for pure NiOOH. Therefore, they ascribed the high OER catalytic performance of Ni(OH)₂/NiOOH mentioned in previous reports to the unintentional incorporation of Fe impurities. Later, Bell's group indicated that the structural conversion of Fe-free Ni(OH)₂/NiOOH under electrochemical conditions obeyed the Bode's scheme.^[62] In contrast, during aging in impurified KOH (< 1 ppm Fe), Fe electrolyte impurities could be incorporated into the matrix of Ni (oxy)hydroxide, resulting in the formation of NiFe-LDH and hence a significant deviation from Bode's model. They proposed that the Fe sites within the NiFe-LDH phase should be accountable for the

significantly improved OER activity over Fe-free Ni (oxy)hydroxide. Given the above findings, later contributions regarding the conversion of $\text{Ni(OH)}_2/\text{NiOOH}$ under electrochemical conditions typically utilized purified KOH electrolytes to exclude the interference from Fe impurities.

As proposed for amorphous hydroxides that plentiful inherent defects could provide high structural flexibility to facilitate the *in situ* transformation into the active phase,^[63-64] defect engineering has been utilized to activate metal hydroxide crystals via enhancing the reconstruction ability. For example, the group of Song demonstrated that cationic vacancies could promote the restructuring of $\alpha\text{-Ni(OH)}_2$ into $\gamma\text{-NiOOH}$.^[65] They synthesized $\alpha\text{-Ni(OH)}_2$ with variable nickel vacancy (V_{Ni}) content and identified the dependence of the OER activity on the V_{Ni} concentration. Besides, the precatalytic oxidation peak assigned to $\text{Ni}^{2+}/\text{Ni}^{3+}$ transition, which was associated with the formation of $\gamma\text{-NiOOH}$ as active species, was also found to grow with the adding nickel vacancy into $\alpha\text{-Ni(OH)}_2$. Post-OER XPS analysis indicated that the $\alpha\text{-Ni(OH)}_2$ rich in cation defects suffered more significant reconstruction. Accordingly, the presence of V_{Ni} was speculated to assist the transformation into $\gamma\text{-NiOOH}$, yielding increased OER active species and thus enhanced catalytic performance. This hypothesis was further supported by DFT calculations, which demonstrated that raising the V_{Ni} concentration of $\alpha\text{-Ni(OH)}_2$ improved the intrinsic conductivity and decreased the theoretical energy for phase conversion.

In addition to defect engineering, the selective leaching of cation and/or anion under electrochemical conditions, which may simultaneously introduce defects into the catalyst, has also been demonstrated to promote the *in situ* derivation of reactive species from metal hydroxides.^[66-70] For instance, the group of Song studied the reconstruction behavior of cobalt oxychloride, $\text{Co}_2(\text{OH})_3\text{Cl}$.^[70] In the as-synthesized $\text{Co}_2(\text{OH})_3\text{Cl}$, Co atoms were octahedrally coordinated by either six O anions or four O and two Cl anions. After electrochemical activation, Cl^- anions were almost totally removed from the lattice of $\text{Co}_2(\text{OH})_3\text{Cl}$, resulting in the activation-derived $\text{Co}_2(\text{OH})_3\text{Cl}$ components (AC- $\text{Co}_2(\text{OH})_3\text{Cl}$) with boosted intrinsic activity and long-term stability. With the aid of *ex situ* and *operando* characterization techniques, it was found that AC- $\text{Co}_2(\text{OH})_3\text{Cl}$, with structure framework like $\beta\text{-CoOOH}$, had abundant undercoordinated Co sites due to the breaking of Co-Cl bonds. Accordingly, a structural model consisting of four-oxygen-coordinated Co (Co(4O))

and six-oxygen-coordinated Co atoms (Co(6O)) was proposed for AC-Co₂(OH)₃Cl. Theoretical calculations further demonstrated that the Co(4O) was the thermodynamically preferred site for OER catalysis. Therefore, the coordinately unsaturated Co(4O) sites formed via Cl⁻ leaching were supposed to be the origin of enhanced OER activity.

Figure 2.12 Crystal structure of layered LiMO₂ (M = transition metal).^[6]

Layered Lithium Transition Metal Oxide. Layered lithium transition metal oxide (LiMO₂; M = transition metals), a type of compound widely studied as the cathode material in lithium-ion batteries, has recently been employed as OER catalysts. Like the structure of metal oxyhydroxide, LiMO₂ is composed of edge-sharing M³⁺O₆ octahedral layers, despite that the intercalation species between layers are Li⁺ cations (Figure 2.12). Through the channel provided by the two-dimensional arrangement of MO₆ units, Li⁺ can be facily extracted in either chemical or electrochemical way. The influence of delithiation on the OER activity of layered LiMO₂ has attracted many research interests.^[71-74] For example, Lu et al. reported that electrochemical delithiation of layered LiCoO₂ in organic electrolyte could optimize the electronic structure and thus result in Li_{0.5}CoO₂ with enhanced OER performance in aqueous medium.^[71]

Electrochemical delithiation of LiMO₂ also can occur during water oxidation in the aqueous electrolyte, potentially inducing structural transformation and affecting the catalytic performance. It has been demonstrated that *in situ* electrochemical delithiation resulted in more active surface structure than *ex situ* chemical delithiation.^[73] In contrast with chemically delithiated LiMO₂, fully lithiated oxides underwent irreversible Li⁺

extraction during the first CV scan and exhibited higher specific activity, thus suggesting the critical role of *in situ* transformation.

Several studies have revealed the reconstruction-derived structure for layered LiCoO_2 after OER, which, however, are not in agreement with each other. Lee et al. reported that surface crystalline LiCoO_2 evolved into a spinel-like LiCo_2O_4 structure in neutral electrolyte whereas into an amorphous phase in alkaline medium.^[75] Nonetheless, the HRTEM detection by Gardner et al. showed that spinel LiCo_2O_4 was the reconstructed structure for LiCoO_2 after electrolysis in 1 M NaOH, and this phase transformation was suggested to be responsible for the activation of LiCoO_2 .^[76] In contrast, the group of Manthiram, with the help of *ex situ* Raman spectroscopy, noticed that a spinel-like Co_3O_4 was the derived phase after electrochemical lithium removal in 0.1 M KOH electrolyte.^[74] Despite the discrepancy in identified active phases, which could be attributed to different electrochemical measurement conditions and/or characterization techniques, the consistency in observing lithium reduction and structural change suggests that layered structure is less thermodynamically preferred than spinel structure for delithiated LiCoO_2 under OER conditions. The finding of Zhu et al. suggests that the incorporation of appropriate foreign metal, e.g. Fe, may impede the lithium removal as well as the restructuring of LiCoO_2 during OER and thus enhance the structural and functional stability.^[6] In contrast with the undoped phase, Fe doped LiCoO_2 ($\text{LiCo}_{0.8}\text{Fe}_{0.2}\text{O}_2$) did not display the irreversible anodic peak assigned to significant lithium removal in the first anodic sweep in 0.1 M KOH. $\text{LiCo}_{0.8}\text{Fe}_{0.2}\text{O}_2$ after stability test was found to preserve the layered structure despite losing partial lithium and change in layer distance, which was considered to account for the durability superior to that of LiCoO_2 . The preservation of layered structure after OER was also observed for Ni-rich LiMO_2 compounds.^[73, 77] This may be explained by the phase instability of Ni-rich spinel oxides or the cooperative effect between mixed metals. Recently, Ren et al. reported that the growth of amorphous NiOOH layer on electrochemically delithiated LiNiO_2 during OER yielded an adaptive heterojunction (delithiated $\text{LiNiO}_2/\text{NiOOH}$) which could facilitate the generation of superoxo/peroxo-like $(\text{O}_2)^{n-}$ species that are beneficial for triggering the LOM.^[32]

2.5 Outstanding Questions

As discussed in the aforementioned literature review, Fe incorporation, either as a bulk dopant or impurity, can significantly improve the catalytic performance of Co- or Ni-based OER electrocatalysts.^[5-6, 60, 78-80] Growing studies have identified the indispensable role of Fe in Co/Ni-Fe catalytic systems and proposed Fe as the highly active site.^[60, 78, 81-82] Besides, as Fe is more earth-abundant, cheaper, and less toxic than Co and Ni,^[83-84] pristine Fe-based materials have the potential to be the desirable OER catalysts that are highly efficient, cost-effective, and environmentally friendly. However, Fe-based OER catalysts have not been as extensively investigated as Co- or Ni-based ones, and the knowledge about the local chemical structure required by the most active Fe sites is insufficient.

Another rising concern about TMO electrocatalysts is the occurrence of surface reconstruction during OER. Drastic surface changes under OER conditions may destroy the original surface atomic arrangements, which is accompanied by the *in-situ* formation of new surface structures. Such surface reconstruction may induce prominent activity improvement due to the increase in surface reactive zone and/or the formation of better surface-active sites. However, the controllable derivation of advanced OER catalyst from TMO precatalysts via surface reconstruction is challenging. That is because the surface reconstruction process of TMOs during OER is highly complex, which is still poorly understood.

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Chapter 3

Experimental Methodology

*This chapter presents methods adopted to synthesize target materials as well as characterization techniques employed to study these materials. First, the reasons for the selection of experimental methodologies are described. Then, the procedures of the synthesis of transition-metal oxides are introduced. Lastly, the principles behind the physical characterizations, the details of electrochemical measurements, and the theory of *ab initio* calculation are elaborated.*

3.1 Rationale for Selection

Because the fine control of morphology is not necessary for this thesis, the methods selected to prepare transition-metal oxide materials are as simple as possible, such as sol-gel method and hydrolysis method. To confirm the crystal structures of as-synthesized materials, X-ray diffraction technique is employed. To determine the valence state and the cation distribution for as-prepared oxides, X-ray absorption spectroscopy is used. To analyze the chemical states of transition metal cations and oxygen atoms in the near-surface regions of oxides, X-ray photoelectron spectroscopy is utilized. To record the surface morphologies of as-synthesized oxide particles, field emission scanning electron microscopy is applied. To study the surface structural changes of oxide catalysts after electrochemical measurements, high-resolution transmission electron microscopy is adopted. To estimate the compositional ratio of metal cations on the oxide catalyst surface, energy-dispersive X-ray spectroscopy is utilized. To analyze the leaching of transition metals from oxide catalysts during the electrochemical tests, inductively coupled plasma mass spectrometry is applied. To measure the specific surface area of as-synthesized oxide particles, Brunauer–Emmett–Teller method is adopted. To evaluate the catalytic performance of oxide catalysts in alkaline electrolytes for water oxidation cyclic voltammetry test is used. To understand the electronic structures of oxide materials, density functional theory computations are performed to obtain the density of states.

3.2 Synthesis Methods

Perovskites were synthesized by a conventional sol-gel method.^[1] For $A\text{FeO}_3$ ($A = \text{Y, Gd, Pr, and La}$), 10 mmol A-site metal nitrate ($A = \text{Y, Gd, Pr, and La}$), 10 mmol $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 20 mmol ethylenediaminetetraacetic acid (EDTA), 40 mmol citric acid ($\text{C}_6\text{H}_8\text{O}_7$) and 100 mL ammonium hydroxide (NH_4OH) were dissolved into 200 mL de-ionized water (DI water). In the same way, for $\text{SrCo}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ ($x = 0, 0.05, 0.2$ and 0.5), stoichiometric amounts of $\text{Sr}(\text{NO}_3)_2$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were mixed with DI water, EDTA, NH_4OH , and $\text{C}_6\text{H}_8\text{O}_7$. The mixture solution was continuously stirred and heated at 260 °C to become a homogeneous gel. Next, the gel was heated at 200 °C for 5 hours for

the formation of a precursor. At last, the precursor was calcined at 1000 °C in air for 5 hours to form perovskite particles. To prepare cubic-structured $\text{SrCoO}_{3-\delta}$, the corresponding precursor successively underwent calcination in air at 1000 °C for 12 hours, quenching in air, and annealing in oxygen atmosphere at 300 °C for 96 hours.^[2]

Spinel $\text{ZnFe}_{2-x}\text{Cr}_x\text{O}_4$ ($x = 0, 0.5, 1, 1.5, 2$) were prepared by a conventional sol-gel auto combustion method. 30 mmol nitrate salts (consisting of stoichiometric amounts of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), 60 mmol $\text{C}_6\text{H}_8\text{O}_7$, 30 mmol urea and 20 mL nitrite acid were successively added into 200 mL DI water. The aqueous mixtures were continuously stirred and heated at 90 °C until the formation of homogeneous gels. Subsequently, the gels were heated at 170 °C for 12 hours to produce precursors, which then were calcined at 800 °C in air for 6 hours.

β -FeOOH was prepared by a previously reported hydrolysis method.^[3] The mixture of 10 mL of 0.5 mol/L aqueous FeCl_3 and 70 mL DI water was dried at 100 °C for 24 hours to form precipitates, which later were repeatedly washed with DI water and ethanol and then dried at 80 °C for 12 hours.

3.3 Physical Characterization

3.3.1 X-Ray Diffraction (XRD)

XRD is a powerful technique for revealing the atomic arrangements, i.e., the crystal structures, of matter. When X-rays encounter the material being investigated, part of them is elastically scattered by the electrons of the atoms they hit. The elastically scattered X-ray beam will interfere with each other, and diffraction created by constructive interference takes place when Bragg's law conditions are satisfied (Figure 3.1). The Bragg's law is mathematically expressed as

$$n\lambda = 2d\sin\theta \quad (3.1)$$

where n is a whole number, λ the X-ray wavelength, d the spacing between planes in the atomic lattice of the material, and θ the diffraction angle in degrees. At a given wavelength, a specific substance has a characteristic XRD pattern in terms of diffraction angles and beam intensities. Thus, by comparing the peak positions and the relative peak intensities

in a diffraction pattern with known patterns in a database, the substances in the material under investigation can be identified. However, XRD requires specimens with long-range ordered atomic arrangements since amorphous/poorly crystalline structures will randomly scatter the incident X-rays. In this thesis, the XRD patterns of oxides were collected to confirm the crystal structure and the phase purity.

Figure 3.1 Schematic illustration of Bragg's law conditions. When the conditions are satisfied, constructive interference occurs, and a diffracted beam is created. Otherwise, destructive interference fails the formation of a diffracted beam.^[4]

3.3.2 X-Ray Absorption Spectroscopy (XAS)

XAS is an element-specific spectroscopic technique that uses energy-tunable X-rays produced by synchrotrons to detect the physical and chemical states of atoms in matter. When X-rays hit a sample, part of them is absorbed due to the photoelectric effect (Figure 3.2), in which a core-level electron absorbing a photon is ejected from the atom that the electron initially resides in (the electron is called as photoelectron). The prerequisite of the photoelectric effect is that the energy of the photon being absorbed cannot be smaller than the binding energy of the electron, i.e., the energy needed to migrate the electron to a continuum state.

Figure 3.2 Illustration of the photoelectric effect. After absorbing an X-ray photon, an electron in the core level is ejected to the continuum.^[5]

Figure 3.3 An incident X-ray beam with an intensity of I_0 hits a sample with a thickness of t , and a beam with an intensity of I is transmitted.^[5]

The probability of incident X-rays being absorbed follows Beer's Law:

$$\ln (I_0 / I) = \mu t \quad (3.2)$$

where I_0 and I are the intensities of incident and transmitted X-rays, respectively, t is the sample thickness, and μ is the linear absorption coefficient (Figure 3.3). For XAS measurement, the concern is the variation of μ with the energy of incident X-rays. For most X-ray energies, μ is a smooth function of the X-ray energy (E), as expressed in the equation

$$\mu = \frac{\rho Z^4}{A E^3} \quad (3.3)$$

where ρ , Z , and A respectively are sample density, atomic number, and atomic mass. When the X-ray energy equals the binding energy of a core-level electron of an atom within the sample, the photoelectric effect occurs, the absorption of X-rays sharply increases, and an absorption edge is observed on the XAS spectrum. For each element, the binding energies of core-level electrons are specific and well-known. Therefore, the element of interest can be probed by varying the X-ray energy to be near and above a core-level binding energy of that element.

Figure 3.4 Two regions in an XAS spectrum: XANES and EXAFS.^[6]

As shown in Figure 3.4, an XAS spectrum typically can be divided into X-ray absorption near-edge spectroscopy (XANES) and extended X-ray absorption fine-structure spectroscopy (EXAFS). XANES is in the energy region of 50-100 eV above the absorption edge, which is strongly sensitive to the formal oxidation state and the coordination chemistry of the selected element. The shift of the position of an absorption edge can be employed to estimate the average valence state of the element concerned. EXAFS corresponds to the oscillations from 50 eV above the absorption edge. Photoelectrons are backscattered by neighboring atoms, after being ejected from the absorbing atoms due to the photoelectric effect. In the EXAFS region, the photoelectrons have high kinetic energy and thus behave like waves. When the forward-propagating photoelectron waves interfere with the backscattered waves, the measured absorption coefficient is modulated, and its

maxima and minima respectively correspond to constructive and destructive interference. Therefore, the oscillations in EXAFS contain local geometrical information of the absorbing atoms. The distances, coordination number, and atomic species of the neighbors surrounding the absorbing atoms can be determined by fitting EXAFS spectra. In Chapter 4, Fe K edge XANES was employed to confirm the Fe valency for a series of as-synthesized ferrites. In Chapter 5, Zn, Fe, and Cr K edge XANES and EXAFS were utilized to analyze the oxidation states and site distribution of Zn, Fe, and Cr in spinel oxides. XAS data were processed with the software Athena, and EXAFS fitting was carried out with the software Artemis.

3.3.3 X-Ray Photoelectron Spectroscopy (XPS)

XPS is an electron spectroscopic technique that can provide chemical information within ~10 nm of a sample surface. It can not only detect elemental compositions at the surface region but also measure the chemical state of these elements. Apart from hydrogen and helium, all elements can be detected by XPS, and the detection limits are in the parts per thousand range (ppt). The working principle of XPS is based on the photoelectric effect (Figure 3.2). The surface of a specimen in vacuum is irradiated by X-ray beams with a specific energy. After absorbing the energy of an incident X-ray photon, a core-level electron of an atom in the sample escapes from the very top surface. The kinetic energy of the emitted electron, which is called as photoelectron, can be determined by the following equation,

$$E_{kinetic} = E_{photon} - (E_{binding} + \varphi) \quad (3.4)$$

where $E_{kinetic}$ is the kinetic energy of the photoelectron, E_{photon} the energy of the incident X-ray photon, $E_{binding}$ the binding energy of the photoelectron, and φ the work function related to the spectrometer. Because there will be a specific value of the binding energy associated with each core atomic orbital for every element, the photoelectron's kinetic energy is element-specific and is also related to the electronic configuration of the atom from which it is emitted. In an XPS spectrum, the position of peaks is indicative of the elements present at the surface, and the intensity of these peaks is directly proportional to the concentrations of these elements. Furthermore, chemical shifts in the spectrum, i.e., small shifts in the

peak positions, can provide information about the local bonding environment of the elements identified. In Chapter 5, XPS was employed to determine the valences of transition-metal elements, i.e., Zn, Fe, and Cr, in as-synthesized spinel oxides. In Chapter 6, XPS was used to analyze the changes in the oxidation states of Sr, Co, Fe, and O of perovskite oxides after electrochemical measurements. The fitting of XPS spectra was performed with XPSPEAK41 software.

3.3.4 Electron Microscopy

A microscope is a tool that produces magnified images of objects. Electron microscopes are capable of capturing significantly smaller details than light microscopes, because of the shorter wavelength of electrons than that of visual light. Scanning electron microscope (SEM) and transmission electron microscope (TEM) are two common types of microscopes using high voltage electrons as the illumination source.

In a SEM, images are created by using a focused beam of electrons with high energy to scan the surface of a specimen in high vacuum. Because of the interaction between incoming electrons and atoms at the surface, various signals containing compositional and topographical information are produced, among which the secondary electrons produced by inelastic scattering are commonly used to image the three-dimensional appearance of a specimen. To reduce surface charging caused by the low conductivity of oxide samples, a thin coating of gold was applied at the top of oxides before SEM characterization. Typically, a SEM can achieve a resolution of better than 10 nanometers. Compared with the conventional SEM, field emission SEM (FESEM), which uses a field emission gun to generate extremely focused electron beams, can produce clearer images due to its higher resolution. In Chapter 5 and 6, FESEM images of as-prepared materials were collected to compare their morphologies.

With much higher accelerating voltage and thus smaller wavelength of electrons, a TEM typically has a resolution of better than 1 nm and thus allows visualizing finer details, even the single column of atoms. In contrast with a SEM, the electron beams in a TEM pass through the entire thickness of samples and ultimately hit the imaging screen to produce images. TEM can be used to investigate the morphological, crystallographic, and

compositional information of materials. To be penetrated by electrons, the sample usually is an ultrathin section with a thickness of less than 200 nm or a suspension on a copper grid. The wavelength of electrons in a TEM usually is much smaller than the atomic spacing in specimens, and hence electrons in a TEM behave more like waves rather than particles. When Bragg's law conditions are satisfied, electron diffraction occurs, and a diffraction pattern, i.e., an image of bright regular dots or rings, is formed on the viewing screen. In Chapter 6, high-resolution transmission electron microscopy (HRTEM) was utilized to confirm the crystalline structures of pristine perovskite oxides and their surface amorphization after OER measurements.

3.3.5 Energy-Dispersive X-Ray Spectroscopy (EDS)

Figure 3.5 Illustration of characteristic X-ray generation. An electron is kicked out from an inner shell (K shell) by the incident beam. Subsequently, the hole left in the inner shell is replenished by an electron from an outer shell (L or M shell), which coincides with the emission of an X-ray photon (K_{α} or K_{β}) with element-specific energy.^[7]

EDS can qualitatively as well as quantitatively analyze the elemental composition of a specimen (only the elements with an atomic number larger than three can be measured). When high-energy electrons from the primary beam of TEM are focused on a specimen, characteristic X-rays can be produced by the interaction of incident electron beams with

the atoms in the sample material (Figure 3.5). An incident electron may dislodge an electron from the inner shell of an atom in the sample, therefore leaving a vacancy in this shell. For the stabilization of the excited atom, the vacancy is replenished by an electron from an outer shell with a higher energy level. Due to the energy difference between the inner and the outer shells, an X-ray photon is emitted, the energy of which is element-specific because each element has a unique atomic structure and hence specific ionization energies for each electron shell. In an energy-dispersive spectrum, a plot of intensity versus X-ray energy, the sample elements are differentiated by their characteristic X-ray peaks, and their relative concentrations are estimated from the corresponding peak intensity. The detection limit of EDS in TEM is in the range of ~0.01-0.1 wt%. It is an effective technique for not only major and minor element analysis but also trace-element analysis. For elements with similar electronic structures, their characteristic X-ray peaks may overlap and thus are hard to tell apart. In Chapter 6, EDS is employed to estimate the surface strontium, cobalt, and iron ratios of electrode materials after electrochemical tests.

3.3.6 Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

ICP-MS can be utilized to quantitatively analyze the trace elements in liquid specimens. When hit by a high-frequency inductively coupled plasma, the sample is transited into ions of its constituent elements, which later are separated according to their mass-to-charge ratios. In Chapter 6, ICP-MS was utilized to quantify strontium, cobalt, and iron ions in the alkaline electrolytes before and after electrochemical measurements.

3.3.7 Brunauer–Emmett–Teller (BET) Surface Area Analysis

At a micro level, the real surface area of an oxide catalyst is much larger than its geometric surface area determined by macroscopic measurements. Since the apparent activity of a solid catalyst is influenced by not only the inherent activity but also the surface area accessible for reactants, it is necessary to determine its real surface area to obtain the universally comparable value of the intrinsic activity. BET method is a routine approach to measure the real surface area for oxides. The BET method is based on the analysis of

probe gas molecular isothermal adsorption on a specimen according to BET theory. By measuring the number of adsorbates at the first layer, the surface area can be calculated out with the knowledge of an effective cross-sectional area of the probe molecule. Various gases can be used as the probe and give different results. In most cases, nitrogen (N_2) is popular, due to its inertness and low price. In this thesis, the BET specific surface areas of as-prepared oxide were measured for calculating the intrinsic activity of oxide catalysts.

3.4 Electrochemical Measurements

Figure 3.6 Setup of a three-electrode electrochemical cell in O_2 -saturated KOH electrolyte.^[8]

Electrochemical Cell Setup. A three-electrode cell setup, consisting of a glassy carbon electrode (GCE) as the working electrode (WE), a platinum plate as the counter electrode (CE), a reference electrode (RE), and O_2 -saturated KOH electrolyte, was utilized for electrochemical characterization.^[9] To remove oxygen bubbles continuously formed on the WE surface upon water oxidation, the WE is rotated, or the electrolyte is stirred. In Chapter 4 and 6, a saturated calomel reference electrode (SCE) was used as the RE, and a Hg/HgO (1.0 M KOH) reference electrode was used in Chapter 5.

Electrode Preparation. An oxide electrode was fabricated by drop-casting the ink containing oxide catalyst onto a GCE with a geometric surface area of 0.196 cm^2 . For the preparation of ink with oxide particles homogeneously dispersed, 5 mg oxide catalyst, 2 mg

acetylene black (AB), 750 μL DI water, 225 μL isopropanol (IPA), and 25 μL Nafion® perfluorinated resin solution (5 wt% in water) were mixed and subsequently ultrasonicated for 30 minutes. Before drop-casting, GCEs were successively polished with alumina slurry, ultrasonicated in a solution consisting of ethanol and DI water, and dried at room temperature in air. 10 μL ink was drop-casted onto a GCE and then dried at ambient condition. To evaluate the influence of carbon additives on catalytic activity, 10 μL ink of pure AB was dropped onto a GCE to make a control experiment.

Cyclic Voltammetry (CV). CV is a powerful and common electrochemical technique to study the electron transfer-initiated chemical reactions during catalysis.^[10] It records the currents varying with the applied potential in an electrochemical cell. In this thesis, CV measurements were performed to estimate the catalytic activities of oxides for water oxidation.

Electrochemical Data Analysis. The OER currents measured by CV were corrected with the capacitive currents via averaging the positive-going and the negative-going currents of a CV scan. All potentials were referenced to the reversible hydrogen electrode (RHE) scale ($E_{\text{RHE}} = E_{\text{SCE}} + 0.245 + 0.0591 \times \text{pH}$; $E_{\text{RHE}} = E_{\text{Hg/HgO}} + 0.098 + 0.0591 \times \text{pH}$) unless otherwise stated. The applied potentials were iR -corrected with the measured current i and the uncompensated ohmic electrolyte resistance R determined by electrochemical impedance spectra,

$$E_{iR\text{-corrected}} = E_{\text{applied}} - iR \quad (3.5)$$

The OER kinetic current was normalized to the oxide surface area measured by nitrogen BET analysis to obtain the intrinsic activity.

3.5 Density Functional Theory (DFT) Calculation

DFT is a quantum mechanical computation method widely employed to investigate the electronic properties of metal oxides.^[11] Compared to traditional theoretical methods, e.g. Hartree-Fock theory, DFT requires much lower computational cost. Over the past few decades, DFT has been intensively used to reveal the physical origins of the activity trends observed for OER catalysts. Besides, DFT calculation is also emerging as an effective approach to rationally design OER catalysts and predict catalytic activity. In this thesis,

DFT calculations were performed to link the catalytic activity of metal oxides to their electronic structures.

The Schrödinger Equation and Wave Function. In 1926, Erwin Schrödinger, an Austrian theoretical physicist, discovered the Schrödinger equation, the cornerstone of quantum mechanics.^[12] The general form of time-dependent Schrödinger equation (TDSE) is

$$i\hbar \frac{\partial \psi}{\partial t} = \hat{H}\psi \quad (3.6)$$

where i is the imaginary unit ($i = \sqrt{-1}$), $\hbar$ the Dirac constant, ψ the wave function (a set of solutions to the equation), t time, and $\hat{H}$ the Hamiltonian operator. As the symbol $\frac{\partial}{\partial t}$ indicates, a TDSE describes the evolution of a system with time. And when $\hat{H}$ is independent of time, the Schrödinger equation is called as time-independent Schrödinger equation (TISE), of which the general form is

$$\hat{H}\psi = E\psi \quad (3.7)$$

Here, E is the total energy of the system, i.e., the sum of kinetic energy and potential energy. For each solution ψ_n , there is an associated eigenvalue E_n , a real number satisfying the TISE. If TISE is soluble, the full-time dependence of the wavefunction is readily known. In quantum mechanics, all information regarding a given system is provided by the system's wavefunction, ψ , which can be obtained by solving the Schrödinger equation.

Born-Oppenheimer (BO) Approximation. For a many-body system, where multiple nuclei and electrons interact with each other, the Hamiltonian operator can be written as

$$\hat{H} = -\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 - \frac{\hbar^2}{2M_I} \sum_I \nabla_I^2 - \sum_{i,I}^N \frac{Z_I e^2}{r_{i-I}} + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{r_{i-j}} + \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J e^2}{|R_I - R_J|} \quad (3.8)$$

where m_e is the mass of an electron with charge e and M_I is the mass of a nucleus I with charge $Z_I e$. The first and the second term in the above equation define the kinetic energy of electrons and that of nuclei, respectively. The last three terms depict the electron-nucleus, electron-electron, and nucleus-nucleus interaction, successively. The Schrödinger equations in real systems are too complicated to be soluble. Yet, it is possible to simplify the expression of $\hat{H}$ by separating electronic and nuclear motion. Due to the significant mass difference between an electron and a nucleus, electrons make much more rapid responses to variation in their surroundings than nuclei can. According to this observation,

Max Born and J. Robert Oppenheimer in 1927 proposed BO approximation: when considering the motion of electrons, nuclei stay at the instantaneous position; when considering the motion of nuclei, the distribution of electrons is always at its equilibrium.^[13]

As a result, the Schrödinger equation can be solved by two less complicated successive steps. First, nuclei in the system are supposed to be at fixed positions, and the Schrödinger equation describing electron motion is solved. Next, with the electron wavefunction obtained from the first step, the Schrödinger equation containing only nuclei is solved.

For a given set of electrons moving in the potential generated by a set of fixed nuclei, the time-independent Schrödinger equation is written as

$$\left[-\frac{\hbar^2}{2m} \sum_{i=1}^N \nabla_i^2 - \sum_{i=1}^N V(\vec{r}_i) + \sum_{i=1}^N \sum_{j<1} U(\vec{r}_i, \vec{r}_j) \right] \psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_n) = E \psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_n) \quad (3.9)$$

where m is the electron mass, N is the number of electrons, $\psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_n)$ is the electronic wave function and $\vec{r}_i$ defines the spatial and spin coordinates of an electron. The three terms in the bracket represent the electron kinetic energy, the potential energy of electrons in the field of the fixed nuclei, and electron-electron interaction energy, respectively. However, the present form of a many-body Schrödinger equation is still too complicated to be soluble and is not separable into simpler equations. To solve the problem, many attempts have been made, and among them, DFT is a powerful tool for calculating electronic structure.^[11]

DFT. The computational cost for the wavefunction ψ is enormous while the information provided by ψ is redundant. The use of electron density $n(\vec{r})$ instead of ψ allows to not only limit the redundant information but also significantly reduce calculation amount.

DFT has its roots in the Thomas-Fermi model for the electronic structure of many-body systems.^[14-15] Until 1964, the exact relationship between electronic density and energy is developed by Walter Kohn and Pierre Hohenberg, who proved two fundamental mathematical theorems, Hohenberg-Kohn (HK) theorems.^[16] The first theorem demonstrates that the ground-state electron density $n(\vec{r})$ corresponds to a solely potential field of the system, which determines all the properties of the system. This means all the ground-state properties of a system, such as wave function and energy, are uniquely determined by its ground-state electron density $n(\vec{r})$. As a result, the number of spatial coordinates involved in the solution of a many-body Schrödinger equation is reduced to

only three, when the electron density $n(\vec{r})$, rather than the wave function, is used as the solution. According to the first HK theorem, the ground-state energy E is a unique functional of $n(\vec{r})$, i.e., the ground-state energy of a system can be expressed as $E(n(\vec{r}))$. The second HK theorem further proves that the true ground-state electron density, $n_0(\vec{r})$, minimizes the value of $E(n(\vec{r}))$. Thus, $n_0(\vec{r})$ and thus other properties of a system can be determined by successfully minimizing the value of $E(n(\vec{r}))$.

However, the form of the functional $E(n(\vec{r}))$ is not provided by the HK theorems. This problem was solved by Walter Kohn and Lu Jeu Sham,^[17] who further developed HK theorems and obtained the Kohn-Sham Equation, the Schrödinger-like equation involving only one single electron and expressed as follow

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}) + V_H(\vec{r}) + V_{xc}(\vec{r}) \right] \psi_i(\vec{r}) = \varepsilon_i \psi_i(\vec{r}) \quad (3.10)$$

where the first item in the bracket describes the electron kinetic energy, and the following three items, in order, represent ion Coulomb potential, classical electronic Coulomb potential, and exchange-correlation potential. In Kohn-Sham DFT, an interacting many-body system is simplified to non-interacting particles moving in an effective potential. By solving a set of single-particle Kohn-Sham equations, the ground state of a system can be found, and thus the system's full Schrödinger equation is solvable.

Exchange-Correlation Potential. In Kohn-Sham DFT, energy items are exact except for the exchange-interaction energy functional, E_{xc} . Therefore, the selection of appropriate E_{xc} functional is crucial to the accuracy of DFT results and developing new E_{xc} form is one of the hottest topics of DFT.

Local Density Approximation (LDA) is the simplest and easiest approximation to $E_{xc}[n(\vec{r})]$. It is derived from the uniform electron gas model, where the electron density is constant at all points in space, i.e., $n(\vec{r}) = \text{constant}$. In LDA, $E_{xc}[n(\vec{r})]$ is assumed to be a sum of contributions from each point, which can be mathematically expressed as

$$E_{xc}^{LDA}[n(\vec{r})] = \int d^3r n(\vec{r}) \varepsilon_{xc}(\vec{r}) \quad (3.11)$$

where $\varepsilon_{xc}(n)$ is the exchange-correlational energy at per point in a uniform electronic system. Since the LDA uses only local electron density, it is not suitable for long-range correlation systems and systems with a large gradient charge density, such as organic molecules and transition metal oxide.

To improve the LDA, Generalized Gradient Approximation (GGA) is developed, which includes both the electron density and its first derivative in the functional E_{xc} . There are many methods to include the information of the gradient of density, and thus there are various GGA functionals, E_{xc}^{GGA} . Two most widely employed E_{xc}^{GGA} for solids are the Perdew–Wang functional (PW91)^[18] and the Perdew–Burke–Ernzerhof functional (PBE)^[19]. Due to a more accurate approximation to the real situation, GGA works better than LDA for systems with a large gradient charge density. However, GGA also fails to correctly deal with the strong electron correlation effect in transition metal and rare earth compounds.

To address this issue, the GGA+U method is developed, which includes an orbital dependent Hubbard U term into GGA. Within this method, the U term is exerted on the highly localized orbitals and the self-interaction term is eliminated. The choice of the U values is dependent on the properties under investigation and the pseudopotential applied. As evidenced in previous literature, an appropriate value of the U term makes an obvious improvement in predicting the electronic properties of transition metal oxides.^[20]

Self-Consistent Field (SCF) Method. The solution to a Schrödinger equation is required to be self-consistent and the method of approximation for calculating the wave function and energy in the ground state is called SCF method or Hartree-Fock method. The calculation process is started with a trial electron density $n(\vec{r})$, which is used to solve the Kohn-Sham Equation and thus obtain the wave function solutions. With these wave functions, the electron density $n_{ks}(\vec{r})$ can be calculated out. If the calculated electron density $n_{ks}(\vec{r})$ equals to the initial density $n(\vec{r})$, the true ground-state electron density is found out and thus the total energy can be calculated out. Otherwise, the trial electron density $n(\vec{r})$ is updated in some way and the above process is iterated.

Density of States (DOSs) Calculation. DOS is a primary quantity used to describe the electronic properties of a metal oxide. It can be obtained from DFT calculations and displayed as the number of electron states versus energy. The intensity of DOS at specific energy denotes the number of states available for occupation at that energy level. For the DOS at energy lower than the Fermi energy, the available states are occupied by electrons. The Fermi energy corresponds to the energy of the highest occupied electronic state at $T = 0\text{ K}$, and hence the DOS above the Fermi level are unoccupied.

In this thesis, DFT computation was performed with the Vienna Ab Initio Simulation Package (VASP) software.^[21-22] The interaction between atomic cores and valence electrons is modeled by the projector augmented-wave (PAW) method,^[23] and the exchange-correlational effects of valence electrons are described by the GGA method with a PBE functional.^[19] To address the on-site Coulomb interaction of transition-metal d orbitals, the GGA+U approach is adopted by using the standard Dudarev implementation in VASP. In the Dudarev method, a Hubbard effective parameter $U_{eff} = U - J$ is used, with $J = 0$ and $U_{eff} = U$. The values of U_{eff} for Fe, Zn, Cr, and Co sites are set to be 4.0, 7.1, 3.2, 3.3 eV, respectively, which are taken from previous literatures.^[24-25] In Chapter 4, the magnetic configurations of all the ferrites investigated are set to be G-type antiferromagnetic, and a γ -centred $7 \times 7 \times 5$ k-point mesh is used for $AFeO_3$ ($A = Y, Gd, Pr, \text{ and } La$), a $5 \times 5 \times 5$ mesh for $ZnFe_2O_4$, and a $4 \times 4 \times 14$ mesh for β -FeOOH. In Chapter 5, for $ZnFe_{2-x}Cr_xO_4$ ($x = 0-2$), a γ -centred $5 \times 5 \times 5$ k-point mesh is applied to the standard Fd-3m spinel structure models. In Chapter 6, for $SrCoO_3$, $SrCo_{0.75}Fe_{0.25}O_3$, $Ba_{0.5}Sr_{0.5}Co_{0.75}Fe_{0.25}O_3$ and $LaCoO_3$, a γ -centred $6 \times 6 \times 6$ k-point mesh is applied to $2 \times 2 \times 2$ cubic perovskite supercells. In all calculations, the plane-wave cut-off energy is 520 eV. After structural relaxation with a force convergence of $0.02 \text{ eV}\text{\AA}^{-1}$ and an energy tolerance of 10^{-6} eV , the ground-state electronic properties of structural models are computed using the tetrahedron method with Blöchl corrections.^[26]

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Chapter 4

Understanding the Role of Octahedral Tilting in Fe-Based Oxides for Water Oxidation

Fe-based materials are promising candidates for cost-efficient electrocatalysts towards water oxidation. To figure out the optimal geometric structure for catalytically active Fe sites, the specific OER activities of FeO₆ octahedron in perovskites LaFeO₃, PrFeO₃, GdFeO₃, YFeO₃, spinel ZnFe₂O₄, and β-FeOOH are investigated and negatively correlated with the geometric tilting degree. With the aid of theoretical calculation, the catalytic performance of these Fe-based catalysts is further correlated with their bulk electronic properties.

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4.1 Introduction

Fe (oxy)hydroxides and oxides ever were considered as poor OER catalysts, inferior to CoO_xH_y or NiO_xH_y.^[1-3] However, recent studies demonstrate that Fe can play a highly active role in catalyzing OER. The existence of Fe in Ni/Co (oxy)hydroxides is found to be critical to superior OER activity.^[4-5] Besides, the OER activity trends revised by Burke et al. demonstrate that FeOOH, among the first-row transition metal oxyhydroxides, has the highest intrinsic activity in alkaline electrolytes.^[6] Furthermore, Fe-based oxides, CaCu₃Fe₄O₁₂, CaFeO₃, and SrFeO₃, were reported to be highly efficient OER electrocatalysts.^[7] Considering that there are abundant resources of ferrites in the Earth, Fe-based materials are promising commercial catalysts.^[8] To help the rational design of Fe-based OER catalysts, it is essential to figure out the local structural requirements of the most active Fe sites.

In this chapter, several crystalline structures, including perovskite, spinel, and oxyhydroxide, were specially selected to adjust the geometry of FeO₆ octahedra. In perovskites AFeO₃ (A = Y, Gd, Pr, and La), the Fe cations in the B site are acknowledged to be active for OER catalysis, whereas the rare earth metal cations in the A site are considered to be inactive.^[9] Yet, the coordination geometry of Fe in AFeO₃ is influenced by the size of A-site cations.^[9] In normal spinel ZnFe₂O₄, Zn²⁺ in the tetrahedrally-coordinated site has filled d orbitals and hence is regarded to be catalytically inactive, while Fe in the octahedrally-coordinated site plays a dominant role in OER catalysis.^[10-11] It is found that the OER activities of β -FeOOH, ZnFe₂O₄, and AFeO₃ (A = Y, Gd, Pr, and La) are correlated with the tilting degree of their FeO₆ octahedra. Furthermore, two electronic parameters related to such geometric tilting, i.e., the O 2p band centre and the charge-transfer energy, were used to explain the observed activity trend. This investigation helps to understand the factors critical to the OER catalysis on Fe-based materials.

4.2 Results and Discussion

4.2.1 Material Characterization

Figure 4.1 Structural models of (a) an ideal perovskite oxide, (b) GdFeO_3 -type perovskite oxide, (c) ZnFe_2O_4 spinel oxide, and (d) $\beta\text{-FeOOH}$.

As illustrated in Figure 4.1, FeO_6 octahedra in perovskites are completely corner-linked. In the ideal form, FeO_6 octahedra are regular polyhedral, with Fe–O–Fe bond angles of 180° (Figure 4.1a). In most cases, perovskites deviate from the ideal cubic phase to stabilize the crystal structure. GdFeO_3 -type perovskite, mainly driven by the misfit of A-site cation size, is one of the most common distorted forms. In this distortion, essentially rigid FeO_6 octahedra are tilted, and hence Fe–O–Fe bond angles are smaller than the ideal value, 180° , bringing about the decrease of crystal symmetry (Figure 4.1b). In this chapter, single phases of AFeO_3 ($\text{A} = \text{Y}, \text{Gd}, \text{Pr}, \text{and La}$) were prepared by a simple sol-gel method. As confirmed by X-ray diffraction (XRD) characterization, all of them are stoichiometric GdFeO_3 -type perovskites, crystalizing in orthorhombic structure with the $Pnma$ space

group (Figure 4.2a-d and Table 4.1). With identically trivalent valence state, the size of A cations in AFeO₃ follows the order: La³⁺ > Pr³⁺ > Gd³⁺ > Y³⁺ (Table 4.2).^[12] The smaller the A-site ionic radius is, the more distorted the corresponding AFeO₃. In contrast with AFeO₃, FeO₆ octahedra in spinel ZnFe₂O₄ are purely edge-linked, with Fe-O-Fe bond angles close to 90° (Figure 4.1c). In β -FeOOH, double chains of edge-sharing FeO₆ are linked by corners, yielding multiple values of Fe-O-Fe bond angle (Figure 4.1d). In this chapter, as-synthesized spinel ZnFe₂O₄ (Figure 4.2e) is purely crystallized in cubic structure with *Fd-3m* space group and β -FeOOH (Figure 4.2f) is a pure phase with *I-4m* space group.

Two variables were calculated to evaluate the distortion degree of FeO₆ octahedra in these Fe-based materials, that is, the internal deformation index δ and the average Fe-O-Fe angle $\langle \text{Fe-O-Fe} \rangle$. δ is employed to describe the deformation extent of FeO₆ from a regular octahedron and determined by the equation as follow

$$\delta = \frac{1}{n} \sum_i \left[\frac{(r_i - r)}{r} \right]^2$$

where r_i , r and n denote the Fe-O bond length, average Fe-O bond length, and the number of Fe-O bonds in a FeO₆ octahedron, respectively. A δ equal to zero indicates the octahedron is regular and the index is larger when the internal deformation is greater. The other parameter $\langle \text{Fe-O-Fe} \rangle$ is adopted to demonstrate the geometric tilting degree of FeO₆ octahedra. For orthogonal octahedra, $\langle \text{Fe-O-Fe} \rangle$ is 180° and increasing tilting degree results in the reduction of $\langle \text{Fe-O-Fe} \rangle$. The data of Fe-O bond lengths and Fe-O-Fe bond angles used to calculate the above two variables for Fe-based materials are summarized in Table 4.3 - 4.5.

Figure 4.2 Rietveld refined XRD profiles of as-prepared ferrites.

Table 4.1 Rietveld refined lattice constants and reliability factors for AFeO₃, ZnFe₂O₄, and β -FeOOH.

Sample	Space group	Lattice Constants			χ^2	R_p (%)	R_{wp} (%)
		a (Å)	b (Å)	c (Å)			
LaFeO ₃	<i>Pnma</i>	5.563	7.849	5.551	1.173	3.79	4.82
PrFeO ₃	<i>Pnma</i>	5.585	7.797	5.490	1.160	3.43	4.32
GdFeO ₃	<i>Pnma</i>	5.610	7.669	5.349	1.136	2.86	3.63
YFeO ₃	<i>Pnma</i>	5.597	7.608	5.283	1.180	2.36	2.97
ZnFe ₂ O ₄	<i>Fd-3m</i>	8.441	8.441	8.441	1.357	1.35	1.71
β -FeOOH	<i>I 4/m</i>	10.512	10.512	3.035	1.420	1.93	2.50

Table 4.2 Shannon ionic radii data for ions in AFeO₃ (A = Y, Gd, Pr, and La). The ionic radii are affected by the valence state, coordination number, and spin state of the element. For the ions in this table, the coordination number of A³⁺ is seven, of Fe³⁺ (HS) is six, and of O²⁻ is two.

Ions	O ²⁻	Fe ³⁺	La ³⁺	Pr ³⁺	Gd ³⁺	Y ³⁺
Ionic radius (Å)	1.38	0.645	1.16	1.126	1.053	1.019

Table 4.3 Fe-O distances, Fe-O-Fe angles, and distortion parameters in AFeO₃ (A = Y, Gd, Pr, and La). Data are obtained from the Rietveld refinement results.

	LaFeO ₃	PrFeO ₃	GdFeO ₃	YFeO ₃
Fe1-O1 * 2 (Å)	1.990(5)	2.0014(26)	1.96761(5)	2.0006(17)
Fe1-O2 * 2 (Å)	2.057(18)	1.991(11)	2.02235(4)	2.059(5)
Fe1-O2 * 2 (Å)	1.946(19)	2.032(11)	1.98690(4)	1.988(5)
Average Fe-O (Å)	1.99767	2.00813	1.99229	2.01587
Deformation index	$5.2194e^{-4}$	$7.51e^{-5}$	$1.2948e^{-4}$	$2.3543e^{-4}$
Fe1-O1-Fe1 (°)	160.7(17)	153.8(6)	154.013(1)	143.86(29)
Fe1-O2-Fe1 (°) * 2	157.9(8)	153.5(4)	150.321(0)	143.94(23)
Average Fe-O-Fe (°)	158.83333	153.6	151.55167	143.91333

Table 4.4 Fe-O distances, Fe-O-Fe angles, and distortion parameters in ZnFe₂O₄. Data are obtained from the Rietveld refinement results.

	ZnFe₂O₄
Fe2-O1 (Å) * 3	2.0246(18)
Average Fe-O (Å)	2.0246
Deformation index	0
Fe2-O1-Fe2 (°) * 3	94.854
Average Fe-O-Fe (°)	94.854

Table 4.5 Fe-O distances, Fe-O-Fe angles, and distortion parameters in β -FeOOH. Due to the complex connectivity of FeO₆ octahedra in β -FeOOH, data are obtained from the Inorganic Crystal Structure Database.

	β-FeOOH
Fe1-O1 (Å)	2.048
Fe1-O1 (Å) * 2	2.204
Fe1-O2 (Å)	2.033
Fe1-O2 (Å) * 2	2.006
Average Fe-O (Å)	2.0835
Deformation index	0.00251
Fe1-O1-Fe1 (°)	86.619
Fe1-O1-Fe1 (°) * 2	93.044
Fe1-O2-Fe1 (°)	97.764
Fe1-O2-Fe1 (°) * 2	130.763
Average Fe-O-Fe (°)	105.33283

Figure 4.3a demonstrates that the values of δ for AFeO₃ as well as ZnFe₂O₄ approach to zero, indicating that their FeO₆ octahedra are essentially undeformed, while that of β -FeOOH is slightly larger. Besides, the average Fe-O bond distance of every sample is about 2.0 Å, although that of β -FeOOH is insignificantly longer. In contrast, the values of $\langle \text{Fe-O-Fe} \rangle$ are distinctly different and follow the trend, AFeO₃ (La > Pr > Gd > Y) > β -FeOOH >

ZnFe₂O₄, as demonstrated in Figure 4.3b. It is worth noting that the single value of the Fe-O-Fe angle in ZnFe₂O₄ is larger than the smallest one in β -FeOOH (see Table 4.4 and 4.5).

Figure 4.3 (a) Deformation index (x axis) and average Fe-O length (y axis) and (b) Average Fe-O-Fe angle in ferrites.

Figure 4.4 (a) Fe K-edge XANES spectra and (b) Fe valence states of Fe-based materials.

Fe K-edge X-ray absorption near-edge spectroscopy (XANES) was employed to evaluate the valence states of Fe ions in these ferrites (Figure 4.4a). The edge position is defined as the energy at the highest first derivative of the absorbance, and its shift reflects the change in valency. With the known Fe valency in standard reference materials, i.e., Fe₃O₄ and Fe₂O₃, the oxidation states of Fe in other ferrites can be derived using linear interpolation

method. As displayed in Figure 4.4b, iron cations in AFeO₃, ZnFe₂O₄, and β -FeOOH are trivalent. Moreover, the occupancy of the iron cation of the octahedral site in ZnFe₂O₄ was confirmed by extended X-ray absorption fine-structure spectroscopy (EXAFS). In the Fourier transformation (FT) spectra of EXAFS (Figure 4.5), the peak at ~ 2.5 Å is present in the Fe K-edge FT spectrum but absent from the Zn K-edge FT spectrum, which is indicative of that Zn cations reside in the tetrahedral site while Fe cations occupy the octahedral site in ZnFe₂O₄.^[10, 13]

Figure 4.5 Fourier transformation of (a) Zn and (b) Fe K-edge EXAFS spectra for ZnFe₂O₄.

Based on the above analysis, the major environmental variable for FeO₆ octahedra in AFeO₃, ZnFe₂O₄, and β -FeOOH is $\langle \text{Fe-O-Fe} \rangle$, which indicates the degree of octahedral tilting, given the insignificant difference in the average Fe-O bond length, internal deformation extent, and Fe valency.

4.2.2 Electrochemical Performance

Figure 4.6a demonstrates the kinetic OER currents of ferrites in 0.1 M O₂-saturated KOH electrolyte. The specific activity was extracted by normalizing the OER current to the Brunauer–Emmett–Teller (BET) surface area of oxides (Table 4.6). Figure 4.6b compares the specific OER activities of ferrites with that of rutile IrO₂ nanoparticles,^[14] the gold standard. It can be observed that the catalytic performance of Fe-based perovskites outperforms ZnFe₂O₄ spinel and β -FeOOH. Among AFeO₃ catalysts, LaFeO₃, exhibiting

intrinsic activity comparable to that of IrO₂,^[14] takes the first place, followed successively by PrFeO₃, GdFeO₃, and YFeO₃.

Table 4.6 BET specific surface areas of AFeO₃ (A = Y, Gd, Pr, and La), ZnFe₂O₄, and β -FeOOH.

Samples	S _{BET} (m ² /g)
LaFeO ₃	1.45
PrFeO ₃	1.23
GdFeO ₃	2.69
YFeO ₃	2.71
ZnFe ₂ O ₄	1.97
β -FeOOH	88.73

Figure 4.6 (a) Capacitance- and iR -corrected OER currents of AFeO₃ (A = Y, Gd, Pr, and La), ZnFe₂O₄, and β -FeOOH in 0.1 M KOH. (b) Intrinsic OER activities of AFeO₃ (A = Y, Gd, Pr, and La), ZnFe₂O₄, β -FeOOH. The OER activity of rutile IrO₂ nanoparticles is included for comparisons. Data were extracted from the first cycle of CV.

Figure 4.7 Evolution of specific OER activity with the average Fe-O-Fe angle.

As shown in Figure 4.7, a positive correlation is identified between the specific OER activity and the average Fe-O-Fe bond angle, $\langle \text{Fe-O-Fe} \rangle$. As indicated by the trendline, it can be expected that the closer to 180° the $\langle \text{Fe-O-Fe} \rangle$, the higher the catalytic activity. Nevertheless, there is a small discrepancy that ZnFe₂O₄ has higher inherent activity but smaller $\langle \text{Fe-O-Fe} \rangle$ than β -FeOOH. This seeming divergence is probably due to the following causes. First, the more deformed FeO₆ octahedron and the stretched Fe-O bond in β -FeOOH (Figure 4.3a) may be detrimental to its OER activity. Second, there are several values of Fe-O-Fe bond angle in β -FeOOH, and the smallest one may be heavily weighted against its activity. Since this minor discrepancy can be justified, it still can be concluded from Figure 4.7 that the specific OER activity of Fe-based oxides is positively related to $\langle \text{Fe-O-Fe} \rangle$ and hence inversely correlated to the geometric tilting degree of FeO₆ octahedra. Disclosing the physical origin of this relationship is essential to the development of highly active Fe-based catalysts.

4.2.3 Density of States Analysis

In recent years, transition metal-oxygen covalency has been reported to be an influential factor for the high OER activity of TMOs.^[7, 15-18] TM-O covalency is associated with the interfacial charge-transfer rate during the OER process, and the enhancement of covalency is expected to yield the increase in inherent activity.^[18] It has been reported that the

electronic structures of perovskite oxides are susceptible to the variation in geometric factors, such as the change of metal-oxygen-metal bond angles.^[19-21] Therefore, the dependence of the specific activity of FeO_6 octahedra on the geometric tilting degree probably is governed by the Fe-O covalency.

Figure 4.8 Partial DOS plots of the O 2p and the Fe 3d orbitals of ferrites.

To verify this conjecture, density functional theory (DFT) computation was carried out to analyze the electronic structures of AFeO₃, ZnFe₂O₄, and β -FeOOH. Figure 4.8 shows the partial density of state (DOS) plots of Fe 3d and O 2p orbitals. It can be observed that for each structural model, the DOS at the Fermi energy (E_F) is zero and the band gap is less than 3 eV (Table 4.7), indicating that these Fe-based materials are semiconductors. Besides, the valence band near the Fermi level is primarily occupied by O 2p states, and the conduction band (unoccupied states above E_F) is mainly dominated by Fe 3d states. The above observations are in agreement with previous theoretical^[8, 22] and experimental^[23-26] studies.

Table 4.7 DFT calculated band gap, E_g for AFeO₃ (A = Y, Gd, Pr, and La), ZnFe₂O₄, and β -FeOOH.

Samples	E_g^{DFT} (eV)
LaFeO ₃	2.29
PrFeO ₃	2.29
GdFeO ₃	2.28
YFeO ₃	2.14
ZnFe ₂ O ₄	1.69
β -FeOOH	2.11

To estimate the Fe-O covalency degree, two electronic parameters, that is, the O 2p-band centre ($\bar{\epsilon}_{O\ 2p}$) and the charge-transfer energy (Δ), are calculated according to the PDOS data shown in Figure 4.8. As illustrated in Figure 4.9a, $\bar{\epsilon}_{O\ 2p}$ is the first moment of the occupied O 2p states,^[27] the shift of which reflects the variation of metal-oxygen hybridization as well as the degree of covalency.^[17] The DFT calculated O 2p band centre (vs. E_F) has been demonstrated to be a good activity descriptor for perovskite-type catalysts, and a narrower energy gap between the O 2p band centre and the Fermi level is indicative of higher catalytic performance.^[28-29] However, the experimental findings reported by Hong et al. demonstrate charge-transfer energy as an activity descriptor more general than O 2p band centre (vs. E_F), considering that the OER mechanism of semi-metallic oxides is different from that of semiconducting ones.^[27] For semiconductors, the charge-transfer energy determined by experimental approaches can track the DFT-calculated energy

difference between the unoccupied TM 3d and occupied O 2p band centres (Figure 4.9a), i.e., the TM-O covalency.^[27] A lower charge-transfer energy denotes greater TM-O covalency and hence indicates higher catalytic activity. To reliably evaluate the Fe-O covalency, both $\bar{\epsilon}_{O\ 2p}$ and Δ , are calculated for the Fe-based materials investigated in this chapter. As summarized in Table 4.8 and shown in Figure 4.9a, $\bar{\epsilon}_{O\ 2p}$ follows the trend, AFeO₃ (La > Pr > Gd > Y) > ZnFe₂O₄ > β -FeOOH, while Δ follows an inverse trend.

Figure 4.9 (a) Schematic representation of the O 2p band centre ($\bar{\epsilon}_{O\ 2p}$) and the charge-transfer energy (Δ); the unoccupied Fe 3d and the occupied O 2p band centres of AFeO₃ (A = Y, Gd, Pr, and La), ZnFe₂O₄, and β -FeOOH are shown on the right. Evolution of (b) O 2p band centre (vs. E_F) as well as (c) charge-transfer energy with the average Fe-O-Fe angle.

Table 4.8 DFT calculated O 2p band centre, unoccupied Fe 3d band centre, and charge-transfer energy of AFeO₃ (A = Y, Gd, Pr, and La), ZnFe₂O₄, and β -FeOOH.

Samples	O 2p-band centre (eV)	Fe 3d-band centre (eV)	Charge-transfer energy (eV)
LaFeO ₃	-2.3343	2.77934	5.11365
PrFeO ₃	-2.42938	2.74261	5.17199
GdFeO ₃	-2.45221	2.98168	5.43389
YFeO ₃	-2.54521	2.93824	5.48345
ZnFe ₂ O ₄	-3.12405	2.54655	5.6706
β -FeOOH	-3.16408	2.83914	6.00321

In Figure 4.9b-c, the O 2p band centre (vs. E_F) as well as the charge-transfer energy is related to the average Fe-O-Fe bond angle of ferrites. By reducing the average Fe-O-Fe angle, the O 2p band centre is moved down, and the charge-transfer energy is increased. This observation agrees well with the conjecture that the octahedral tilting degree in ferrites influences the covalency of Fe-O bonds. As indicated by the grey trendlines in Figure 4.9b-c, the dependence of Δ on $\langle\text{Fe-O-Fe}\rangle$ is lower than that of $\bar{\epsilon}_{O\ 2p}$, suggesting that the position of Fe 3d band is less sensitive to the octahedral tilting degree than that of the Fermi level. It is noteworthy that both $\bar{\epsilon}_{O\ 2p}$ and Δ indicate that β -FeOOH has Fe-O covalency weaker than that of ZnFe₂O₄. As mentioned above, electronic structures are closely related to structural distortion. Hence, the small internal deformation of FeO₆ octahedron and the slight elongation of Fe-O bonds probably decrease the Fe-O covalency in β -FeOOH, resulting in OER activity inferior to that of ZnFe₂O₄.

Figure 4.10 demonstrates the close relationship between the Fe-O covalency, indicated by $\bar{\epsilon}_{O\ 2p}$ and Δ , and the OER activity. Besides, Δ has a better correlation with the catalytic activity in comparison with $\bar{\epsilon}_{O\ 2p}$, which agrees with the conclusion made by Hong et al. that Δ can better reflect the OER activity than $\bar{\epsilon}_{O\ 2p}$.^[27] The above analysis demonstrates that FeO₆ octahedral tilting plays an important role in catalyzing OER. With increasing the octahedral tilting degree, the Fe-O covalency is weakened, which can be reflected by a lower $\bar{\epsilon}_{O\ 2p}$ and a larger Δ , and hence the inherent OER activity of FeO₆ octahedra is

decreased.

Figure 4.10 Evolution of specific OER activity with the Fe-O covalency.

4.3 Conclusion

In summary, the OER catalytic performance of a series of ferrites was negatively related to the geometric tilting degree of FeO₆ octahedra. The physical origin of this relationship is attributed to the Fe-O covalency, which can be indicated by the O 2p band centre (vs. E_F) and the charge-transfer energy obtained from DFT calculation. It is unveiled that the FeO₆ octahedral tilting will weaken the Fe-O covalency and therefore decrease the catalytic efficiency over Fe sites.

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Chapter 5

Identifying Metal-Oxygen Hybridization as an Influential Parameter in $\text{ZnFe}_{2-x}\text{Cr}_x\text{O}_4$ Spinel Oxides for Water Oxidation

The rational design of oxygen evolution electrocatalysts is inseparable from a good knowledge of the physicochemical properties governing the catalytic behaviors. In this chapter, to identify the influential electronic parameter at the octahedral (O_h) site of spinel oxides for water oxidation, catalytic activities of $\text{ZnFe}_{2-x}\text{Cr}_x\text{O}_4$ ($x = 0 - 2$) were investigated. With catalytically inactive Zn^{2+} occupying the tetrahedral (T_d) site in spinel oxides, the possible interference from T_d - O_h superexchange interaction is avoided. It is revealed that the composition-dependent activity of $\text{ZnFe}_{2-x}\text{Cr}_x\text{O}_4$ is governed by the metal-oxygen hybridization at the O_h site.

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5.1 Introduction

To expedite the development of advanced catalysts, a good understanding of the factors critical to the oxygen evolution catalysis on transition metal oxides (TMOs) is essential.^[1] At present, two popular approaches are employed to investigate the OER electrocatalysts. One is to *in situ* detect the changes of oxide surface under OER conditions,^[2-4] and the other is to build a link between the desirable catalytic performance and the specific electronic structures of TMOs.^[5] The latter has successfully identified several activity descriptors,^[6-9] among which, transition-metal e_g occupancy, in combination with metal-oxygen covalency, has been demonstrated to well explain the OER activity trends observed for perovskite-type TMOs.^[7]

Given the success of e_g occupancy as a descriptor to rationalize the diversity in the OER activities of perovskites and design perovskite-type catalysts with high activity, it has been tried to apply e_g filling to other oxide families, for example, spinel oxides.^[10] Different from a perovskite oxide, where only octahedral (O_h) interstitials can be occupied by TM cations and hence are considered as catalytically active sites, a spinel oxide offers not only O_h but also tetrahedral (T_d) interstitials (as shown in Figure 5.1a), resulting in a complex situation. Due to the stronger metal-oxygen covalency of O_h coordination than that of T_d coordination, TM cations in O_h site are proposed to be superior to the same element in T_d site for catalyzing the OER.^[10] Nevertheless, the superexchange interaction between magnetic cations in T_d and O_h sites is generally stronger than that between O_h -site magnetic cations,^[11] which therefore may affect the catalytic efficiency over O_h -site transition metal (TM_{O_h}) cations.

To reveal the electronic parameter of TM_{O_h} cations governing the OER activity of spinel oxides without interference from T_d - O_h electronic interaction, $ZnFe_{2-x}Cr_xO_4$ ($x = 0, 0.5, 1, 1.5$, and 2) were synthesized. In $ZnFe_2O_4$ and $ZnCr_2O_4$, the T_d site is primarily occupied by catalytically inactive Zn^{2+} with $3d$ orbitals filled, and O_h site by Fe^{3+} in the high spin state (HS) or Cr^{3+} .^[12] As shown in Figure 5.1b, the e_g orbital of Fe^{3+} (HS) is occupied by two electrons whereas that of Cr^{3+} by zero electrons.^[12] Thus, the nominal average e_g number of O_h -site TM cations (TM_{O_h}) in $ZnFe_{2-x}Cr_xO_4$ decreases from 2 to 0 with the increase of Cr substitution. In addition, because the d orbitals of Zn^{2+} are fully occupied by

electrons, the superexchange interaction in $\text{ZnFe}_{2-x}\text{Cr}_x\text{O}_4$ mainly takes place between the O_h -site cations, which may tune the electronic configurations of Fe and/or Cr cations.

Figure 5.1 (a) Structural model of $\text{ZnFe}_{2-x}\text{Cr}_x\text{O}_4$ ($x = 0-2$) spinel oxide. (b) Electronic configuration of TM 3d orbitals in the spinel structure, i.e., Zn(II) in T_d site, Fe(III) (high spin) in O_h site, and Cr(III) in O_h site.

5.2 Results and Discussion

5.2.1 Material Characterization

XRD characterization and Rietveld refinement results confirmed that all the as-prepared $\text{ZnFe}_{2-x}\text{Cr}_x\text{O}_4$ spinel oxides are crystallized in a cubic structure with $\text{Fd-}3\text{m}$ space group (Figure 5.2a-e and Table 5.1). As demonstrated in Figure 5.2f, the lattice constants ($a = b = c$) of $\text{ZnFe}_{2-x}\text{Cr}_x\text{O}_4$ monotonically reduce with the increment in Cr content, which agrees with previous reports that the smaller radius of octahedrally-coordinated Cr^{3+} than Fe^{3+} ions leads to the decrease of lattice size with increasing Cr substitution.^[13-14]

Figure 5.2 (a-e) Rietveld refined XRD profiles of as-prepared ZnFe_{2-x}Cr_xO₄ spinel oxides. (f) Evolution of lattice constant with the Cr content.

Table 5.1 Rietveld refined lattice parameters and reliability factors for $\text{ZnFe}_{2-x}\text{Cr}_x\text{O}_4$.

Sample	Space group	Lattice parameters $a = b = c$ (Å)	χ^2	R_p (%)	R_{wp} (%)
ZnFe_2O_4	$Fd-3m$	8.4407(1)	1.357	1.35	1.71
$\text{ZnFe}_{1.5}\text{Cr}_{0.5}\text{O}_4$	$Fd-3m$	8.4128(1)	1.625	1.68	2.21
ZnFeCrO_4	$Fd-3m$	8.3811(2)	1.797	2.16	2.88
$\text{ZnFe}_{0.5}\text{Cr}_{1.5}\text{O}_4$	$Fd-3m$	8.3566(1)	1.814	2.50	3.27
ZnCr_2O_4	$Fd-3m$	8.3286(1)	3.961	3.81	5.70

Figure 5.3 (a-e) FESEM images of as-synthesized $\text{ZnFe}_{2-x}\text{Cr}_x\text{O}_4$ ($x = 0, 0.5, 1, 1.5,$ and 2) spinel oxides. (f) Evolution of BET specific surface area with the Cr content.

Table 5.2 BET specific surface areas and average particle sizes of $\text{ZnFe}_{2-x}\text{Cr}_x\text{O}_4$.

$\text{ZnFe}_{2-x}\text{Cr}_x\text{O}_4$	BET specific surface area ($\text{m}^2 \text{g}^{-1}$)	Average particle size (μm)
ZnFe_2O_4	1.97	3.04
$\text{ZnFe}_{1.5}\text{Cr}_{0.5}\text{O}_4$	3.83	1.56
ZnFeCrO_4	2.66	2.26
$\text{ZnFe}_{0.5}\text{Cr}_{1.5}\text{O}_4$	6.37	0.94
ZnCr_2O_4	6.55	0.92

Figure 5.4 (a) Zn, (b) Fe, and (c) Cr K-edge XANES spectra for $\text{ZnFe}_{2-x}\text{Cr}_x\text{O}_4$. (d) Evolution of absorption edge positions with the Cr content.

The FESEM images of $\text{ZnFe}_{2-x}\text{Cr}_x\text{O}_4$ demonstrate that the change in Cr content has an insignificant influence on the morphology (Figure 5.3a-e), which is consistent with the minor difference in the Brunauer–Emmett–Teller (BET) specific surface areas of $\text{ZnFe}_{2-x}\text{Cr}_x\text{O}_4$ (Figure 5.3f and Table 5.2).

X-ray absorption near-edge spectroscopy (XANES) was employed to estimate the valence states of Zn, Fe, and Cr ions in $\text{ZnFe}_{2-x}\text{Cr}_x\text{O}_4$ (Figure 5.4a-c). The absorption edge position is defined as the energy at the highest first derivative of the absorbance, and its shift reflects the change of valence states of the absorbing element. Figure 5.4d demonstrates that irrespective of the detected element, the edge positions have almost no fluctuation with the change in Cr content, suggesting that the valence states of TM cations in $\text{ZnFe}_{2-x}\text{Cr}_x\text{O}_4$ keep almost constant.

Figure 5.5 Fe 2p and Cr 2p XPS spectra of $\text{ZnFe}_{2-x}\text{Cr}_x\text{O}_4$.

Figure 5.6 Zn 2p XPS spectra of $\text{ZnFe}_{2-x}\text{Cr}_x\text{O}_4$.

For the determination of the valence states of transition-metal cations in $\text{ZnFe}_{2-x}\text{Cr}_x\text{O}_4$, X-ray photoelectron spectroscopy (XPS) measurements were carried out. Figure 5.5 shows the Fe 2p and the Cr 2p XPS spectra. The observations that the binding energies of Fe $2p_{1/2}$ and Fe $2p_{3/2}$ are around 724.6 eV and 711.2 eV, respectively, and that satellite peaks for Fe $2p_{1/2}$ and Fe $2p_{3/2}$ are centred at 732.6 eV and 718.8 eV, respectively, indicate that Fe ions in $\text{ZnFe}_{2-x}\text{Cr}_x\text{O}_4$ have a valence of three.^[15-16] It also can be observed that the binding energies of Cr $2p_{1/2}$ and Cr $2p_{3/2}$ are about 586.2 eV and 576.5 eV, respectively, suggesting that Cr ions in $\text{ZnFe}_{2-x}\text{Cr}_x\text{O}_4$ also have a valence of three.^[17-18] Figure 5.6 displays the Zn

2p XPS spectra. The two peaks located at ~ 1045 and ~ 1022 eV can be assigned to Zn $2p_{1/2}$ and Zn $2p_{3/2}$, respectively, demonstrating that Zn ions in $\text{ZnFe}_{2-x}\text{Cr}_x\text{O}_4$ have a valence of two.^[19-20] The above XPS analysis agrees well with the above results of XANES characterization.

Figure 5.7 Fourier transformation of (a) Zn, (b) Fe, and (c) Cr K-edge EXAFS spectra. (d) The number of coordinated oxygen anions for transition metal cations in $\text{ZnFe}_{2-x}\text{Cr}_x\text{O}_4$.

Figure 5.8 Fitted Zn K-edge EXAFS $k^3\chi(R)$ spectra.

Extended X-ray absorption fine-structure spectroscopy (EXAFS) was employed to disclose the geometrical occupation information of TM ions in $\text{ZnFe}_{2-x}\text{Cr}_x\text{O}_4$. Octahedrally-

coordinated and tetrahedrally-coordinated cations can be distinguished by their difference in interatomic distances as revealed by the Fourier transformation (FT) of EXAFS spectra. No matter the absorbing element is in the O_h or T_d site, the single scattering from its closest oxygen anions leads to the appearance of a peak at $\sim 1.5 \text{ \AA}$ in the FT spectrum, and the scattering from its neighboring metal ions in either O_h or T_d site results in a peak emerging at $\sim 3.0 \text{ \AA}$.^[21-22] Nevertheless, if the absorbing cation is in O_h site, the scattering from its nearest O_h -site metal cations yields a peak additionally existing at $\sim 2.5 \text{ \AA}$.^[21] Because of the scattering phase-shift, the distance between atoms shown in a FT spectrum is about $0.5 \text{ \AA}$ shorter than the real value.^[23] Figure 5.7a-c demonstrate that both Fe and Cr cations in $\text{ZnFe}_{2-x}\text{Cr}_x\text{O}_4$ have two values of cation-cation bond distance (i.e., ~ 2.5 and $\sim 3.0 \text{ \AA}$) while Zn cations possess a single value of cation-cation bond distance ($\sim 3.0 \text{ \AA}$).

Figure 5.9 Fitted Fe K-edge EXAFS $k^3\chi(R)$ spectra.

Figure 5.10 Fitted Cr K-edge EXAFS $k^3\chi(R)$ spectra.

Moreover, EXFAS fitting results reveal the number of coordinated oxygen anions for TM cations in $\text{ZnFe}_{2-x}\text{Cr}_x\text{O}_4$ (see Figure 5.8-5.10 and Table 5.3-5.5 for details). Figure 5.7d shows that the oxygen coordination number for either iron or chromium ions is six and that for zinc ions is four, indicating that $\text{ZnFe}_{2-x}\text{Cr}_x\text{O}_4$ are normal spinel oxides with $\text{Fe}^{3+}/\text{Cr}^{3+}$ in the O_h site and Zn^{2+} in the T_d site. Besides, the FT spectra in Figure 5.7a-c demonstrate the slight shift of peak positions with the change in Cr content, which may be caused by the reduction in lattice volume as octahedrally-coordinated Fe substituted by smaller Cr cations.

Table 5.3 Fitting parameters for Zn K-edge EXAFS spectra.

Sample	Path	R (Å)	Coordination number N	N_error	σ^2 (Å ²)
ZnFe ₂ O ₄	Zn-O	1.96	3.9	0.2	0.0048
	Zn-M_M	3.54	9	0.6	0.0021
	Zn-Zn	3.65	5.1	0.5	0.002
ZnFe _{1.5} Cr _{0.5} O ₄	Zn-O	1.96	3.8	0.2	0.0041
	Zn-M_M	3.52	8.6	0.7	0.0018
	Zn-Zn	3.62	5.4	0.6	0.0016
ZnFeCrO ₄	Zn-O	1.96	3.7	0.2	0.0041
	Zn-M_M	3.51	8.6	0.7	0.0018
	Zn-Zn	3.61	4.8	0.5	0.0016
ZnFe _{0.5} Cr _{1.5} O ₄	Zn-O	1.96	3.8	0.2	0.0037
	Zn-M_M	3.5	9	0.8	0.0016
	Zn-Zn	3.6	4.8	0.5	0.0015
ZnCr ₂ O ₄	Zn-O	1.95	3.9	0.3	0.0033
	Zn-M_M	3.48	9.4	0.9	0.0015
	Zn-Zn	3.58	4.9	0.6	0.0013

Table 5.4 Fitting parameters for Fe K-edge EXAFS spectra.

Sample	Path	R (Å)	Coordination number N	N_error	σ^2 (Å ²)
ZnFe ₂ O ₄	Fe-O	2.02	5.8	0.4	0.0065
	Fe-M_M	3.02	5.3	0.4	0.003
	Fe_Zn	3.5	2.8	0.5	0.0027
ZnFe _{1.5} Cr _{0.5} O ₄	Fe-O	2.02	6.3	0.5	0.0072
	Fe-M_M	3	5.4	0.5	0.0033
	Fe_Zn	3.49	2.9	0.6	0.003
ZnFeCrO ₄	Fe-O	2.02	5.8	0.6	0.0054
	Fe-M_M	3	4.9	0.5	0.0025
	Fe_Zn	3.49	2.6	0.5	0.0022
ZnFe _{0.5} Cr _{1.5} O ₄	Fe-O	2.01	6	0.7	0.0059
	Fe-M_M	2.98	5.3	0.7	0.0027
	Fe_Zn	3.47	2.8	0.6	0.0024

Table 5.5 Fitting parameters for Cr K-edge EXAFS spectra.

Sample	Path	R (Å)	Coordination number N	N_error	σ^2 (Å ²)
ZnFe _{1.5} Cr _{0.5} O ₄	Cr-O	1.99	5.7	0.6	0.003
	Cr-M_M	2.98	4.9	0.6	0.0038
	Cr_Zn	3.47	2.3	0.6	0.0034
ZnFeCrO ₄	Cr-O	1.98	5.7	0.6	0.0048
	Cr-M_M	2.96	4.6	0.6	0.0023
	Cr_Zn	3.45	2	0.4	0.002
ZnFe _{0.5} Cr _{1.5} O ₄	Cr-O	1.98	5.8	0.6	0.0049
	Cr-M_M	2.95	4.8	0.5	0.0023
	Cr_Zn	3.45	2.1	0.4	0.0021
ZnCr ₂ O ₄	Cr-O	1.99	6	0.6	0.0047
	Cr-M_M	2.94	5.2	0.5	0.0022
	Cr_Zn	3.44	2.2	0.4	0.002

Table 5.6 Ionic radii in angstrom of chromium and iron in the function of ionic charge and spin state (high spin = HS, low spin = LS). Ions in this table are with a coordination number of six.

Ion	2+	3+	4+	5+	6+
Cr (LS)	0.73	0.615	0.55	0.49	0.44
Cr (HS)	0.80				
Fe (LS)	0.61	0.55	0.585		0.25 (4)
Fe (HS)	0.78	0.645			

The results obtained from the above X-ray absorption spectroscopy and XPS analysis are consistent with the expectation that ZnFe_{2-x}Cr_xO₄ are normal spinel oxides, in which Fe³⁺ and Cr³⁺ ions primarily occupy the O_h site while Zn²⁺ are located at the T_d site. Besides, the results derived from Rietveld refinement of XRD patterns demonstrate that the lattice constants of ZnFe_{2-x}Cr_xO₄ reduce with increasing Cr/Fe ratio, which is attributed to the larger cation size of Fe³⁺ than Cr³⁺ at the O_h site. In view of the revised ionic radii reported by Shannon,^[24] the cation size follows the order of Fe³⁺ (HS) > Cr³⁺ > Fe³⁺ (LS) (Table

5.6). Therefore, the Fe^{3+} in $\text{ZnFe}_{2-x}\text{Cr}_x\text{O}_4$ synthesized in this chapter should be in the HS state and thus with e_g occupancy of two.

5.2.2 Electrochemical Performance

Figure 5.11 (a) CV curves of $\text{ZnFe}_{2-x}\text{Cr}_x\text{O}_4$ in 1 M KOH electrolyte. Redox features are shown in the inset. (b) OER activity as a function of the Cr content (left y axis) as well as the nominal average e_g filling of TM_{Oh} cations (right y axis).

Figure 5.11a shows the Cyclic voltammetry (CV) curves of $\text{ZnFe}_{2-x}\text{Cr}_x\text{O}_4$ at a scan rate of 2 mV s^{-1} in 1 M KOH electrolyte. For ZnCr_2O_4 , an anodic redox peak emerges at $\sim 1.30 \text{ V}$ (anodic) vs. RHE, which is ascribed to the oxidation of Cr^{3+} to Cr^{6+} .^[25] With Cr is increasingly substituted by Fe, this redox feature gradually disappears, suggesting that the Fe/Cr ratio in the oxide surface is consistent with that in the bulk. To obtain the specific activity, the OER kinetic currents of $\text{ZnFe}_{2-x}\text{Cr}_x\text{O}_4$ were normalized to their surface areas measured by the nitrogen BET method. Figure 5.11b demonstrates the evolution of the specific OER activity with the Cr content in $\text{ZnFe}_{2-x}\text{Cr}_x\text{O}_4$, which follows a volcano-shaped trend with a summit at $x = 1$. The dependence of OER activity on composition may result from that the superexchange interaction between TM_{Oh} cations transfers e_g electrons from Fe to Cr. As the e_g electron number of Fe^{3+} (HS) and Cr^{3+} is two and zero, respectively, the nominal average e_g filling of TM_{Oh} cations in $\text{ZnFe}_{2-x}\text{Cr}_x\text{O}_4$ reduces from two to zero with increasing Cr content (right y-axis, Figure 5.11b). Despite having an optimal nominal

average e_g filling and the highest OER activity among $\text{ZnFe}_{2-x}\text{Cr}_x\text{O}_4$, ZnFeCrO_4 is inferior to perovskite oxide catalysts with e_g occupancy close to unity.^[7] This suggests that the actual tuning effect of Cr substitution on the e_g occupation of ZnFe_2O_4 is insignificant.

5.2.3 Density of States Analysis

Figure 5.12 Comparison of DFT optimized lattice parameters of $\text{ZnFe}_{2-x}\text{Cr}_x\text{O}_4$ with the experimental values.

Density functional theory (DFT) calculation was performed to analyze the electronic structures of $\text{ZnFe}_{2-x}\text{Cr}_x\text{O}_4$ spinel oxides. Figure 5.12 compares the lattice constants optimized by DFT computation with the experimental values. Figure 5.13 displays the partial density of state (PDOS) plots of Zn 3d, Fe 3d, Cr 3d, and O 2p orbitals for $\text{ZnFe}_{2-x}\text{Cr}_x\text{O}_4$, from which it can be noticed that the density of states (DOSs) at the Fermi level are empty and the band gaps are smaller than 3 eV. This result is consistent with the findings of previous DFT+U studies^[26-27] and experiments^[28-30]. Besides, there is a distinct difference in the band gaps of $\text{ZnFe}_{2-x}\text{Cr}_x\text{O}_4$ (Table 5.7), which suggests the difference in their conductivity. Figure 5.14 shows the OER activity of $\text{ZnFe}_{2-x}\text{Cr}_x\text{O}_4$ as a function of the band gap, from which little correlation is identified. As electrons do not have to pass through the oxide particles in the catalyst composite (oxides mixed with carbon materials) and hence the intrinsic conductivity of oxides is not a critical factor for OER catalysis.^[30]

Figure 5.13 Partial DOS plots of TM (TM = Zn, Fe, and Cr) 3d and O 2p orbitals in $\text{ZnFe}_{2-x}\text{Cr}_x\text{O}_4$.

Table 5.7 DFT calculated lattice parameters and electronic band gaps of $\text{ZnFe}_{2-x}\text{Cr}_x\text{O}_4$.

$\text{ZnFe}_{2-x}\text{Cr}_x\text{O}_4$	Lattice parameter	Electronic band gap
	a^{DFT} (Å)	E_g^{DFT} (eV)
ZnFe_2O_4	8.497	1.21
$\text{ZnFe}_{1.5}\text{Cr}_{0.5}\text{O}_4$	8.477	1.14
ZnFeCrO_4	8.456	1.22
$\text{ZnFe}_{0.5}\text{Cr}_{1.5}\text{O}_4$	8.436	1.71
ZnCr_2O_4	8.416	2.53

Figure 5.14 OER activity as a function of the band gap of $\text{ZnFe}_{2-x}\text{Cr}_x\text{O}_4$.

It also can be observed from Figure 5.13 that the DOSs close to the Fermi level are mainly occupied by O 2p as well as Fe/Cr 3d states whereas the d electrons of Zn (located at 7-9 eV below E_F) make a minor contribution to the top valence band. As the DOSs near the Fermi level are regarded to play a crucial role in binding the reaction intermediates,^[31] the interaction between O 2p band and TM_{Oh} (i.e. Fe and/or Cr) 3d band is expected to be vital to influence the OER activities of $\text{ZnFe}_{2-x}\text{Cr}_x\text{O}_4$, while the electronic structures of Zn ions in T_d site are insignificant. Moreover, it can be noticed that the characteristics of the Fe 3d band become weaker whereas those of the Cr 3d band get greater with increasing the Cr content in $\text{ZnFe}_{2-x}\text{Cr}_x\text{O}_4$. Therefore, to evaluate the influence of TM_{Oh} -O electronic interactions on OER activity, the PDOS of the Fe 3d band is superimposed with that of the Cr 3d band of $\text{ZnFe}_{2-x}\text{Cr}_x\text{O}_4$ (Figure 5.15a).

Figure 5.15 (a) Partial DOS plots of TM_{Oh} 3d and O 2p orbitals. (b) Illustration of calculating the percentage of O 2p states hybridized with TM_{Oh} 3d states. (c) Hybridization intensity as a function of the Cr content.

The importance of the hybridization between TM 3d and O 2p states to OER catalysis has been emphasized by previous studies on TMOs with superior catalytic activity.^[7, 32-33] It is expected that the increase in hybridization will enhance the metal-oxygen covalency and thus the catalytic activity of a TMO.^[8] As shown in Figure 5.15b, the hybridization between O 2p and TM_{Oh} 3d states is indicated by the overlapped region of the two bands, that is, the gray shaded area, and the intensity of TM_{Oh} -O hybridization can be reflected by the degree of overlap. Hence, the proportion of O 2p states that are mixed with TM_{Oh} 3d states was adopted as an indicator to evaluate the TM_{Oh} -O hybridization intensity for $\text{ZnFe}_{2-x}\text{Cr}_x\text{O}_4$.

$x\text{Cr}_x\text{O}_4$. Figure 5.15c shows that the evolution of the hybridization degree with the Cr content in $\text{ZnFe}_{2-x}\text{Cr}_x\text{O}_4$ follows a volcano-shaped trend with a summit at $x = 1$. Besides, as shown in Figure 5.16, the hybridization intensity of Fe 3d and O 2p orbitals positively whereas that of Cr 3d and O 2p orbitals negatively varies with the increment of Cr content, suggesting that both Fe and Cr cations in $\text{ZnFe}_{2-x}\text{Cr}_x\text{O}_4$ are catalytically active sites for water oxidation.

Figure 5.16 Evolution of Fe-O (red circles) and Cr-O (blue triangles) hybridization intensity with the Cr content.

Figure 5.17a shows the classical OER mechanism, in which the redox chemistry of surface TM cations dominates the reaction and four steps of coupled electron-proton transfer are involved.^[34-35] In recent years, several studies have demonstrated that the OER mechanism on perovskite oxides are related to the bulk electronic properties.^[36-37] It has been reported that the involvement of lattice oxygen into producing oxygen molecules can be triggered by increasing the metal-oxygen covalency of perovskite-type catalysts, resulting in an OER mechanism essentially different from the traditional one.^[36] Nevertheless, the large energy gap between the O 2p band centres and the Fermi level (Figure 5.15a) suggests that the lattice oxygen anions in $\text{ZnFe}_{2-x}\text{Cr}_x\text{O}_4$ are not active enough to participate in the OER catalysis.^[36] Therefore, the volcano-shaped trend observed for the OER activities of $\text{ZnFe}_{2-x}\text{Cr}_x\text{O}_4$ should be rationalized based on the conventional concerted proton-electron transfer mechanism shown in Figure 5.17a. In the traditional OER mechanism, the catalytic efficiency is dependent on the electronic interaction between oxygenated intermediates and

TM sites on the oxide surface.^[7, 35] Figure 5.17b shows the positive relationship between the specific OER activity and the $\text{TM}_{\text{Oh}}\text{-O}$ hybridization intensity of $\text{ZnFe}_{2-x}\text{Cr}_x\text{O}_4$, which is consistent with previous findings that OER catalytic performance is closely related to the metal-oxygen hybridization.^[7-8] This direct correlation is explained by that TM-O covalency positively varying with the increment of hybridization intensity expedites the charge transfer rate between the surface transition-metal active sites and the oxygenated intermediates and hence enhance the catalytic activity.^[8]

Figure 5.17 (a) Conventional OER mechanism. (b) Evolution of specific activity with the $\text{TM}_{\text{Oh}}\text{-O}$ hybridization parameter.

5.3 Conclusion

The specific OER activity of $\text{ZnFe}_{2-x}\text{Cr}_x\text{O}_4$ spinel oxides shows a volcano-shaped dependence on the Cr content. It is attributed to that the gradual replacement of Fe by Cr modulates the $\text{TM}_{\text{Oh}}\text{-O}$ hybridization intensity, considering that the DFT-calculated hybridization parameter also follows a volcano-shaped trend with the Cr content. The positive correlation identified between the specific activity of $\text{ZnFe}_{2-x}\text{Cr}_x\text{O}_4$ and the $\text{TM}_{\text{Oh}}\text{-O}$ hybridization intensity highlights the critical role of metal-oxygen hybridization at the O_{h} site in catalyzing the OER.

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Chapter 6

Revealing the Active Phase on Fe-Modified $\text{SrCoO}_{3-\delta}$ Perovskite Oxides for Water Oxidation

Surface reconstruction into an amorphous layer during the oxygen evolution reaction (OER) has been reported for some perovskite-type catalysts. However, it is still unknown whether the observed OER activity is exclusively governed by the amorphous surface layers or also strongly correlated with the remaining bulk. It is attempted to address this confusion by investigating the catalytic behaviors of $\text{SrCoO}_{3-\delta}$ (SC) and Fe-modified SC in alkaline solution. Two approaches were used to introduce Fe into SC, that is, bulk Fe doping ($\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$, SCF02) and surface incorporating Fe ions from Fe^{3+} -spiked electrolyte (SC + Fe^{3+}). The surface reconstruction phenomena of SC and SCF02 after electrochemical measurements were verified by multiple experimental techniques. With different remaining bulk perovskites, SCF02 and SC + Fe^{3+} were found to exhibit roughly equal catalytic activities, confirming the dominant role of the in situ derived surface components in determining the catalytic performance.

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6.1 Introduction

Among the transition metal (TM) oxides investigated as the electrocatalysts for oxygen evolution reaction (OER), perovskite oxide family has attracted many research interests owing to its great flexibility in composition and structure. By tailoring the bulk properties, several highly active perovskites, such as $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF) and $\text{SrNb}_{0.1}\text{Co}_{0.7}\text{Fe}_{0.2}\text{O}_{3-\delta}$, have been developed. For these perovskite compounds, their superior inherent OER activities were suggested to be directly originated from the well-engineered electronic properties of the as-synthesized materials. However, the reasonability of this explanation is on the basis that the surface properties of these crystalline compounds remain unchanged during the OER process, which has undergone the challenges from growing findings on the surface instability of perovskite oxides under electrochemical conditions.^[1-6] For instance, Shao-Horn's group noticed the quick surface amorphization of BSCF upon catalyzing OER in basic electrolytes, along with the dissolution of Ba and Sr.^[1] Such drastic surface rearrangements was also observed for other efficient perovskites, for example, $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (SCF02), whereas not for inferior ones, i.e., LaCoO_3 .^[1-2] Later, with the assistance of *operando* techniques, Schmidt's group detected the growth of $(\text{Co}, \text{Fe})\text{O}_x\text{H}_y$ on the BSCF perovskite surface under OER conditions, and they regarded the *in situ* formed surface species as the real catalyst accounting for the measured catalytic performance.^[4]

Although the dynamic surface changes of perovskite oxides have been obtaining intensive research attention, little focus has been put on the role in OER catalysis played by the bulk perovskites underlying the reconstructed surface layers. As the contribution made to the apparent OER activity by the amorphized surface has not yet been unambiguously distinguished from that by the remaining bulk, it is elusive whether the measured activity is directly affected by the bulk perovskite's electronic structure or more related to the *in situ* developed metal (oxy)hydroxides. Resolving this confusion is important to the rationalization of observed OER activity trend, the understanding of factors determining activity, and the design of new catalytic materials. Given previous reports that incorporating Fe ions in the electrolyte can positively affect the OER catalytic performance of Co- or Ni-based (oxy)hydroxides and oxides,^[7-9] it can be inferred that the $\text{Co/NiO}_x\text{H}_y$

in situ evolved from a Co/Ni-based perovskite is also subjected to the influence of electrolyte Fe ions while the underlying bulk oxide is not, which thus make it possible to unravel the roles of the remaining bulk and the reconstructed surface in catalyzing OER.

Figure 6.1 (a) Cubic $\text{SrCoO}_{3-\delta}$ perovskite is modified by Fe ions in two ways. Rietveld refined XRD profiles of as-prepared (b) SC and (c) SCF02. HRTEM images of pristine (d) SC and (e) SCF02.

In this chapter, with cubic $\text{SrCoO}_{3-\delta}$ (SC) perovskite chosen as the model catalyst, the OER activities of $\text{SrCoO}_{3-\delta}$ that are respectively modified by bulk Fe doping (SCF02) and surface Fe decorating (the incorporation of Fe ions from the electrolyte, $\text{SC} + \text{Fe}^{3+}$) are compared, as illustrated in Figure 6.1a. With the aid of multiple experimental techniques, it was confirmed that both SC and SCF02 experienced quick surface amorphization and Sr leaching during OER while their bulk perovskite structures well-maintained. Upon the spiking of 0.1 mM Fe^{3+} into the 0.1 M KOH electrolyte, the apparent OER activity of SC was significantly enhanced, which thus is comparable to that of SCF02 in Fe-free KOH solution. This observation highlights the key role of oxide-electrolyte interface in catalyzing OER. Accordingly, for perovskite oxides suffering reconstruction during OER, it is the *in situ* formed surface $(\text{Co}, \text{Fe})\text{O}_x\text{H}_y$, instead of the remaining bulk phase, that determine the observed catalytic performance.

6.2 Results and Discussion

6.2.1 Material Characterization

Table 6.1 Rietveld refined lattice constants and reliability factors for as-synthesized perovskite powders.

Sample	Structure	Space group	Lattice constants $a = b = c$ (Å)	χ^2	R_p (%)	R_{wp} (%)
$\text{SrCoO}_{3-\delta}$	cubic	$Pm\bar{3}m$	3.8451	1.649	2.09	2.72
$\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$	cubic	$Pm\bar{3}m$	3.8570	1.589	1.89	2.49

The as-synthesized SC crystalizes in a simple cubic perovskite structure, as evidenced by the XRD patterns and Rietveld refinement results (Figure 6.1b and Table 6.1). As shown in Figure 6.1c and Figure 6.2, the cubic perovskite structure remains unchanged as the Co ions in B sites are gradually replaced by Fe ions, which agrees with previous reports that appropriate content of Fe dopants can stabilize the cubic structure of SC perovskite.^[10-11] Hence, the possibility can be excluded that the difference in crystal structure results in variation in the catalytic performance.

Figure 6.2 Observed XRD profiles of as-prepared $\text{SrCo}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ perovskites.

Figure 6.3 FESEM images of as-synthesized $\text{SrCo}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ perovskites.

The high-resolution transmission electron microscope (HRTEM) images of pristine SC and SCF02 perovskites (Figure 6.1d-e) reveal their highly crystalline surfaces as well as bulk phases. The interplane distances of 2.7 Å and 2.2 Å can be assigned to the [110] crystal plane in SC and the [111] crystal plane in SCF02, respectively (Table 6.1). Besides, for all the $\text{SrCo}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ ($x = 0, 0.05, 0.2$ and 0.5 , denoted as SC, SCF005, SCF02 and SCF05, respectively), the corresponding field emission scanning electron microscope (FESEM) images (Figure 6.3) demonstrate that their morphologies and particle sizes are almost the same, which is consistent with that their Brunauer-Emmett-Teller (BET) specific surface areas are in the same order (Figure 6.4 and Table 6.2).

Figure 6.4 BET measurements of as-synthesized perovskite powders.

Table 6.2 BET specific surface area of as-synthesized perovskite powders.

Samples	S_{BET} (m^2/g)
$\text{SrCoO}_{3-\delta}$	0.5997
$\text{SrCo}_{0.95}\text{Fe}_{0.05}\text{O}_{3-\delta}$	0.3851
$\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$	0.3739
$\text{SrCo}_{0.5}\text{Fe}_{0.5}\text{O}_{3-\delta}$	0.3996

6.2.2 Surface Evolution and Catalytic Behaviors

Figure 6.5 (a) OER currents and (b) specific OER activities of $\text{SrCo}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$. The electrochemical data were taken from the 100th CV scans.

The Fe-free (Fe concentration is lower than 1 ppb) 0.1 M KOH electrolyte was prepared with KOH pellets (Sigma Aldrich, 99.99%) and Milli-Q water ($18.2 \text{ M}\Omega \cdot \text{cm}$).^[12] Figure 6.5 compares the OER activities of $\text{SrCo}_{1-x}\text{Fe}_x\text{O}_3$ in the Fe-free KOH electrolyte. It is observable that the OER activity of SC is increased as a result of Fe doping and the maximum activity is exhibited by SCF02, which agrees with previous findings that the optimal Fe doping level in Co-based oxides and (oxy)hydroxides is approximately 20%.^[8, 10, 13] The SCF02 catalyst was used for further investigation.

Cyclic voltammetry (CV) scans of SC and SCF02 in the Fe-free KOH electrolyte at a rate of 10 mVs^{-1} are demonstrated in Figure 6.6a-b. For either SC or SCF02, an oxidation process, in-between 1.4 V and 1.5 V, appears in the forward-going scan of the first CV cycle. Such broad oxidation peak disappears in the subsequent scans and hence suggests that the perovskite surface is irreversibly changed. From the second cycle, two new sets of redox features before the occurrence of OER can be observed. The first one (in-between 1.0 and 1.3 V) can be ascribed to the conversion between Co(II)/Co(III) , and the second one can be assigned to the transition between Co(III)/Co(IV) .^[14] During the continuous potential cycling, the two redox peaks become more markedly, and simultaneously the OER currents of both SC and SCF02 are gradually enhanced. These observations suggest that the SC and SCF02 may undergo surface restructuring, as the variation in OER activity accompanied by structural changes during electrochemical testing has been frequently

reported for perovskite oxides in recent years. After 50 cycles, the surface of either SC or SCF02 reaches a relatively stable state, given that the OER activity and the capacitance are almost unchanged.

Figure 6.6 Representative CV scans of (a) SC and (b) SCF02 in Fe-free 0.1 M KOH electrolyte. (c) O 1s and (e) Sr 3d XPS spectra of pristine and cycled SC. (d) O 1s and (f) Sr 3d XPS spectra of pristine and cycled SCF02. (g) HRTEM detection of tested SC and SCF02. (h) Averaged concentration of Sr leaching into the KOH electrolyte per cycle at different stages.

As shown in Figure 6.6c-f and Figure 6.7, the potential surface changes of SC and SCF02 before and after OER are probed with X-ray photoelectron spectroscopy (XPS). Table 6.3 and 6.4 summarize the related peak-fitting parameters. Figure 6.6c-d present the O 1s spectra of SC and SCF02 before and after electrochemical cycling. In the as-prepared SC or SCF02, two types of oxygen can be distinguished, that is, the lattice oxygen (529.5 - 529.8 eV) from the perovskite oxide and the oxygen (~531.7 eV) from surface SrCO_3 and/or $\text{Sr}(\text{OH})_2$.^[15-17] Additionally, an insignificant peak (~533.1 eV) from molecular water can be observed in the O 1s spectrum of as-prepared SC.^[18-19] After electrochemical

cycling, the intensity of the peak from lattice oxygen greatly decreased, indicating the loss of initial perovskite-structured surfaces. An extra peak emerging at ~ 535.6 eV in the O 1s spectra of cycled perovskites can be attributed to the oxygen from Nafion (the electrode binder).^[20] Figure 2e-f display the Sr 3d XPS spectra, which further supports that the surface structures of SC and SCF02 are rearranged. In as-synthesized perovskites, there are two types of Sr, one (Sr 3d_{5/2}: 131.4 - 132.0 eV) from the perovskite lattice and the other (Sr 3d_{5/2}: 133.1 - 133.7 eV) from SrCO₃ and Sr(OH)₂.^[15-17] After OER measurements, the relative intensities of Sr from perovskite lattice is weakened (for SCF02) or even absent (for SC), hinting the reconstructed surfaces are Sr deficient.

Figure 6.6g shows the HRTEM images of cycled perovskites to further evidence the restructuring during catalysis process. For both SC and SCF02 after 100 CV cycles, an amorphized surface is formed with a depth of approximately ten nanometers, while the crystalline bulk phase is well retained. In addition, inductively coupled plasma mass spectrometry (ICP-MS) analysis of electrolytes (Figure 6.6h and Table 6.5-6.6) demonstrates that the loss of Sr during the cycling tests, which agrees with the XPS results shown in Figure 6.6e-f. The dissolution rate of Sr during potential cycling is evaluated by normalizing the content of Sr leaching into the electrolyte to the duration of CV scan (Figure 6.6h and Table 6.5). In view of the much higher Sr leaching rate within the first ten CV cycles than that in the following cycles, it is expectable that the surface reconstruction is most rapid during the initial testing.

Figure 6.7 Co 2p XPS spectra of pristine and cycled (a) SC and (b) SCF02. Insignificant variation in the cobalt oxidation state was observed.

Table 6.3 Fitting parameters for the XPS spectra of pristine and cycled $\text{SrCoO}_{3-\delta}$.

Pristine SC					Cycled SC			
Sr								
	3d _{3/2}	3d _{5/2}	3d _{3/2}	3d _{5/2}	3d _{3/2}	3d _{5/2}		
Binding energy (eV)	135.7	133.7	133.8	132.0	135.2	133.5	/	
FWHM (eV)	1.61	1.61	1.49	1.49	2.3	2.3		
Co								
	2p _{1/2}	2p _{3/2}	2p _{1/2}	2p _{3/2}	2p _{1/2}	2p _{3/2}	2p _{1/2}	2p _{3/2}
Binding energy (eV)	796.6	781.6	795.1	780.0	796.5	781.47	795.06	780.06
FWHM (eV)	3.05	3.05	1.66	1.66	2.6	2.6	1.63	1.63
O								
Binding energy (eV)	533.1	531.7	529.8	535.7	532.3	529.9		
FWHM (eV)	1.86	1.84	2.05	2.03	2.59	2.13		

Table 6.4 Fitting parameters for the XPS spectra of pristine and cycled $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$.

Pristine SCF02					Cycled SCF02			
	Sr							
	3d _{3/2}	3d _{5/2}	3d _{3/2}	3d _{5/2}	3d _{3/2}	3d _{5/2}	3d _{3/2}	3d _{5/2}
Binding energy (eV)	134.8	133.1	133.2	131.4	135.5	133.8	133.0	131.2
FWHM (eV)	1.40	1.40	2.36	2.36	3.44	3.44	0.78	0.78
	Co							
	2p _{1/2}	2p _{3/2}	2p _{1/2}	2p _{3/2}	2p _{1/2}	2p _{3/2}	2p _{1/2}	2p _{3/2}
Binding energy (eV)	796.7	781.7	795.3	780.3	796.8	781.8	795.1	780.1
FWHM (eV)	3	3	2.05	2.05	3.27	3.27	1.75	1.75

O						
Binding energy (eV)	/	531.7	529.5	535.6	532.3	529.8
FWHM (eV)		2.29	3.33	2.43	2.80	2.24

Table 6.5 The concentration of Sr leaching into the electrolyte during 1-10, 10-50, and 50-100 cycles and the concentration of dissolved Sr normalized to the cycle time.

Samples	Concentration of leached Sr (ppb)*			Averaged concentration of leached Sr per cycle (ppb)		
	1-10	10-50	50-100	1-10	10-50	50-100
	cycles	cycles	cycles	cycles	cycles	cycles
SC	6.77 ± 0.08	3.24 ± 0.04	3.63 ± 0.05	0.677 ± 0.008	0.081 ± 0.001	0.0726 ± 9E-4
SCF02	7.15 ± 0.10	2.57 ± 0.02	2.21 ± 0.02	0.715 ± 0.010	0.0643 ± 5E-4	0.0442 ± 3E-4

*The concentration of trace Sr in the untested 0.1 M KOH electrolyte is 0.776 ± 0.018 .

Table 6.6 ICP-MS analysis of Co and Fe concentrations in the electrolyte after 1-10, 10-50, and 50-100 cycles.

Samples	Co Concentration (ppb)*			Fe Concentration (ppb)*		
	1-10	10-50	50-100	1-10	10-50	50-100
	cycles	cycles	cycles	cycles	cycles	cycles
SC	0.0169 ± 0.0022	0.0103 ± 0.0027	0.0121 ± 0.0031	0.805 ± 0.113	0.69 ± 0.12	0.695 ± 0.020
SCF02	0.018 ± 0.002	0.0139 ± 0.0010	0.0147 ± 0.0061	1.05 ± 0.12	0.965 ± 0.085	0.872 ± 0.055

*The concentration of trace Co and Fe in the untested 0.1 M KOH electrolyte is 0.0160 ± 0.0015 and 0.748 ± 0.133 . Hence, the leaching of B-site cations from SC as well as SCF02 during potential cycling is insignificant.

Figure 6.8 (a) 2nd and 10th CV scans of SC in Fe³⁺-spiked KOH solution by contrast with the 100th CV scan in Fe-free solution. (b) Capacitive regions of the CV scans in (a). (c) Evolution of capacitive current with the CV scan rate. (d) Representative CV scans of α -FeOOH. (e) Geometric current densities of blank GCE, pure AB carbon and SC in Fe-free and Fe³⁺-spiked electrolytes.

After cycling in Fe-free electrolyte for 100 times, SC surface reached a relatively steady state (Figure 6.6a), and subsequently 0.1 mM Fe³⁺ was immediately spiked into the 0.1 M KOH electrolyte. Figure 6.8a shows the CV profiles of SC in Fe³⁺-spiked KOH electrolyte. The OER currents of SC is sharply increased and kept stable during ten continuous CV scans. As displayed in Figure 6.9, when the concentration of spiked Fe³⁺ (Fe³⁺_{spiked}) reaches 0.1 mM, the performance improvement approaches the maximum. Figure 6.8b shows that the capacitive region of CV scans in Fe-free KOH electrolyte is almost overlapped with that in Fe³⁺-spiked electrolyte, suggesting little change in the electrochemical active surface area (ECSA). Figure 6.10 displays the measurement of the double-layer capacitance (C_{dl}), an indicator of ECSA,^[21] for SC in Fe-free and Fe³⁺-spiked electrolytes. As demonstrated in Figure 6.8c, the two values of C_{dl} are almost the same, which demonstrates that the variation of ECSA cannot account for the activity enhancement shown in Figure 6.8a.

Figure 6.9 Evolution of the geometric activity with the concentration of Fe^{3+} spiked into the alkaline electrolyte.

Hence, the promoting effect of $\text{Fe}^{3+}_{\text{spiked}}$ on the OER activity of SC is considered. The equilibrium solubility of $\text{Fe}(\text{OH})_4^-$ at pH 13 is about 10^{-6} M.^[22] Therefore, most of the 0.1 mM $\text{Fe}^{3+}_{\text{spiked}}$ should become FeO_xH_y precipitate, which is confirmed to be α -FeOOH (Figure 6.11). Nevertheless, Figure 6.8d demonstrates that the OER activity of α -FeOOH is inferior and suffers rapid deactivation within 50 CV scans. Therefore, the noticed activity improvement cannot result from the α -FeOOH that may adsorb onto the oxide electrode surface. In addition, there is possibility that $\text{Fe}^{3+}_{\text{spiked}}$ ions are deposited onto the catalyst surface and thus promote the catalytic efficiency. This conjecture is supported by the enhanced catalytic performance of pure acetylene black (AB) carbon as well as blank glassy carbon electrode (GCE) tested in Fe^{3+} -spiked KOH solution (Figure 6.8e and Figure 6.12). It is worth noting that regardless of the presence of $\text{Fe}^{3+}_{\text{spiked}}$, the lack of SC brings about poor activity, which suggests that the good activity measured for SC + Fe^{3+} is indispensable from the interaction between $\text{Fe}^{3+}_{\text{spiked}}$ ions and the reconstructed SC surface.

Figure 6.10 Double-layer capacitance measurements for SC in Fe-free and Fe^{3+} -spiked electrolytes. Double-layer capacitances are equal to the slopes obtained from the linear fitting of the two sets of data.

Figure 6.11 Rietveld refined XRD pattern of α -FeOOH collected from the brown precipitate after adding $\text{Fe}(\text{NO}_3)_3$ into 0.1 M KOH. The reliability factors are $R_p = 1.92\%$, $R_{wp} = 2.43\%$, and $\chi^2 = 1.11$.

Figure 6.12 Cyclic voltammograms (10 mVs^{-1}) of SC oxide catalyst (containing $50 \mu\text{g}$ oxide and $20 \mu\text{g}$ AB), pure carbon catalyst (containing $20 \mu\text{g}$ AB) and blank GCE in Fe-free (dashed lines) and Fe^{3+} -spiked (solid lines) 0.1 M KOH electrolytes.

Figure 6.13 Tafel plots for SCF02 in Fe-free (100th cycle) and Fe³⁺-spiked (2nd and 10th cycles) electrolytes.

As previously suggested, the rearrangement of a perovskite (ABO_3) surface during the OER can be related to the dissolution of metal cations and the rapid redeposition of hard-to-dissolve ones (such as the transition metals in the B site) on the catalyst surface.^[2-4] Hence, it can be inferred that the $\text{Fe}^{3+}_{\text{spiked}}$ ions are involved in the dissolution/redeposition cycle along with Co ions,^[23] resulting in the growth of $(\text{Co}, \text{Fe})\text{O}_x\text{H}_y$ akin to the amorphized SCF02 surface. This inference is supported by the nearly unaltered OER currents of SCF02 tested in Fe^{3+} -spiked electrolyte (Figure 6.13).

It is noteworthy that the optimized $\text{Fe}^{3+}_{\text{spiked}}$ concentration is ~ 0.1 mM (Figure 6.9), which is much higher than the critical value (ca. 10^{-6} M) required for the alkaline electrolyte being saturated with soluble Fe species.^[22] A similar result has been reported for amorphous $\text{CoO}_x + \text{Fe}^{3+}$ catalyst (where the optimized $\text{Fe}^{3+}_{\text{spiked}}$ concentration is 0.3 mM).^[9] Over a CoO_xH_y host, the dissolution of Fe from the electrode and the deposition of Fe from the electrolyte during OER are concomitant.^[23] Hence, to ensure sufficiently high content of Fe being incorporated into the reconstructed surface, the deposition rate of Fe, which is positively correlated with the Fe content in the electrolyte, should be equal to or much higher than the dissolution rate.^[23] Then, the concentration of $\text{Fe}^{3+}_{\text{spiked}}$ beyond the solubility limit is expected to make sure that the electrolyte immediately adjacent to the catalyst's surface is always saturated with soluble Fe species. Therefore, a sufficient

amount of Fe ions can be maintained in the reconstructed surface of SC, which yields the highest catalytic activity.

6.2.3 Structure-Activity Relationship

Figure 6.14 (a) Specific activity comparison. The inset shows the EIS spectra. (b) The structure-activity relationship among SC, SC + Fe³⁺, and SCF02.

For the estimation of the specific OER activity (i_s), OER currents are normalized to the BET surface area of catalyst materials. Figure 6.14a demonstrates that the OER activity of SC is better than that of rutile IrO₂ nanoparticles,^[24] which is consistent with previous studies that cubic SC is a promising oxygen evolution electrocatalyst.^[25-26] Both types of Fe modification bring about the significant enhancement of catalytic performance, yielding activities similar to that of BSCF.^[27] In addition, the incorporation of Fe into SC results in noticeable decrease in the Tafel slope. The insignificant difference in the Tafel slopes of SC + Fe³⁺ and SCF02 possibly results from the slightly different Fe content present in their surfaces (Figure 6.15), which is consistent with that the Tafel slopes of Co_{1-x}Fe_xOOH are found to be related to the Fe content.^[8] Moreover, the inset of Figure 6.14a demonstrates the electrochemical impedance spectra (EIS), which reflects that the charge transfer rate of SC is markedly increased due to Fe incorporation.^[13, 28]

Figure 6.15 High angle annular dark field (HADF) of (a) cycled SCF02 and (b) cycled SC + Fe³⁺ with point scanning transmission electron microscopy (STEM) EDS analysis. Surface Sr, Co, and Fe metal ratios determined by STEM EDS are summarized in (c).

Based on the above results of physical and electrochemical characterizations, the structure-activity relationship among SC, SC + Fe³⁺, and SCF02 is summarized in the schematic diagram displayed in Figure 6.14b. While merely incorporating Fe ions into the near-surface region, SC + Fe³⁺ demonstrates a specific activity markedly higher than that of SC, suggesting that, as opposed to the remaining bulk structure, the catalyst's surface environment determines its catalytic activity towards OER. This conclusion is further supported by comparing SC + Fe³⁺ with SCF02, both of which have similar catalytic activity and surface (oxy)hydroxide layers. This suggests that the remaining SC and SCF02 perovskites, which have different bulk properties, such as the B-site composition and the electronic structure (Figure 6.16), make little contribution to the observed OER activity. Given the above discussion, for perovskites suffering surface restructuring during the catalysis process, the true active components may differ from the pristine surface structures.

Consequently, it is important to identify the correlations among the initial bulk properties, the reconstruction process, and the ultimate activity.

Figure 6.16 Partial DOS plots for (a) SrCoO_3 and (b) $\text{SrCo}_{0.75}\text{Fe}_{0.25}\text{O}_3$. (c) O p band centres (vs. E_F) of SrCoO_3 (SC), $\text{SrCo}_{0.75}\text{Fe}_{0.25}\text{O}_3$ (SCF02), $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.75}\text{Fe}_{0.25}\text{O}_3$ (BSCF) and LaCoO_3 (LC). The dependence of the OER catalytic performance on the O p band centre (vs. E_F) of perovskite oxides has been proposed in previous literatures.^[1, 27]

6.3 Conclusion

With the aid of XPS, HRTEM and ICP-MS, it is revealed both SC and SCF02 experienced surface restructuring and Sr leaching during electrochemical testing in Fe-free KOH electrolyte. Upon further tested in Fe³⁺-spiked KOH electrolyte, SC exhibited markedly increased OER activity, due to incorporating Fe³⁺_{spiked} into the amorphized surface layers. This observation highlights that the OER activity is governed by the oxide-electrolyte interface. Besides, for SC + Fe³⁺ and SCF02, their comparability in activity is accompanied by the difference in bulk phase yet the resemblance in (Co, Fe)O_xH_y surface layer, which further proves that the remaining perovskite has an insignificant effect on the catalytic performance. Accordingly, understanding factors controlling the reconstruction behaviors of perovskites is vital for future catalyst development, because the *in situ* formed surface components determine the catalytic performance.

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Chapter 7

Conclusions and Recommendations

This chapter first presents a general discussion about how the hypotheses are adequately proven in this thesis. Based on research results obtained in this thesis, future work regarding the development of efficient oxygen evolution electrocatalysts is recommended. Besides geometric effect, the roles of Fe valency and oxygen deficiency on the OER activity of FeO_6 octahedra need further investigation to develop desirable Fe-based catalysts. In addition, the promoting effect of iron spiked into electrolyte on Co/Ni-containing oxides can be utilized to construct highly active catalytic systems for water oxidation. Moreover, given the dynamic interaction between the oxide electrode surface and the electrolyte environment during oxygen evolution reaction, the spiking of synergetic metal ions into the electrolyte may be a facile approach to improve the activity of metal oxide catalyst.

7.1 General Discussion

In this thesis, earth-abundant transition metal (TM) oxides have been investigated as electrocatalysts for the oxygen evolution reaction (OER) under alkaline conditions, and the relationships between the bulk properties of initial oxide materials and the measured catalytic performance have been explored.

Fe oxides and (oxy)hydroxides are among the most promising cost-effective OER electrocatalysts. Therefore, it is necessary to explore the catalytically critical geometric structure for Fe sites. This thesis first addresses the effect of geometric tilting degree on OER catalysis by putting FeO_6 octahedra into crystalline ordered environments, including AFeO_3 ($\text{A} = \text{Y, Gd, Pr, and La}$) perovskites, ZnFe_2O_4 spinel, and $\beta\text{-FeOOH}$. In perovskites AFeO_3 , corner-shared FeO_6 octahedra are acknowledged to be catalytically active for water oxidation, and the octahedral tilting degree is under the influence of the size of catalytically inactive A-site cations. In normal spinel ZnFe_2O_4 , as Zn^{2+} cations in the tetrahedral (T_d) site have filled d orbitals and hence are catalytically inactive, Fe cations in the octahedral (O_h) site play a dominant role in OER catalysis. Average Fe-O-Fe angle was calculated to indicate the geometric tilting degree in these ferrites. It is positively correlated with the OER activity, and the optimal value is expected to be 180° . With the help of theoretical computation, two electronic parameters associated with Fe-O covalency, i.e., O 2p band centre and charge-transfer energy, are well correlated with the average Fe-O-Fe angle and the OER activity of ferrites. This proves the hypothesis that the degree of geometric tilting can influence the intrinsic reactivity of FeO_6 octahedron by altering the Fe-O covalency. Besides geometric effect, composition-dependent catalytic behavior has been frequently reported for mixed-metal oxides. Elucidating the physical origin of the compositional influence is essential for science-based catalyst design. To identify the electronic parameter of O_h -site TM (TM_{O_h}) cations influential in the OER catalysis on spinel oxides, $\text{ZnFe}_{2-x}\text{Cr}_x\text{O}_4$ ($x = 0 - 2$) normal spinels are investigated as OER catalysts. Due to the preference of catalytically inactive Zn^{2+} to occupy the T_d site,^[1] the superexchange interaction in $\text{ZnFe}_{2-x}\text{Cr}_x\text{O}_4$ mainly exists between TM_{O_h} cations (Fe and/or Cr), which thus avoids the interference from T_d - O_h electronic interaction. The site distribution and the oxidation states of Zn, Fe, and Cr ions in $\text{ZnFe}_{2-x}\text{Cr}_x\text{O}_4$ are verified by X-ray absorption spectroscopy

(XAS). The specific OER activity of $\text{ZnFe}_{2-x}\text{Cr}_x\text{O}_4$ is found to have a volcano-shaped dependence on the Cr content. With the aid of *ab initio* calculation, the hybridization degree between TM_{Oh} 3d and O 2p orbitals is revealed, and a volcano-shaped relationship is also identified between the TM_{Oh} -O hybridization degree and the Cr content, which may be due to the superexchange interaction between TM_{Oh} cations. Most importantly, the specific activity of $\text{ZnFe}_{2-x}\text{Cr}_x\text{O}_4$ is found to be positively related to the TM_{Oh} -O hybridization intensity, which proves the hypothesis that there exists an electronic parameter of TM_{Oh} cations crucial to the composition-dependent OER activity of $\text{ZnFe}_{2-x}\text{Cr}_x\text{O}_4$ spinel oxides. The relationships found between the bulk physicochemical properties and the OER catalytic performance of TM oxides once were attributed to the optimized binding strength between OER intermediates and the TM sites on the well-defined surface structures of as-synthesized oxides.^[2-4] However, this explanation has been challenged by growing reports regarding the surface structural transformation of perovskite as well as spinel oxides under OER conditions.^[5-9] For oxides undergoing surface reconstruction during OER, the surface species *in situ* formed is proposed as the real catalyst.^[7-8] Nevertheless, it is elusive whether the apparent activity is still subjected to the strong influence of the remaining bulk phase. To resolve this issue, the enhancement effect of Fe incorporation, either by bulk doping or surface decorating, on the catalytic performance of cobalt-based (oxy)hydroxides is utilized to differentiate the activities contributed by the reconstructed surface layers and the underlying bulk phase. By continuously cycling in Fe-free alkaline electrolyte, both $\text{SrCoO}_{3-\delta}$ and $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ perovskites underwent surface amorphization along with the leaching of A-site cation. Subsequently, the reconstructed $\text{SrCoO}_{3-\delta}$ was further cycled in Fe^{3+} -spiked electrolyte to incorporate Fe ions into the amorphized surface layers, resulting in an increased OER activity which is comparable to that of $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$. This proves the hypothesis that the *in situ* derived surface components primarily account for the measured activity while the underlying bulk phase plays an insignificant role.

7.2 Future Work

In Chapter 4, the role of the geometric tilting degree of FeO_6 octahedra in catalyzing OER has been revealed. However, the intrinsic OER activity of LaFeO_3 , the most active ferrite

investigated in Chapter 4, is mediocre. Therefore, to advance the development of desirable Fe-based catalysts, it is critical to elucidate the local structural requirements of the most active Fe sites besides an average Fe-O-Fe angle close to 180° . Changing the A-site cation of perovskite oxide is capable of changing not only lattice parameters, as demonstrated in Chapter 4, but also the valency of B-site cations and oxygen vacancy content. Substituting trivalent A-site cation with divalent alkali earth metals, such as Sr^{2+} and Ba^{2+} , while maintaining Fe in the B site of perovskites, the oxidation states of Fe may vary, and oxygen vacancies may form. Perfect SrFeO_3 is crystallized in a cubic perovskite structure, with Fe-O-Fe angles close to 180° (Figure 7.1).

Figure 7.1 Crystal structure of perfect SrFeO_3 perovskite oxide. Green, gold, and red balls represent strontium cations, iron cations, and oxygen anions, respectively.

Nevertheless, it is hard to prepare fully oxidized SrFeO_3 . Hence, the incorporation of oxygen vacancies is unavoidable for SrFeO_3 synthesized by conventional sol-gel methods at atmospheric pressure. When A-site cations are totally replaced by Ba^{2+} , BaFeO_3 with hexagonal-type perovskite structure and oxygen deficiency is more facile to synthesize. However, in this type of BaFeO_3 , FeO_6 octahedra are not only corner-sharing but also face-sharing. In contrast, $\text{Ba}_{1-x}\text{Sr}_x\text{FeO}_{3-\delta}$ ($0 \leq x \leq 1$), with only a small amount of Sr doping, is crystallized in a cubic perovskite structure, just like SrFeO_3 . This is verified by the X-ray diffraction (XRD) patterns displayed in Figure 7.2, which shows that as-synthesized $\text{SrFeO}_{3-\delta}$ and $\text{Ba}_{0.8}\text{Sr}_{0.2}\text{FeO}_{3-\delta}$ are with highly similar crystal structures. And the comparative left shift of the diffraction peaks of $\text{Ba}_{0.8}\text{Sr}_{0.2}\text{FeO}_{3-\delta}$ indicates the increase in lattice constants, which results from the larger cation size of Ba^{2+} than Sr^{2+} . Because the

configuration of FeO_6 octahedra in hexagonal-type $\text{BaFeO}_{3-\delta}$ is quite different from that in SrFeO_3 and it is difficult to synthesize the pure phase of $\text{BaFeO}_{3-\delta}$ (Figure 7.2),^[10] $\text{BaFeO}_{3-\delta}$ is not included in the following discussion. It is expectable that the Fe valency and the oxygen vacancy content can be tuned by varying the barium content in $\text{Ba}_{1-x}\text{Sr}_x\text{FeO}_{3-\delta}$ ($0 < x \leq 1$) cubic perovskites. Hence, the roles of Fe^{4+}O_6 octahedra and oxygen deficiency in the OER catalysis may be revealed by investigating the catalytic behaviors of these ferrites. Besides activity, the durability of Fe-based OER electrocatalysts also needs to be improved, as the deactivation of Fe-based perovskites during OER in alkaline media has been noted by several reports.^[11-13] By varying the A-site element in AFeO_3 perovskite oxides and examining the resulting stability, the intrinsic factors that result in the instability of Fe-based catalytic materials may be identified.

Figure 7.2 XRD patterns of as-prepared $\text{BaFeO}_{3-\delta}$, $\text{Ba}_{0.8}\text{Sr}_{0.2}\text{FeO}_{3-\delta}$, and $\text{SrFeO}_{3-\delta}$ perovskite oxides.

It has been reported that Fe species in the alkaline electrolyte can enhance the OER activity of Co/Ni (oxy)hydroxide.^[14-15] As has been confirmed in Chapter 6, the cobalt-based oxyhydroxide *in situ* derived from $\text{SrCoO}_{3-\delta}$ perovskite is also subjected to the influence of electrolyte Fe levels. Hence, it can be expected that the activity of Ni (oxy)hydroxide *in situ* formed on nickelate perovskites can be promoted by potential cycling in Fe^{3+} -spiked

electrolyte. Hexagonal perovskite BaNiO_3 (BN), which can be facily prepared by a sol-gel method, has been reported to undergo surface amorphization upon water oxidation.^[16] It can be expected that the surface of BaNiO_3 transforms into Ni-based (oxy)hydroxide during OER along with A-site cation leaching, as what has been found for $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF).^[5] Figure 7.3 displays the XRD pattern of as-prepared BaNiO_3 hexagonal perovskite. As demonstrated in Figure 7.4, after testing in Fe-free electrolyte for 100 cycles, the OER currents and the Ni redox behaviors of BaNiO_3 approached stable states, indicating that the reconstruction-derived surface was relatively steadied. Then, the self-reconstructed BaNiO_3 was immediately testing in Fe^{3+} -spiked KOH electrolyte. As shown in Figure 7.5, under the positive influence of $\text{Fe}^{3+}_{\text{spiked}}$, the activity of BaNiO_3 perovskite is increased by ~ 22 fold and the Tafel slope is decreased by $\sim 60 \text{ mV dec}^{-1}$, which meets the expectation. It is noteworthy that the promoting effect of Fe on the catalytic performance of BaNiO_3 is significantly larger than that on $\text{SrCoO}_{3-\delta}$. This agrees with previous findings that the activity increment due to Fe incorporation is often more prominent on NiO_xH_y than CoO_xH_y .^[14-15, 17]

Figure 7.3 XRD patterns of as-prepared BaNiO_3 hexagonal perovskite and the reference.

According to a recent report regarding Fe-modified MO_xH_y ($M = \text{Co}$ and Ni), OER activity is related to the amount of Fe ions dynamically stabilized on the host material MO_xH_y , which is determined by the balance between Fe dissolution and redeposition.^[17] The Fe

redeposition rate is found to be correlated with the content of Fe in the electrolyte. In this work, the equilibrium level of Fe in the electrolyte is. When the trace Fe in the electrolyte is higher than 0.1 ppm, the number of Fe sites present in the interface is suggested to be limited by the adsorption ability of the host material rather than the redeposition rate. Hence, it can be expected that enlarging the surface area accessible to the electrolyte is beneficial for increasing the number of Fe sites dynamically stabilized on the host. However, due to the calcination temperature as high as 850°, BaNiO₃ particles synthesized by the sol-gel method are micrometer-sized, as evidenced by their 0.9 m²g⁻¹ Brunauer-Emmett-Teller (BET) specific surface area. It can be expected that reducing the particle size of BaNiO₃ perovskite to nanometer-scale allows more Ni sites exposed under OER conditions and larger surface area accessible to the electrolyte, yielding a perfect matrix for Fe³⁺_{spiked} in the electrolyte to adsorb onto and thus collectively forming a highly efficient catalytic system. Schmidt's group has proposed a flame spray (FS) method to prepare nanometer-sized perovskite oxide particles and successively synthesized ultra-small BSCF, La_{0.2}Sr_{0.8}CoO_{3-δ}, and Pr_{0.5}Ba_{0.5}CoO_{3-δ} perovskite nanoparticles by this means.^[18-19] Hence, it is recommended to synthesize nanosized BaNiO₃ particles by novel approaches, such as the FS method, to prepare a precatalyst that can evolve into an idealized host under OER conditions for dynamically stable Fe sites.

Figure 7.4 Cyclic voltammograms of BaNiO₃ perovskite in 0.1 M KOH electrolyte.

Figure 7.5 Tafel plots of BaNiO₃ perovskite in Fe-free and Fe³⁺-spiked KOH solutions.

In addition, heteroatom doping is usually a practical approach to increase the catalytic performance of TM oxides, and there are many reports about the synergic effect between transition metals.^[20-21] However, due to the restriction of synthesis methods, heteroatom doping is not always a practical way. Besides, the content of dopants may result in a difference in the catalytic performance, and hence considerable effort is required to find out the optimal doping amount. Therefore, a more facile and more efficient approach to utilize the synergic effect between transition metals is necessary. Given the above findings that the catalyst surface can dynamically interact with the electrolyte environment during OER, it is recommended that the spiking of synergic ions into the electrolyte may open a promising and efficient way to utilize the synergic effect between transition metals for activity enhancement.

7.3 Conclusion

The three hypotheses in this thesis have been adequately validated by experimental design, and the outcomes are reflected in the original hypothesis. The hypothesis concerning the role of geometric tilting in the OER catalytic performance of FeO₆ octahedron is proven by setting FeO₆ octahedra into a series of pure Fe-based oxides. The OER catalytic

activities of these ferrites are negatively related to the tilting degree of FeO_6 octahedra, which is rationalized through the Fe-O covalency. The direct correlation identified between the $\text{TM}_{\text{Oh}}\text{-O}$ hybridization degree and the composition-dependent OER activity of normal spinel $\text{ZnFe}_{2-x}\text{Cr}_x\text{O}_4$ ($x = 0 - 2$) evidences the hypothesis that the OER catalytic performance of spinel oxides can be governed by an electronic parameter of TM_{Oh} cations. The immediately distinct increase in the OER activity of self-reconstructed $\text{SrCoO}_{3-\delta}$ perovskite upon cycling in Fe^{3+} -spiked KOH electrolyte validates the hypothesis that the *in situ* formed surface species is the real active phase on self-reconstructed perovskite oxides.

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