MnO₆ octahedron in transition metal oxide for electrochemical energy conversion and storage

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NANYANG
TECHNOLOGICAL
UNIVERSITY

**MnO₆ OCTAHEDRON IN TRANSITION METAL
OXIDE FOR ELECTROCHEMICAL ENERGY
CONVERSION AND STORAGE**

WEI CHAO

SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

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CONVERSION AND STORAGE**

WEI CHAO

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

2016

Statement of Originality

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

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Abstract

Climate changes and the scarcity of fossil fuels have stimulated extensive studies on electrochemical devices for energy storage and conversion. Among various earth-abundant electrode materials, MnO_6 octahedron-based metal oxides have emerged as one of the most promising candidates, and thus requiring a better understanding on the relationship between the physical properties of MnO_6 octahedron and the corresponding electrochemical performance. A better understanding of Mn gives benefits to rational design of electrode materials for supercapacitor and oxygen electrocatalysis devices. This dissertation firstly investigates the influence of particle size on ORR (oxygen reduction reaction). Without tuning the specific activity, a high mass activity is achieved by nano-engineering MnO_6 octahedron into uniform-sized MnO_2 nanoflakes, which provides more electrochemical-active sites. Second, the uniform-sized MnO_2 nanoflakes serve as the standard active component of pseudocapacitor to understand the interplay between MnO_6 octahedrons and various carbon supports, i.e., AB (acetylene black), rGO (reduced-graphene oxide) and CNTs (carbon nanotubes). MnO_6 octahedrons supported on rGO can be fully utilized at slow rate and gives the highest capacitance; while, CNTs and AB displays better energy storage capability at high scan rates. Third, MnO_6 octahedron is put in the crystal environment of spinel oxides to reveal the role of MnO_6 octahedron in pseudocapacitive performance. By employing spinel ferrites XFe_2O_4 ($\text{X} = \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}$) as the model material, we demonstrate the superior ability of MnO_6 octahedron to change valence state and thus MnFe_2O_4 gives the highest pseudocapacitance. Forth, efforts are devoted to unveil the role of MnO_6 octahedron in oxygen electrocatalysis. The electronic structure of MnCo_2O_4 is tuned via varying the heat treatment temperature and the resulting ORR and OER (oxygen evolution reaction) performance are correlated with valence state and cation distribution. It is proven that the valence state of Mn in MnO_6 octahedron and the fraction of Mn that occupies in the octahedral site govern the ORR/OER activity. The universality of the as-revealed descriptor of MnCo_2O_4 is further validated by extending it to describe the ORR/OER at transition metal spinels.

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Figure 8.6 The XRD patterns of γ - MnO_2 and the standard pattern.

Figure 8.7 The XRD patterns of Mn_2O_3 and the standard pattern.

Figure 8.8 The XRD patterns of δ - MnO_2 and the standard pattern.

Figure 8.9 The XRD patterns of Mn_3O_4 and the standard pattern.

Figure 8.10 The XRD patterns of λ - MnO_2 , LiMn_2O_4 and the standard pattern.

Abbreviations

ORR	Oxygen Reduction Reaction
OER	Oxygen Evolution Reaction
BET	Brunauer-Emmett-Teller
TEM	Transmission Electron Microscopy
XRD	X-ray Diffraction
XAS	X-ray Absorption Spectroscopy
XANES	X-ray Absorption Near Edge Structure
EXAFS	Extended X-Ray Absorption Fine Structure

Chapter 1

Introduction

Exploring efficient electrode materials have become the major challenge for developing renewable and sustainable energy technologies such as fuel cells, lithium ion batteries, metal air batteries, supercapacitors and water electrolyzers. Chapter 1 presents the irreplaceable significance of MnO_6 octahedral configuration in the energy application and calls for a better understanding of the relation between the physical properties of MnO_6 octahedron and the electrochemical performance. The rationale of investigating the MnO_6 octahedron for supercapacitor and oxygen electrocatalysis is provided and the unsolved problems in this area are further analyzed in depth.

1.1 Hypothesis

The fast depletion of fossil fuels and the climate changes led by the increasing CO₂ emission have stimulated the development of sustainable and renewable energy resources such as solar, wind, tide, etc.¹ Unfortunately, these clean energy resources are not always available on demand and therefore need to be converted and stored in the forms of chemical bonds. The electrochemical devices, such as water electrolyzers,^{2,3} fuel cells,^{4,5} supercapacitors,^{6,7} lithium-ion batteries,^{5,8} metal-air batteries^{9,10} and CO₂ reduction^{11,12} are acting as the leading role in energy storage and conversion. The major scientific challenge is to invent efficient and low-cost electrode materials to improve the efficiency of these electrochemical devices.

Notable interest has been drawn to the manganese family, especially manganese-based oxides, which are top electrode materials for various energy applications. For example, LaMnO_{3+δ} perovskite show comparable ORR (oxygen reduction reaction, the cathode half reaction of fuel cell) activity with the state-of-art Pt/C catalyst.¹³ The capacity of Mn-substituted LiCoO₂ in lithium-ion batteries exceeds the theoretical values in the case of Li-rich NMC.¹⁴ The α-MnO₂ has superior specific capacitance in supercapacitors and possesses excellent capacity for lithium-air batteries.¹⁵⁻¹⁷ Manganese complexes were discovered as a promising substitute for ruthenium in CO₂ reduction.¹⁸ The activity of electrodeposited MnO_x is approaching to the state-of-art IrO₂ for OER (oxygen evolution reaction, the anode half reaction of water electrolyzers).¹⁹

If we examine the whole family of manganese-based oxides for renewable energy application, it is found that they share one common characteristic: the basic unit that is in charge of energy storage and conversion is the MnO₆ octahedron – a Mn cation with six-fold oxygen coordination. Interestingly, the best OER material in nature - oxygen evolving complex (OEC) in PSII (photosystem II) - is also built upon the Mn octahedral coordination.^{2,20,21} The active sites are 4 Mn cations and each of them is under an octahedral coordination with six ligands (oxygen and nitrogen).^{20,21} The consistency among the above set of evidences is definitely not a coincidence. It raises our awareness that the dominating role of manganese in energy community must originate from this special MnO₆ configuration and necessitates the investigation on the beautiful science

underlying the MnO_6 octahedron. The rational design of electrode materials for electrochemical devices can be guided by a better understanding of the relationship between the physical-properties of MnO_6 octahedron and the electrochemical performance.

This dissertation presents a series of systematic studies on the structure-performance relation of the MnO_6 octahedron for pseudocapacitor and oxygen electrocatalysis (ORR and OER). We put these 3 electrochemical devices together because of their essentially similar mechanisms of energy storage/conversion. First, they all rely on the surface redox reaction, where only the atoms at/near the surface contribute.²²⁻²⁴ In ORR/OER, the catalyst surface adsorbs the reaction intermediates (O_2^* , OOH^* , O^* , OH^*), which are further transformed into the final products by accepting or donating electrons.² The pseudocapacitor stores energy by taking advantage of the movement of charge carriers such as H^+ , Li^+ , Na^+ and K^+ , which accommodate at the surface of electrode material during charge process and leave from the electrode material during discharge.^{23,25} The lithium ion batteries are also based on the movement of Li^+ , but it is a bulky process where the Li^+ penetrates deeply into the electrode material. Second, the operating potentials for pseudocapacitor and oxygen electrocatalysis are quite similar. In aqueous electrolyte, the potential window for pseudocapacitor measurement is 0.6 ~ 1.5 V vs. RHE;^{17,23,25} ORR is 0.1 ~ 1.2 V vs. RHE^{26,27} and OER is 1 ~ 1.7 V vs. RHE.^{28,29} In contrast, because lithium ion battery reaction takes place in organic electrolyte, the potential window is normally larger than 1 V.^{8,14} Third, because these 3 technologies are based on the surface redox reactions and they are operated under a moderate potential window, the electrode materials normally does not undergo apparent structural changes.^{22,30,31} As a result of the bulky Li^+ diffusion in the lithium ion battery, the original morphology cracks and cannot remain unchanged.³² CO_2 reduction is a surface process but it occurs at a very strong reducing potential,¹¹ where most material would be reduced to metallic state. Moreover, metal-air batteries are associated with structural changes because they are involved with the coverage and decomposition of Li oxides on the surface of electrode material.³³

Tremendous efforts have been devoted to investigate the pseudocapacitor and oxygen electrocatalysis on MnO_6 -based electrode materials.^{34,35} However, most existing studies

focus on discovering new electrode materials and the development strategy has been mostly empirical. The fundamental understanding of the physical origin governing electrochemical performance of MnO_6 octahedron still remains insufficient.

MnO_2 nanomaterials with various morphologies have been intensively studied for supercapacitors and oxygen electrocatalysis.^{34,35} Nevertheless, the existing MnO_2 nanoparticles possess big sizes, mostly larger than 100 nm. The successful synthesis of free-standing uniform-sized MnO_2 nanoparticles which are sufficiently small should provide more electrochemistry insights. Polymerizing MnO_6 octahedron monomers into small nanoparticles is expected to give more active sites and thus efficiently lowering the catalyst loading in ORR. The challenge of material synthesis can be overcome by mimicking the classic shape control of gold nanoparticles, where the positive-charged CTA^+ (the polymer chain of cetrimonium bromide) wraps the negative-charged AuCl_4^- into micelles and consequently morphology control is achieved.³⁶ A similar soft template mechanism can be borrowed for MnO_2 synthesis, where the CTA^+ wraps the MnO_4^- to form micelles.

Considering MnO_2 is non-conductive, the conductive additives are indispensable to the smooth charge transport. It is thus necessary to understand the interplay between the stacking of MnO_6 octahedrons and the conductive support such as various carbon materials. Although the traditional MnO_2 /carbon composites exhibit enhanced pseudocapacitance,^{24,37} it is difficult to estimate the real contribution of metal oxides and thus the influence of various conductive supports on interface electron transport cannot be easily revealed. The flexibility of studying the effect of different conductive supports on interface charge transfer could be brought by the successful synthesis of uniform-sized free-standing MnO_2 nanoparticles. It is proposed the different morphology of carbon support should influence the interface charge transfer.

The role of MnO_6 octahedron in manganese oxides (MnO_x) and perovskites have been quite clear because there is no site occupation argument.^{13,26,29,38,39} The MnO_x is purely built upon MnO_6 octahedrons and the octahedral site of perovskites unambiguously acts as the active site.^{13,26,29,38,39} In contrast, the character of MnO_6 octahedron still remains as a puzzle in spinel oxides, where metal cations can occupy either the tetrahedral or octahedral site. Despite numerous studies have explored the supercapacitor and oxygen

electrocatalysis on spinel oxides, most existing reports are based on the mass activity (normalized to the mass loading of active material) discussion, which cannot reflect the real mechanism underlying the surface-sensitive electrochemical process. Unveiling the mysteries of MnO_6 octahedron in spinels has been hindered by the lack of systematic studies base on the intrinsic specific activity (normalized to the real surface area of electrode materials) analysis. It is believed that the different cation distribution in spinel structure can result in different electrochemical performance. With different metal cations to substitute Fe_3O_4 , the comparison of XFe_2O_4 ($\text{X} = \text{Fe}, \text{Mn}, \text{Co}$ and Ni) could give an opportunity to feature the advantage of Mn in electrochemical performance. EXAFS (extended X-ray absorption fine structure) is a well-published technique that is able to qualitatively tell the cation distribution and EXAFS fitting is capable of quantifying the metal cation occupation.^{40,41} With the help of EXAFS, fixing the nominal formula as MnFe_2O_4 and tuning the cation distribution via heat treatment allow us to differentiate the electrochemical contribution from MnO_4 tetrahedron and MnO_6 octahedron.

The role of MnO_6 octahedron in spinels can be further demonstrated by fixing the nominal formula as MnCo_2O_4 and tuning the electronic structure via controlling the heat treatment temperature. With the aid of XAS (X-ray absorption spectroscopy), the physical properties (e.g., valence state and cation distribution) could be correlated with the electrochemical performance. It is assumed that the valence state of the Mn in MnO_6 octahedron and the fraction of Mn that occupies in the octahedral site simultaneously govern the ORR/OER activity.

1.2 Objectives and Scope

The overall objective of this dissertation is to experimentally probe the relationship between the physical properties of MnO_6 octahedron-based electrode materials and the electrochemical performance, i.e., pseudocapacitor and oxygen electrocatalysis. First, we take advantage of the nanotechnology to control the stacking of MnO_6 octahedrons into small MnO_2 nanoparticles (less than 100 nm) and examine the resulting ORR performance which originates from the size effect. Subsequently, the small MnO_2 nanoparticles are physically mixed with various carbon supports (acetylene black,

reduced-graphene oxide and carbon nanotube) by ultrasonication to give insights of the influence of carbon supports on pseudocapacitive behavior. Third, the MnO_6 octahedron is put in the crystal environment of spinel oxides, where the coexistence of tetrahedral and octahedral sites allows the formation of a large number of oxides. We synthesize various spinel ferrites XFe_2O_4 ($\text{X} = \text{Fe}, \text{Mn}, \text{Co}$ and Ni) and study the influence of substitution on pseudocapacitive behavior. The in-situ XAS technique is employed to reveal the physical origin of the different pseudocapacitive behavior as a function of substitution element. Considering the metal cation occupation is sensitive to the heat treatment temperature, cation distribution of MnFe_2O_4 is further tuned by varying the synthesis temperature and the resulting occupation is quantified by EXAFS fitting. The comparison between MnO_4 tetrahedron and MnO_6 octahedron is made by investigating the trend of MnFe_2O_4 pseudocapacitance as a function of heat treatment temperature. Fourth, we aim to reveal the role of MnO_6 octahedron in ORR/OER. The electronic structure of MnCo_2O_4 is tuned by varying the synthesis temperature. The resulting valence state and cation distribution are characterized by XAS and related to the ORR/OER performance.

1.3 Dissertation Overview

The thesis addresses the relationship between the physical properties of MnO_6 octahedron-based transition metal oxides and the electrochemical performance, i.e., pseudocapacitor and oxygen electrocatalysis.

Chapter 1 provides the significance of MnO_6 octahedron in energy conversion and storage, a rationale for the research on pseudocapacitor and oxygen electrocatalysis and outlines the goals and scope.

Chapter 2 reviews the literature concerning the development of MnO_6 octahedron-based transition metal oxides as renewable energy materials and the state-of-art understanding of the physical property that governs the performance of pseudocapacitor and oxygen electrocatalysis.

Chapter 3 discusses the principles underlying the experiment design and validates the experimental methodology employed in this dissertation. It covers the synthesis of electrode material, electrode fabrication, electrochemical characterization, analysis method of electrochemical data and material characterization.

Chapter 4 is devoted to the synthesis of uniform-sized MnO_2 nanoparticle which is sufficiently small and its application for ORR. The hypothesis on the size effect will be presented by correlating the mass activity and specific activity with the stacking size of MnO_6 octahedrons.

Chapter 5 elaborates the interplay between MnO_6 octahedrons and various carbon supports (acetylene black, reduced-graphene oxide and carbon nanotube). The hypothesis that the different carbon supports affect the interface charge transfer will be tested by screening the pseudocapacitive behavior of MnO_2/C (C = carbon).

Chapter 6 focuses on the pseudocapacitive performance of spinel ferrites XFe_2O_4 (X = Fe, Mn, Co and Ni). The concept that X (the substituted element) and its occupation are instrumental to the pseudocapacitance will be verified and the physical origin will be explored by in-situ XAS technique and EXAFS fitting.

Chapter 7 elaborates the role of MnO_6 octahedron in ORR/OER. By fixing the nominal formula as MnCo_2O_4 and tuning the electronic structure via heat treatment, the activity descriptor for MnCo_2O_4 spinel oxides will be established. Its universal applicability will be demonstrated by further extending to explain the ORR/OER activity of all transition metal spinels.

Chapter 8 draws together the threads of this thesis and discusses the extent to which the hypothesis is proven. Recommended future work is provided and the preliminary results are presented.

1.4 Findings and Outcomes/Originality

This research led to several novel outcomes by:

1. Correlating the stacking size of MnO_6 octahedrons with ORR mass activity and specific activity;
2. Establishing the relationship between the pseudocapacitive behavior of MnO_6 octahedron-based oxide and different carbon supports;
3. Elucidating the physical origin of different pseudocapacitive behavior brought by various element substitution in spinel ferrites XFe_2O_4 ($\text{X} = \text{Fe}, \text{Mn}, \text{Co}$ and Ni);
4. Comparing the pseudocapacitive performance of MnO_4 tetrahedron versus MnO_6 octahedron and consolidating the important role of MnO_6 octahedron in energy storage;
5. Demonstrating that the different ORR/OER behavior of MnCo_2O_4 spinel oxides originates from the physical property of MnO_6 octahedron;
6. Developing a universal descriptor to describe the ORR/OER activity of transition metal spinel oxides.

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Chapter 2

Literature Review

The scarcity of fossil fuels and climate changes has stimulated extensive studies on electrochemical devices for energy storage and conversion. Among various earth-abundant electrode materials, manganese (Mn) -based metal oxides have emerged as one of the most promising candidates, and thus requires better understanding on the relationship between the physical properties of Mn and the corresponding electrochemical performance. In this Review, we combine supercapacitors and oxygen electrocatalysis (ORR and OER) due to the synergy between their energy storage/conversion mechanism: both rely on the surface-sensitive redox reactions. A better understanding of Mn gives benefits to rational design of electrode materials for supercapacitor and oxygen electrocatalysis devices.

2.1 The importance of MnO_6 octahedron in energy storage and conversion

The life of human beings has been relying on fossil fuels for centuries. The fast depletion of petroleum resources and the climate change resulting from the increasing CO_2 emission urgently require the development of sustainable and renewable energy production from solar, wind, tide, etc.^{1,2} Because these renewable resources are not always available on demand, energy needs to be converted and stored in the forms of chemical bonds via the electrochemical devices,¹ such as water electrolyzers,^{1,3} fuel cells,^{4,5} supercapacitors,^{6,7} lithium-ion batteries,^{8,9} metal-air batteries,^{8,10} CO_2 reduction,^{11,12} etc. One of the major challenges on these electrochemical devices is to invent efficient and low-cost electrode materials for use.

Figure 2.1 Monetary (\$/g) of Pt, Ir, Ru, Mn and Co. Extracted from Mineral Commodity Summaries 2016 with permission (ref. 13).

Throughout the history of electrochemical devices, the best electrode materials with top performance usually contain scarce elements, e.g., Pt (~35 \$/g, Figure 2.1)¹³ for fuel cells and hydrogen production, Ir (~17 \$/g)¹³ and Ru (~2 \$/g)¹³ for supercapacitors and OER (oxygen evolution reaction). Electrode materials with particular promise for large-scale application fall within the family of Mn (~0.000004 \$/g)-based oxides¹³, where the basic building block is MnO_6 octahedron – Mn cation with six-fold oxygen coordination. For example, $\text{LaMnO}_{3+\delta}$ ^{14,15} and $\alpha\text{-MnO}_2$ ¹⁶ show comparable ORR (oxygen reduction

reaction) activity with commercial Pt/C. The Mn-substituted LiCoO_2 in lithium-ion batteries displays high capacity (200 mAh/g), even can exceed the theoretical values in the case of Li-rich NMC.⁹ $\alpha\text{-MnO}_2$ has superior energy storage capability in supercapacitors^{17,18} and Li-air batteries.^{19,20} The electrodeposited MnO_x exhibits outstanding bi-functional activities in both ORR and OER.²¹

Figure 2.2 (a) Turnover frequencies (TOF) of state-of-art catalysts for oxygen evolution reaction at 0.3 V overpotential. Reproduced from ref. 22 with permission by Royal Society of Chemistry. (b) The X-ray crystallographic structure of OEC in PSII (oxygen evolving complex in photosystem II). Reproduced from ref. 24 with permission by Nature Publishing Group.

Since Mn is present in the form of MnO_6 octahedrons within the Mn-based oxides as mentioned, the excellent performance should originate from this particular coordination configuration. This is in concert with the best catalyst (Figure 2.2a) given by nature: OEC in PSII (oxygen evolving complex in photosystem II)²² feeds this planet with O_2 by the four Mn cations under quasi-spherical octahedral coordination (Figure 2.2b).^{23,24} It should be noted that the TOF of metal oxide and Co-Pi (Figure 2.2a) were estimated from the specific activity; and the TOF of PSII was quantified as the reciprocal of the total duration for one catalytic turnover (~ 2.73 ms) divided by 4 Mn atoms.²² These findings call for revealing the beautiful science underlying the irreplaceable role of MnO_6 octahedrons in artificial electrochemical devices, but also for better understanding catalysis in nature. In this Review, we discuss the state-of-the-art relationship between the physical properties of MnO_6 octahedrons and the performance in supercapacitors and oxygen electrocatalysis (ORR and OER). We focus on these two electrochemical technologies because of their similar energy storage/conversion mechanism: both of them are based on the surface-sensitive redox reactions; only the atoms at/near the surface are active.²⁵ A better understanding of MnO_6 octahedrons brings benefits to better design of electrode materials for supercapacitor and oxygen electrocatalysis devices.

2.2 Specific activity versus mass activity

To estimate the electrochemical activity, the current density is usually normalized to the mass loading of the electrode material, giving the so-called mass activity. For the bulky chemistry process such as lithium-ion battery reactions, where the Li^+ diffuses deeply into the material and the original micro-structure cracks with charge/discharge cycles,²⁵ mass activity serves as a reasonable parameter for comparing performance of different materials. However, for the surface chemistry process such as supercapacitor and electrochemical catalysis, where the reaction occurs at/near the surface and the electrode materials normally possess better structural stability, mass activity cannot represent the intrinsic activity.²⁶ Since the interior atoms beneath the surface are not contributing to the charge storage process, we will compare the specific activity, which is normalized to the real surface area of electrode material. The specific activity is equivalent to the intrinsic

performance, because surface area reflects the real number of active sites. With the purpose of telling the intrinsic difference among various electrode materials, it is critical to use specific activity. The mass activity – largely determined by the particle size – is of important engineering meaning of estimating the practical performance. The optimum electrode material should have both high specific activity and mass activity.

2.3 Rational design for supercapacitor electrode material

Figure 2.3 Cyclic voltammetry (CV) curves. The schematic illustration of the energy storage mechanism of MnO_2 in 0.1 M K_2SO_4 electrolyte. Reproduced from ref. 27 with permission by Nature Publishing Group.

The capability of changing valence state. Supercapacitors store energy via fast, reversible redox reactions at/near the surface.^{25,27} All the metal oxides (MnO_2 , Fe_3O_4 , Co_3O_4 , RuO_2 , etc.) exhibit this pseudocapacitive behavior.²⁷ The EDLC (electrochemical double layer capacitor), which stores energy through ion adsorption at the surface, also takes place on metal oxides.²⁸ But the intrinsic capacitance of EDLC is negligible compared with the pseudocapacitance, which attracts more extensive studies. Because the specific activity depends on the redox reaction, the ideal electrode material for pseudocapacitor should be capable of changing its valence state under the operated potential window. To date, the best material is RuO_2 ,²⁹ a rutile crystal where the basic

unit is RuO_6 octahedron. It has three available valence states within the potential window of 1.2 V in acid electrolyte. The Ru valence states can vary between (II) and (IV), and thus RuO_2 gives high specific capacitance.²⁹ Due to the high-cost of Ru (~2 \$/g),¹³ earth-abundant oxides of V, Mn, Fe, Co and Ni are considered as alternative candidates and have been extensively investigated.³⁰⁻³³ Especially MnO_2 , constructed by MnO_6 octahedrons, is distinguished as the best alternative solution. The charge storage mechanism of MnO_2 is mainly based on the surface redox reaction between Mn (III) and Mn (IV) (as shown in Figure 2.3).^{27,34,35} Because Mn only has two accessible valence states within the typical potential window (~1.0 V) in aqueous electrolyte, the specific activity of MnO_2 is inferior to RuO_2 . However, the energy storage capability of Mn can be greatly upgraded by other strategies of material design, for example, nanostructuring MnO_2 ⁶ and employing organic electrolyte.^{36,37} It should be noted that the initial Mn valence state in oxides is considered not to be influential to supercapacitor performance. The successive multiple redox reactions lead to the pseudocapacitive charge storage mechanism.³⁵ With CV (cyclic voltammetry) scans, Mn is subjected to cycles of oxidation and reduction, and meanwhile the charge/discharge takes place. It does not matter what the starting point (the initial valence state) of Mn is; as long as the CV potential window covers the Mn redox potential, Mn will be oxidized/reduced.

Crystal channels for accommodation of charge carriers. As indicated in Figure 2.3, the redox reaction always involves cation (H^+ , Li^+ , Na^+ , K^+) accommodation inside the electrode material and the consequent lattice expansion.²⁷ This characteristic requires the electrode material not only to be good at changing the valence state, but also to have inner void space for charge carrier insertion. Although the valence state of MnO_6 is restricted between 3^+ and 4^+ , it is possible to tune the specific activity by tuning the inner empty space. With different arrangement of MnO_6 octahedrons, the formation of 8 polymorphs has been reported (Figure 2.4).³⁸ Despite of the same ability to change valence state, the larger channel size gives higher specific capacitance (Figure 2.4i).¹⁷ For example, although $\gamma\text{-MnO}_2$ (with 2×2 tunnel size) has higher surface area than $\alpha\text{-MnO}_2$ (with 2×2 tunnel size) and $\delta\text{-MnO}_2$ (with two-dimensional interlayer space), its mass capacitance is 1 time lower than $\alpha\text{-MnO}_2$ and $\delta\text{-MnO}_2$. $\beta\text{-MnO}_2$ and $\lambda\text{-MnO}_2$ crystals are

too densely packed that the specific capacitances are very low; only double-layer capacitance contribute. The lack of intrinsic activity (normalized to surface area) analysis hinders the more accurate comparison, but the positive impact of larger channel size on pseudocapacitance is still apparently observed. This elucidates the origin that most of the manganese oxides that possess superior supercapacitor performance are normally in the forms of α -MnO₂ and δ -MnO₂,^{39,40} because of their large inner void space for charge carrier accommodation.

Figure 2.4 Illustration of 8 polymorphs of manganese oxides with different MnO₆ octahedron arrangement: (a) β -MnO₂, (b) γ -MnO₂, (c) α -MnO₂, (d) δ -MnO₂, (e) λ -MnO₂, (f) LiMn₂O₄, (g) Mn₂O₃, (h) Mn₃O₄. (i) The mass capacitance of α -MnO₂ (17.29 m²/g for α -MnO₂; 123.39 m²/g for m- α -MnO₂), β -MnO₂ (nanorod, 50 nm in diameter and several micrometers in length), γ -MnO₂ (31.56 m²/g), δ -MnO₂ (20.93 m²/g) and λ -MnO₂ (5.21 m²/g) electrodes in 0.1 M Na₂SO₄. Reproduced from ref. 38 and ref. 17 with permission by American Chemical Society.

The channel size dependence demonstrates the pseudocapacitive behavior is essentially similar to battery behavior.⁴¹ Both of them store energy via charge carrier diffusion within the electrode material. The difference is how deep the charge carrier diffuses into the electrode material. Battery is bulky diffusion which drives the charge carrier for a long distance; while in pseudocapacitor, the diffusion is near the surface but not confined to the topmost layer.

Conductivity effect from carbon additives. To ensure the smooth charge transfer at the interface, electrochemical devices normally should be highly conductive. Especially for the semiconductor materials that are built by MnO_6 octahedrons, carbon additives are indispensable. With carbon addition, the CV curve of MnO_2 /carbon mixture is rectangular shape (Figure 2.5a), which is the typical characteristic of pseudocapacitive behavior.⁴² However, the CV curve of pure MnO_2 (95 %, Figure 2.5a, without carbon addition) is highly polarized and the area under the CV loop is significantly smaller than the others, indicating a much smaller capacitance.⁴² It is worth noting that from 95 % to 80 %, even a 15 % difference of carbon addition could drastically enhance the pseudocapacitance, which demonstrates that the conductivity effect is immense. The distorted shape of CV curve and a lower specific activity indicate the high resistance changes the energy storage mechanism and limits the utilization of active components.

Figure 2.5 (a) CV curves as a function of weight percentage of $\alpha\text{-MnO}_2$. 5 % of the electrode composition is PTFE binder and the remainder is carbon additive. (b) CV curves as a function of scanning rate on LbL-MWNT/ MnO_2 (layer-by-layer multiwalled nanotube/ MnO_2) electrode. The MnO_2 has a 200 nm thickness, prepared by dipping in MnO_4^- for 30 min. Reproduced from ref. 42 and ref. 44 with permission by American Chemical Society.

To further improve the electron transfer between MnO_2 and carbon, MnO_2 nanoparticles have been grown onto carbon supports to maximize their contact. Although the enhanced mass capacitances resulting from the synergetic effect between MnO_2 and carbon materials (carbon nanotubes, graphene, etc.) have been reported,^{18,43} we believe the

intrinsic capacitance of MnO_2 cannot be influenced by carbon support. Neither the ability of changing the valence state nor the tunnel size could possibly be altered by mixing with carbon. The role of carbon is considered to be twofold. First, it improves conductivity and as a result, capacitance retention could be greatly enhanced. Growing a thin layer of MnO_2 on carbon nanotube enables the CV curve to be standard rectangular at a very high scan rate of 1000 mV/s (Figure 2.5b).⁴⁴ From 10 mV/s to 1000 mV/s, the capacitance loss is only ~44 %, which indicates the electrode material has very smooth charge transfer and is capable of adapting to a wide range of current densities. Second, carbon acts as supporting material to well separate each metal oxide particle, thus avoiding aggregation and taking the fullest advantage of metal oxides. This explains the enhanced mass activity in metal oxide/carbon composites.

Mass activity as a function of specific surface area. While the pseudocapacitive specific activity of MnO_6 octahedrons is governed by the ability of changing valence state and tunnel size, the pseudocapacitive mass activity is determined by the surface area. Higher surface area gives more active sites, thus higher mass activity. Boosted by the development of nanotechnology, mass capacitance has been greatly enhanced in the past decades. By selecting the right MnO_2 crystal structure and using advanced nanotechnology to mix nano-sized MnO_2 with conductive support, the mass capacitance of ~940 F/g has been achieved.⁶ For the detailed discussion on the nano-structured materials for supercapacitor application, please refer to the nicely published works.^{6,7,45}

2.4 Rational design for oxygen electrocatalysts

The energy storage and conversion mechanism of oxygen electrocatalysis is an anionic redox process (O_2 gas $\leftrightarrow$ oxygen anion) that takes place at the surface of catalysts.⁹ Energy can be stored in the O-O bond by OER and the breakage of O-O bond converts the chemical energy to electricity energy during ORR (Figure 2.6a).²² Due to the sluggish kinetics of oxygen electrocatalysis, it dominates the majority of the energy loss in water electrolyzers and fuel cells (Figure 2.6b), and thereby has been extensively studied.²² To reduce the energy loss, the key challenge is the pursuit of efficient and low-cost catalysts for ORR/OER. Catalysts can be rationally designed by identifying the activity

descriptor,^{46,47} because a better understanding of the property-activity relationship enables us to design catalysts of higher activity.⁴⁸ When a descriptor is successfully identified, the plot of activity as a function of descriptor normally shows a volcano-shaped trend (Figure 2.7).⁴⁶ This is the basic concept of Sabatier principle, where the optimum catalyst should bind the atoms or molecules with an intermediate strength. Too strong binding strength (elementary step 1, Figure 2.7) hinders the desorption of reaction products; too weak binding strength (elementary step 2, Figure 2.7) cannot activate the reactants.

Figure 2.6 (a) Schematic illustration of oxygen and hydrogen cycle for energy storage and conversion. (b) Schematic illustration of overpotentials caused by oxygen and hydrogen electrodes. Blue color lines are for water electrolyzer and orange color lines are for fuel cell. Reproduced from ref. 22 with permission by Royal Society of Chemistry.

Figure 2.7 Schematic illustration of the qualitative Sabatier principle. The descriptor, which governs the binding strength with reaction intermediates, is identified by a volcano trend with activity (net rate). Reproduced from ref. 46 with permission by AAAS.

Since the year of 1977, efforts have been paid to correlate oxygen electrocatalysis activity with several parameters: the potential where metal cations of higher oxidation state form, the enthalpy of transition from a lower to a higher valence state, metal-hydroxide bonding strength, etc.²² However, none has achieved success as great as the molecular orbital theory, which relates the binding strength of reaction intermediates with the filling state of antibonding orbital.⁴⁹

Figure 2.8 Schematic illustrations of energy levels and electron assignments of orbitals. (a) N_2 , (b) O_2 and (c) " He_2 ". Reproduced from ref. 49 with permission by Wiley and Sons.

Molecular orbital theory was initially applied to describe the strength of molecular bond by estimating the electron filling of the antibonding orbital.⁴⁹ For example, when two N atoms are put together (Figure 2.8a), the antibonding orbitals are empty, and thus the resulting N-N bond of N_2 gas is strong.⁴⁹ For He-He interaction (Figure 2.8c), because the antibonding orbitals are fully filled with electrons, the "He-He bond" is so weak that the chemical formula of helium gas is He rather than He_2 .⁴⁹ The intermediate state is O_2 gas (Figure 2.8b), where the antibonding is half-filled with electrons.⁴⁹ As a result, the O-O bond is neither too strong nor too weak. The electron occupation concept was subsequently employed in catalysis science (especially ORR), and consequently stimulated the discovery of d-band center theory,^{50,51} which is one of the most successful theoretical model for ORR at metal catalyst surface.

The basic concept of d-band center theory is to correlate the position of metal d-band with the antibonding filling of metal-oxygen bond. With oxygen atom approaching the metal surface, the coupling between O 2p and metal d orbitals generates the bonding and antibonding states (Figure 2.9).⁵⁰ The filling of the antibonding is determined by its

energy position (relative to Fermi level), which can be tuned by shifting the position of metal d band. If the centroid of metal d band locates far away from the Fermi level (for example, Au), the energy position of antibonding state would be low and thus the resulting antibonding filling tends to be full.⁵⁰ Therefore, the reason for the low activity of Au is that it binds oxygenated species too weakly.⁵ If the metal d-band center is high (for example, Fe), the antibonding state is close to the Fermi level. As a result, the antibonding occupancy would be empty and the problem of Fe is that it binds oxygen too strongly.^{5,50} The ORR activity can be optimized by searching for a metal with an intermediate d-band center: neither too high nor too low.^{5,50}

Figure 2.9 Schematic illustrations of the interaction between an adsorbate (oxygen atom) valence level and the delocalized s-states and localized d-states of a transition metal surface. Reproduced from ref. 50 with permission by Wiley and Sons.

The identification of d-band center as the ORR activity descriptor for metal catalyst was experimentally verified by plotting the activity of various metals as a function of the d-band center. The striking volcano-shaped trend⁵¹ is consistent with the Sabatier principle (Figure 2.10), proving the validity of the d-band center model. Up to date, Pt is the best monometallic catalyst with a medium value of d-band position (as shown in Figure 2.10).⁵¹ However, the problem of pure Pt is that its d-band center locates at a little higher position and consequently the binding strength of Pt with oxygen is a little strong. This generates the strategy of the extensive studies on Pt-based catalysts for ORR: enhancing the activity by alloying Pt with other metals to slightly shift the d-band center downwards.⁵²⁻⁵⁵

Figure 2.10 ORR kinetic current of carbon-supported metal nanoparticle at 0.80 V vs. RHE as a function of the d-band center (relative to the Fermi level). Reproduced from ref. 51 with permission by American Chemical Society.

Previous study employed polycrystalline Pt_3M ($\text{M} = \text{Ni}, \text{Co}, \text{Fe}$ and Ti) alloy films as the model catalysts to screen the ORR trend.⁵⁶ It was found that at the surface of these alloys, the first atomic layer is pure Pt, which sits on the top of PtM alloy. Due to the strain effect of the substrate atoms on the Pt overlayer, the d-band center was tuned by different element M ($\text{M} = \text{Ni}, \text{Co}, \text{Fe}$ and Ti) and correlated with the ORR activity. A volcano-shaped relationship was established between ORR activity and the d-band center (Figure 2.11).⁵⁶ It can be seen that the activity can be drastically enhanced by lowering the d-band position by ~ 0.2 eV (Pt_3Ni).⁵⁶ This is because the binding strength with oxygen is slightly weakened. However, further bringing down the position of the d-band center decreases the activity, which results from the fact that the binding strength with oxygen is so greatly weakened that the adsorption of reactant becomes the limiting step. This volcano-shaped trend was reproduced in the comparison of Pt_3M ($\text{M} = \text{Ni}, \text{Co}, \text{Fe}, \text{Ti}, \text{V}$), where the d-band center was proven to be applicable to both nanoscale surface and extended surface and universal role of d-band center was further consolidated.⁵⁴ A similar strategy was also used in the synthesis of PtCu alloy nanoparticles, where the shell is Pt and the core is PtCu.⁵³ Due to the strain effect, the d-band center of PtCu is slightly lower

than pure Pt and thus the activity of PtCu is 2~3 times higher than pure Pt.⁵³ The d-band center model not only explains the alloy effect, but also elucidates the different activity given by different exposed facets.^{52,57} The arrangement of Pt atoms on the surface varies the d-band position and therefore tunes the ORR activity. For example, the activity ranking of Pt(hkl) follows the sequence (100) < (110) < (111) in 0.1 M KOH.⁵⁷

Figure 2.11 ORR activity of polycrystalline Pt_3M ($\text{M} = \text{Ni}, \text{Co}, \text{Fe}$ and Ti) alloy films as a function of the experimentally measured d-band center (relative to Pt). The calculated activity is in black and the experimentally measured activity is in red. Reproduced from ref. 56 with permission by Wiley and Sons.

Based on the identification of d-band center as the universal activity descriptor for metal catalysts, the ORR activity has been significantly boosted by carefully selecting the alloy element and the facet surface. The d-band center model has guided the landmark discovery of the $\text{Pt}_3\text{Ni}(111)$ alloy, of which the ORR activity is ~90 times higher than the state-of-art Pt/C catalyst (Figure 2.12).⁵²

Figure 2.12 ORR activity of various Pt-based polycrystalline extended surface as a function of the experimentally measured d-band center (relative to Fermi level). Reproduced from ref. 52 with permission by AAAS.

Inspired by the great success of d-band center model for ORR at metal surface, the molecular orbital theory has subsequently been applied to describe the oxygen electrocatalysis at metal oxide surface. Principles like d-electron number,^{58,59} e_g occupancy,^{14,60} covalency of metal-oxygen bond,^{14,50} O-2p band center⁶¹ have been well established to elucidate the ORR/OER catalyzed by metal cations with six-fold oxygen coordination (metal-O₆ octahedron) in perovskite structure.

The electron occupancy of e_g orbitals. In metal-O₆ octahedral coordination, the five metal antibonding d-orbitals split into two energy levels: two e_g orbitals at the higher energy and three t_{2g} orbitals at the lower.⁶² Different from the traditional d-band principle where the whole antibonding d-orbitals act as the activity descriptor, the e_g theory only focuses on the high-lying antibonding σ^* orbitals, namely the e_g orbitals. The inspiration originates from the spatial arrangement of d-orbitals under octahedral coordination (Figure 2.13).⁶² The e_g orbitals directly point to the oxygen ligand, while the t_{2g} orbitals – low-lying antibonding π^* orbitals – have little spatial overlap with the O-2p orbital. The

strong overlap between e_g and O-2p suggests that the binding strength with reaction intermediates should be controlled by e_g , rather than t_{2g} .

Figure 2.13 (a) Spatial arrangement of oxygen ligands (red balls) in a metal-oxygen octahedral coordination with respect to five d-orbitals. (b) The energy levels of the degenerate d-orbitals in octahedral coordination.

By examining the ORR and OER at 13 various perovskites, the activity exhibits a volcano relationship with the e_g occupancy (Figure 2.14),^{14,60} which is in line with the Sabatier principle. Too low e_g occupancy ($e_g < 1$) gives too strong binding strength with oxygen, and too high e_g occupancy ($e_g > 1$) leads to too weak adsorption. The activity reaches the summit of the volcano at a moderate e_g occupancy ($e_g \approx 1$). $\text{LaMnO}_{3+\delta}$ with MnO_6 octahedron ($\text{Mn}^{3.2+}$, $t_{2g}^3 e_g^{0.8}$) is the best for ORR and $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ with CoO_6 octahedron ($\text{Co}^{2.8+}$, $t_{2g}^5 e_g^{1.2}$) has highest OER activity.^{14,60} According to the e_g principle, MnO_6 octahedron with Mn valence state of 2.8+ is hypothesized to be the ideal catalyst for OER. The e_g theory is the first application of coordination chemistry in describing binding strength. Its reliability is further experimentally demonstrated by the numerous following studies.⁶³⁻⁶⁶ Not only perovskites follow this trend, but also the activity of oxygen electrocatalysis at other metal oxides can be explained by e_g occupancy. For example, those polymorphs of manganese oxides with Mn^{3+}O_6 octahedron ($t_{2g}^3 e_g^1$), e.g., MnOOH and Mn_3O_4 , normally have good ORR/OER performance.^{26,67}

Figure 2.14 The ORR and OER activity on various perovskite catalysts in 0.1 M KOH electrolyte. The (a) ORR and (b) OER overpotentials as a function of e_g electron occupancy. Reproduced from ref. 22 with permission by Royal Society of Chemistry.

Interestingly, the crystal symmetry of the 13 perovskite oxides examined for ORR/OER (Figure 2.14) covers 3 types of space groups, i.e., Pnma, R-3c and Pm-3m. Only the Pm-3m ($\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$) is the cubic perovskite, which has spherical metal- O_6 octahedral configuration. The octahedral coordination in other perovskites is quasi-spherical: more than 1 metal-oxygen bonding length is observed, for example, the existence of 3 metal-oxygen bonding lengths in the Pnma crystals (LaCrO_3 , LaFeO_3 , etc. in Table 2.1). Despite of the inconsistent crystal structure among those perovskites, the

octahedral distortion is demonstrated not to affect the overall volcano trend; they all follow the e_g theory. The contradictory conclusion was also claimed in a recent ORR/OER study of Jahn-Teller effect^{68,69} on LaNiO_3 .⁷⁰ The strain-induced elongation and compression along the z axis of octahedral coordination is able to tune the ORR/OER activity.⁷⁰ Up to date, the effect octahedral distortion is still under debate, but all the results point out the importance the molecular picture.

Table 2.1 Summary of M-O (metal-oxygen) bonding lengths for MO_6 octahedral coordination in perovskites. The ORR/OER measurements of these perovskites were covered in previous reports.^{14,60} The M-O bonding length and coordination number are extracted by loading the CIF file and calculated with Artemis and IFEFFIT software packages.⁷¹

Sample	Space group	MO_6 octahedron		Number of M-O bonding lengths	Example of reference
		M-O bonding length (Å)	M-O bonding coordination number		
LaCrO_3	Pnma 62	1.973	6	1	Ref ⁷²
		1.980	6	1	Ref ⁷³
		1.971	6	1	Ref ⁷⁴
LaMnO_3	Pnma 62	1.955	2	3	Ref ⁷⁵
		1.961	2		
		1.981	2		
		1.958	2	3	Ref ⁷⁶
		2.017	2		
		2.116	2		
LaCoO_3	R-3c 167	1.933	6	1	Ref ⁷⁷
		1.932	6	1	Ref ⁷⁸
LaNiO_3	R-3c 167	1.933	6	1	Ref ⁷⁹
		1.935	6	1	Ref ⁸⁰
		1.893	6	1	Ref ⁸¹
LaFeO_3	Pnma 62	1.988	2	3	Ref ⁸²
		2.003	2		
		2.010	2		
		1.485	2	3	Ref ⁸³
		2.004	2		
		2.504	2		

The covalency of metal-oxygen bond. Despite of the universal applicability of e_g theory, simply counting the number of e_g electrons cannot elucidate the comparison of LaMnO_3 , LaCoO_3 and LaNiO_3 , which have the same e_g electron number but different activity (~120 mV overpotential). With taking the effect of the metal cation center into consideration, it is found that the ORR/OER activity is positively influenced by the metal-oxygen bond covalency (Figure 2.15), which could be quantified by O K-edge

XAS (X-ray absorption spectroscopy).^{14,60,84} The metal-oxygen bond covalency seems to be a secondary descriptor, but its core concept is actually in accordance with the molecular approach.

Figure 2.15 Role of metal-oxygen bond covalency on perovskites with the same e_g electron occupancy ($e_g = 1$) (a) The ORR activity as a function of metal-oxygen covalency. Reproduced from ref. 14 with permission by Nature Publishing Group. (b) The OER activity as a function of metal-oxygen covalency. Reproduced from ref. 60 with permission by AAAS.

The position of O p-band center. The effect of metal-oxygen bond covalency not only highlights the limitation of the simplified e_g molecular orbital model, but also inspires the development of band theory, a more robust activity descriptor. With the aid of DFT calculation, a volcano relationship has been established between experimental-measured OER activity of Co-based perovskites and the calculated position of O p-band center (Figure 2.16).^{9,61} Analogous to the role of d-band center in ORR at metal catalyst surface, the O p-band position (relative to the Fermi level) tunes the oxygen adsorption strength, thus tuning the activity. It also successfully explains the stability trend of various perovskites under anodic potential cycling for the OER measurement.^{22,85} A higher O p-band position gives lower formation energy of oxygen vacancy, resulting in a less stable perovskite structure. The O p-band theory unifies the electron orbital occupancy and the electronegativity of the metal cation center. The stronger electronegativity gives lower energy position of metal d orbital, and consequently pushing the O p-band center closer to Fermi level. Further unification is achieved by considering the electronegativity of

ligand (for example, $O > S > Se > Te$): moving from O to Te pushes the ligand p-band center upwards.²² Enhanced HER (hydrogen evolution reaction) activities at sulfides, phosphides,⁸⁶ carbides⁸⁷ and nitrides⁸⁸ have been demonstrated, and ligand-caused oxygen electrocatalysis performance⁸⁹ has also been reported. Although the low electronegativity of Mn limits the activity of MnO_6 octahedron, the ligand effect shed a light on further enhance the performance of MnO_6 octahedron by replacing O with less electronegative ligand.

Figure 2.16 (a) Schematic illustration of O p-band center on transition metal oxides. (b) The OER activity as a function of O p-band center relative to Fermi level. Reproduced from ref. 61 with permission by Nature Publishing Group.

The core concept of molecular orbital principle is to correlate the molecular characteristics of material with the binding strength of reaction intermediates. Therefore, bulk band theory, which includes all the details of each molecular orbital, is believed to be a more accurate descriptor for catalysis. The key is to experimentally obtain the DOS (density of state), which is the electronic structure fingerprint of each material. Technically, with accessible DOS, activity could be predicted any catalysts. Sophisticated techniques have been invented for extracting DOS of metal surface,^{53,90} making great progress on ORR descriptor studies at metal surface. However, estimating the DOS of metal oxide surface still remains challenging,⁹¹ which leads to the absence of mechanistic insight into oxygen electrocatalysis on metal oxide catalysts. Fundamental physics knowledge on DOS extraction should be developed for understanding the universality of ORR/OER on various catalysts, and other kinds of catalysis.

Figure 2.17 (a) ORR CV curves of MnCo₂O₄/N-doped graphene composite (MCF/N-rGO), MnCo₂O₄ + N-doped graphene mixture (MCF+N-rGO), pure MnCo₂O₄ (MCF), pure N-doped graphene (N-rGO) and state-of-art catalysts in O₂-saturated 0.1 M KOH with 1600 rpm. Reproduced from ref. 92 with permission by Royal Society of Chemistry. (b) ORR CV curves of MnCo₂O₄/N-doped graphene composite (MnCo₂O₄/N-rmGO), MnCo₂O₄ + N-doped graphene mixture (MnCo₂O₄ + N-rmGO mixture), Co₃O₄/N-rmGO composite (Co₃O₄/N-rmGO), pure N-doped graphene (N-rmGO) and state-of-art catalyst in O₂-saturated 0.1 M KOH with 1600 rpm. Reproduced from ref. 94 with permission by American Chemical Society.

Conductivity ensured by carbon. Similar to supercapacitors, carbon is also a necessary additive for oxygen electrocatalysis on MnO₆-based metal oxide catalyst. The conductivity should be ensured; otherwise the measured activity would be quite low. It can be clearly seen in Figure 2.17a that without carbon addition, the onset potential of ORR at pure metal oxide (MCF) could be drastically dragged.⁹² The effect of conductivity has been studied in detail by changing the substitution amount of Mn in La_{1-x}Mn_xO₄ thin film (no carbon addition).⁹³ It was found that better conductivity normally gives better activity. As a result, it is crucial to mix metal oxide powders with carbon additives to exclude the effect of conductivity and to accurately estimate the intrinsic activities of metal oxides.

Synergetic effect from carbon. Except for the influence of carbon support on the conductivity, evidences have also indicated that the synergetic effect between MnO₆ octahedron and carbon can greatly improve the oxygen electrocatalysis performance. For example, chemically growing MnCo₂O₄ onto graphene outperforms the

MnCo₂O₄/graphene composite prepared by physical mixing method; further activity enhancement was achieved by introducing N doping to form MnCo₂O₄/N-doped graphene composite (Figure 2.17b).⁹⁴ The same phenomena were also observed in Co₃O₄ catalysts; the ORR activity is even comparable to commercial Pt/C.⁹⁵ Unfortunately, the underlying mechanism remains unclear. It is believed that the electronic structure at the interface of metal oxide and carbon could be changed by an intimate contact between them. The performance of metal cation might be enhanced by the electronic modification from carbon atoms; or the carbon atoms might be activated when the metal cations come closer. Understanding the relationship between the interface electronic structure and the oxygen electrocatalysis activity would offer new strategy for catalysts design.

Mass activity as a function of specific surface area. While the specific activity is governed by the electronic structure like e.g. occupancy, metal-oxygen bond covalency, ligand p-band center and electronic modification by carbon support, the mass activity is mainly controlled by the catalyst surface area (particle size). More surface atoms lead to higher mass activity. By choosing the catalyst with right electronic structure and reducing the particle size with the aid of nanotechnology, mass activity has been significantly improved, for example, CaMnO₄ (~70 A/g at 0.8 V vs. RHE) and CoMn₂O₄ (~60 A/g at 0.8 V vs. RHE).²⁶ It is recommended to refer to the pioneering works, which have comprehensively reviewed the nanostructured catalysts for oxygen electrocatalysis.

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Chapter 3

Experimental Methodology

Chapter 3 presents the necessary role of the experimental methodology employed in this thesis and validates the experiment design. In the section of electrode material synthesis, the method of preparing the target material for each chapter was discussed. Since the fine control of morphology is not demanded in most cases, the selected preparation method should be as simple as possible. Second, the electrochemistry experiments (including electrode fabrication, electrochemical characterization and electrochemical data analysis) were designed according to the standard procedures published in the reliable landmark works and the underlying mechanism for the electrochemistry details were discussed in depth. Third, material characterization required XRD for phase confirmation, TEM for size distribution analysis and XAS for the determination of valence state and cation distribution.

3.1 Electrode material synthesis

Synthesis of MnO₂ nanoflakes. MnO₂ nanoflakes (in Chapter 4 and 5) were synthesized in aqueous solution through a typical hot-injection method (Figure 3.1). Pre-dissolved potassium permanganate (KMnO₄) solution was quickly added into hexadecyltrimethylammonium bromide (CTAB) solution at 140 °C, giving a mixture containing 0.05 M CTAB and 0.01 M KMnO₄. Temperature of oil bath was maintained at 140 °C. MnO₂ was collected by adding acetone and following centrifugation.

Figure 3.1 Schematic illustration of reaction setup for synthesis of MnO₂ nanoflakes.

The wet-chemical synthesis of MnO₂ nanoflakes was conducted in aqueous solution because the selection of Mn precursor is limited. This is different from the synthesis of noble or transition metal nanoparticles, where various precursors (metal chlorides, metal acetylacetonate, etc.) have been invented for synthesis in either aqueous or organic solution.¹⁻⁴ Up to date, only KMnO₄ is available and thus the aqueous solution is the only one choice.⁵⁻⁷ MnO₂ could also be prepared by oxidizing the Mn precursor of a lower valence state (Mn²⁺, Mn³⁺),⁸ but the oxidation reaction normally takes place at high temperature, which results in a lack of uniform size control.

Considering the negative charge of precursor, the surfactant is required to attract the MnO₄⁻ anions and to wrap them within the surfactant micelle for tight morphology control. CTAB,² one of the most popular cationic surfactants, therefore was chosen to serve as the capping agent. Hexadecyltrimethylammonium chloride (CTAC) was also attempted, but its poor capping effect hinders its further application in MnO₂ nanoflakes synthesis. Detailed discussion about CTAC, sodium dodecyl sulfate (SDS) and requirement for heating rate are included in Chapter 4.

Synthesis of MnO₂ nanoflakes/carbon composite. Before oxygen reduction reaction (ORR) test (in Chapter 4), the MnO₂ nanoflakes was loaded onto carbon through ultrasonication method. In order to ensure smooth charge transfer, carbon is an indispensable additive for electrochemical characterization (ORR and supercapacitor) on non-conductive electrode material (for example, metal oxide). The reason has been discussed in depth in Chapter 2.

The carbon loading⁹ procedure is described as follows: firstly, a suspension solution of carbon nanotube (~0.5 mg/ml) was prepared by sonicating the carbon nanotube in ethanol for 3 hours. Here a relatively lower concentration (~0.5 mg/ml) and a long duration ultrasonication (3 hours) are necessary for preparing a homogeneously dispersed carbon suspension. Afterwards, a suspension of as-synthesized MnO₂ NPs (dispersed in ethanol via ultrasonication) was added drop-wise into the carbon solution and the mixture was further sonicated for 2 hours to homogeneously load MnO₂ NPs onto carbon. After ultrasonication, the hints of the successful carbon loading are the sedimentation of MnO₂/C (C = carbon) and the colorless supernatant solution. The MnO₂/C precipitation was collected by centrifuging and was subsequently dried for further use. In order to ensure the mass loading of MnO₂ to be 20 wt%, the concentration of MnO₂ NPs solution used in carbon loading was determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES). The mass loading of 20 wt% was used in Chapter 4 with the purpose of having sufficient amount of conductivity additives.

The MnO₂/C for supercapacitor characterization (in Chapter 5) was prepared with the same method by varying the carbon material (reduced-graphene oxide, carbon nanotube and acetylene black) and the mass loading of MnO₂. Solid state mixing,^{8,10,11} which usually uses mortar to physically mix metal oxide/carbon composite, is also a well-published method for supercapacitor electrode preparation but results in lower homogeneity compared with the solution phase mixing. Because the Chapter 5 aims to study the interplay between MnO₂ and carbon supports, which necessitates the homogeneous blend, carbon loading via ultrasonication was used in Chapter 5.

Synthesis of XFe₂O₄ (X = Mn, Fe, Co and Ni) ferrite nanoparticles. The material design of ferrite nanoparticles characterized for supercapacitor application in Chapter 6

should fulfill the following two requirements. First, the size of spinel ferrites should be sufficiently small. Chapter 6 employs in-situ X-ray absorption (XAS) technique to study the pseudocapacitor mechanism on spinel ferrite nanoparticles. Because the pseudocapacitive behavior is a surface process where the atoms at/near the surface undergo charge storage (see Chapter 2 for explanation),^{6,12,13} only the surface atoms are expected to exhibit physical property variations deviated from the bulky property. However, XAS collects the signal from the bulky particle rather than the surface atoms. Nanoparticles of small size, which possess a high ratio of surface atoms to bulky atoms, are required for reliable data collection. Second, the sizes of XFe_2O_4 ferrite nanoparticles across different element substitutions ($\text{X} = \text{Mn}, \text{Fe}, \text{Co}$ or Ni) should be similar. As a result of size decrease, the electronic structure of the under-coordinated surface atoms could be varied.^{14,15} For example, previous works have demonstrated that the ORR specific activity of Pt reduces with decreasing particle size.¹⁴ From the bulky polycrystalline Pt disk to Pt nanoparticles ($d = \sim 3 \text{ nm}$), the activity gap is as large as an order of one magnitude.¹⁴ Although this size effect is still unclear in supercapacitor performance at metal oxide, the possibility still remains and it is necessary to exclude this concern by keeping the particle sizes of XFe_2O_4 ($\text{X} = \text{Mn}, \text{Fe}, \text{Co}$ and Ni) at the same level.

Figure 3.2 Schematic illustration of the synthesis setup for spinel ferrite nanoparticles.

Based on the above two design principles, the ferrite nanoparticles were synthesized by a modified thermal decomposition method (Figure 3.2),^{16,17} of which the capability of controlling size has been well demonstrated. In a typical synthesis of Fe_3O_4 nanoparticles, the mixture of oleylamine and 3 mmol $\text{Fe}(\text{acac})_3$ was firstly maintained at 110°C for 1 hour to remove the moisture, followed by refluxing at 300°C for 1 hour under Ar atmosphere. Nanoparticle powders were washed with ethanol and hexane by centrifuging.

The washing process was repeated for three times to remove the excessive amount of oleylamine. The synthesis of other ferrites (XFe_2O_4 , $\text{X} = \text{Mn, Ni, Co}$) were identical to the method described above but using a molar ratio of 2:1 when feeding $\text{Fe}(\text{acac})_3$ and $\text{X}(\text{acac})_2$ ($\text{X} = \text{Mn, Ni, Co}$) in oleylamine. The resulting XFe_2O_4 ($\text{X} = \text{Mn, Fe, Co and Ni}$) nanoparticles are sufficiently small and have almost the same particle sizes ($d \sim 9 \text{ nm}$). If the depth of 2 nm is defined as the surface region, the surface region of a 9 nm particle contributes 80% in overall particle.

Temperature is the major factor which controls the cation distribution of spinels.^{18,19} The as-synthesized MnFe_2O_4 was further calcinated at 200, 300 and 400 °C in air for 6 hours to tune the inversion degree. The annealing of 6 hours is necessary for reaching a thermodynamic equilibrium state. Longer duration does not cause changes on cation distribution.¹⁸

Synthesis of various spinels (AB_2O_4). Most of the spinels that characterized for oxygen electrocatalysis (ORR and OER) in Chapter 7 were synthesized by the traditional solid state chemical method.^{20,21} Because the ORR/OER descriptor study in Chapter 7 was based on specific activity (activity normalized to the surface area of catalyst) analysis, the only one criterion for selecting synthesis method is achieving pure spinel phase. Although different preparation methods have been invented (including sputtering,²² co-precipitation,²³ sol-gel,²¹ electrochemical deposition,²⁴ hydrothermal,^{25,26} microwave synthesis,²⁰ etc.), the easiest one – solid state chemical reaction – was employed. Note that the free-standing spinel oxides were prepared for ORR and OER studies in Chapter 7. Despite the hybrid metal oxide/carbon composite gives enhanced activity,^{25,26} the contribution from carbon and the interaction between carbon and metal oxide inhibit the estimation of the true intrinsic activity of metal oxide. Detailed discussion about the role of carbon in hybrid systems is included in Chapter 2. In order to accurately establish a trend as a function of the descriptor (the physical property of spinel metal oxide), free-standing spinels were the most reasonable choice.

Synthesis of various manganese oxides (MnO_x). Similar to Chapter 7, the synthesis method of various manganese oxides is also not important, as long as the correct crystal

phase forms. Therefore, different synthesis methods were applied by referencing to previous works.²⁷

3.2 Electrode fabrication

Electrode fabrication for supercapacitor characterization. The fabrication methods of supercapacitor working electrode can be generally divided into two types: one is pasting,^{8,10} another is drop-and-cast.²⁸

In a typical pasting method, the metal oxide is mixed with carbon, binder and solvent (which dissolves binder) to form a slurry. The blending is mostly conducted with a mortar or stirring. Afterwards, the slurry is manually pasted onto the current collector (nickel foam, graphite paper, metal thin film, etc.) and the electrode is ready for supercapacitor test after drying to evaporate the solvent. This pasting method is the same as the large-scale industrial production of supercapacitor devices.

The drop-and-cast method uses ultrasonication to mix the metal oxide with carbon and binder. Since the blending is proceeded in a low-concentrated solution phase, the homogeneity is better than pasting method. A certain volume (5 ~ 10 μl) of the resulting ink is dropped onto the current collector (most cases, a circular glassy carbon with known diameter). After drying, a thin layer of electrode material forms on the top of glassy carbon. The drop-and-cast is the universal method for ORR/OER electrode preparation, but not popular in supercapacitor study.

In this thesis, all the supercapacitor electrodes for ex-situ measurement were fabricated through the pasting method because of its popularity in this community and the engineering significance. The metal oxide/carbon and polyvinylidene difluoride (PVDF) were mixed in a mass ratio of 90:10 and dispersed in N-methyl pyrrolidone (NMP) with mortar. The resulting slurry was pasted onto nickel foam substrate (1 cm $\times$ 1 cm) with a spatula. After drying at 80 $^{\circ}\text{C}$ in vacuum oven for 12 hours, the electrode was pressed at a 10 MPa pressure to reduce the contact resistance. To exclude the effect of mass loading, electrode material pasting was kept at $\sim 1.5 \text{ mg/cm}^2$. The electrodes for in-situ XAS (X-ray absorption spectroscopy) characterization in Chapter 6 were fabricated by a similar method. Because the X-ray beam needs to penetrate the current collector, elements with

large atomic numbers would block the X-ray signal, giving unreliable results. Graphite paper was therefore chosen as the substrate, where the active materials were pasted.

Electrode fabrication for oxygen electrocatalysis. All the ORR/OER characterization in this thesis uses the thin film disk electrode,²⁹ where the metal oxide forms a thin layer which homogeneously covers the glassy carbon electrode (Figure 3.3).

Figure 3.3 Schematic illustration of drop-casting the catalyst ink onto RDE (rotating disk electrode) and the setup for oxygen electrocatalysis measurement.

Figure 3.4 Examples of ORR CV curves for RDE in 0.1 M KOH. Comparison between LaCu_{0.5}Mn_{0.5}O₃ and the commercial Pt/C. Arrows indicate the scan direction. Reproduced from ref. 29 with permission by Electrochemical Society.

In order to accurately extract the intrinsic activity, either ORR or OER measurement needs to be conducted with a rotating disk electrode (RDE), rather than a static electrode. ORR is a mass transport-limited reaction, where the diffusion rate of O₂ from bulk electrolyte to approach the catalyst surface controls the overall reaction.^{30,31} This is the reason that in ORR measurement under a fixed rotation speed, a saturated current is

observed with increasing applied potential (Figure 3.4).²⁹ To obtain the real kinetics activity and to exclude the effect of O₂ diffusion, mass transport-correction should be performed. The role of RDE is to define the O₂ mass transport, which is the reflection of limiting current in ORR CV curves under a rotation rate. O₂ diffusion does not affect OER and thus there is no limiting current in OER measurement. However, the gas production reaction results in bubble accumulation at the catalyst surface, which blocks the active sites. RDE is beneficial for inhibiting the O₂ bubble nucleation, which even takes place at a current density lower than 1 mA/cm²_{disk}.³² Therefore RDE is necessary for the OER measurement.

Except for rotating, the thickness of the thin film also affects the accurate definition of O₂ mass transport. Earlier ORR/OER studies on metal oxides frequently use PTFE (polytetrafluoroethylene)-bonded ceramic pellets,^{33,34} where the porous microstructure gives high internal surface area. The resulting O₂ mass transport resistance is very high and hard to be defined. Consequently, it is not possible to extract the absolute ORR activity (specific or mass activity). To avoid undefined O₂ mass transport,²⁹ the drop-casted thin film (~1 μm) electrode was used to eliminate its internal surface area.

Before drop-casting, the catalysts inks were prepared by intensely ultrasonicing metal oxides, carbon and Na⁺-exchanged Nafion in the organic solvent for 1 hour. Note that carbon additive is indispensable to ORR/OER electrode fabrication. It ensures smooth charge transfer at catalyst interface, excluding the electrical resistance effect. For example, spinels with different substitution give different electrical conductivity,³⁵ which is able to affect the ORR/OER performance if carbon is not added.³⁶ Detailed discussion about the importance of carbon addition is included in Chapter 2.

Figure 3.5 Chemical structure of Nafion® 112. Reproduced from ref. 37 with permission by Elsevier.

Different from the most studies where commercial Nafion was directly used, Na^+ -exchanged Nafion was prepared to serve as binder in this thesis. As shown in Figure 3.5, each repeating unit in Nafion molecule provides one $-\text{SOH}$ functional group,³⁷ which hydrolyzes into proton upon touching with water. The 5 wt% Nafion solution corresponds to a proton concentration of $\sim 0.05 \text{ M}$.^{29,38} This strong acidity of commercially available Nafion poses the risk of corroding oxide surface and changing the original surface structure.²⁹ To cope with this concern, Na^+ -exchanged Nafion offers an alternative solution through neutralizing the commercial Nafion by NaOH .²⁹ The acidity is eliminated and the replacement of H^+ by Na^+ in Nafion molecule does not affect its binding performance because the binder role originates from the polymeric structure, rather than the functional group.

THF (tetrahydrofuran) was used as solvent to prepare the catalyst ink. Since a long-term exposure of oxide to THF has been proposed to cause surface amorphization,³⁹ changing the original electronic structure and resulting in poor reproducibility, freshly-prepared ink was immediately used to drop-cast the electrode.

3.3 Electrochemical characterization

Supercapacitor characterization. The supercapacitor measurements were performed using the standard three-electrode system in $1 \text{ M Na}_2\text{SO}_4$ electrolyte. Platinum foil and Ag/AgCl electrode (filled with saturated- KCl solution) were used as counter and reference electrodes, respectively. Another popular setup for supercapacitor test is the two-electrode system, where only working electrode and counter electrode are involved. However, due to the missing of reference electrode, the applied potential cannot be well defined by counter electrode. In order to accurately estimate the specific capacitance of electrode material, three-electrode system was preferred in this thesis.

The cyclic voltammetry (CV) curves were collected within the potential window of $0 \sim 0.9 \text{ V}$ vs. Ag/AgCl to avoid the side reactions. In aqueous electrolyte, if the applied potential is too low (less than -0.2 V vs. Ag/AgCl , as shown in Figure 3.6), the hydrogen evolution reaction is triggered and the drastically increasing current density is observed. With too high applied potential (larger than 1.0 V vs. Ag/AgCl , Figure 3.6), the oxygen

evolution reaction takes place and the current density increases.⁴⁰ To exclude the charge transfer contributed by the side reactions and to ensure the current signal purely comes from the supercapacitance or EDLC (electrical double layer capacitance), the potential window should be kept within a safe range. Thus 0 ~ 0.9 V vs. Ag/AgCl was employed.

Figure 3.6 CV curves of Ti foil and carbon black electrode (pasted on Ti foil) in 1 M NaCl electrolyte. Reproduced from ref. 40 with permission by Electrochemical Society.

As Chapter 4 aims to probe the influence of different carbon supports on charger transfer, the rate capability of supercapacitor performance should be revealed. Therefore, the CV scan rate was varied from 2 to 500 mV/s for capacitance retention study in Chapter 4. In contrast, the target in Chapter 5 is to compare the capability of energy storage across different transition metals (Mn, Fe, Co and Ni) in spinels oxides. A higher scan rate requires the electrode material to make fast response to the rapidly changing voltage. As a result, the conductivity becomes another factor governs the specific capacitance.⁶ In order to make sure that X (X = Mn, Fe, Co and Ni) is the single variable and the intrinsic capacitance is not affected by conductivity, the specific capacitance analysis in Chapter 5 was only based on 5 mV/s. V-t curve (charge-discharge at a constant current density) is another technique to estimate the specific capacitance. Considering the similar essential mechanism of V-t curve and CV curves, priority was given to CV for capacitance comparison.

The stability performance was characterized by conducting V-t curves for 1000 cycles in Chapter 5. To ensure an apparent pseudocapacitance fading, the current density of 3 A/g was used because the low current density cannot give detectable capacitance change.

Figure 3.7 In-situ XAS setup used in experiments, with the one side of the graphite paper facing the incoming X-ray and the other side with deposited XFe_2O_4 nanoparticles (NPs) in contact with 1 M Na_2SO_4 electrolyte. CE, RE, and WE stand for counter, reference and working electrodes, respectively.

Figure 3.7 shows the three-electrode electrochemical cell for in-situ XAS measurement in Chapter 6. In traditional transmission mode, the X-ray has to go through three obstacles: the electrolyte, a layer of electrode material pasted on the current collector and the graphite paper. The electrolyte blocks most of the X-ray signal. To avoid the involvement of electrolyte, the fluorescent mode was employed (Figure 3.7).⁴¹ In this case, the X-ray beam only needs to travel through the graphite paper for twice. As long as the thickness of graphite paper is small enough ($\sim 1 \mu\text{m}$), the signal loss would be negligible. With this setup, the fine structure of spinel ferrites as a function of applied potential was studied in depth. The working electrode was held at a constant potential and the X-ray signal collection started when the current reached the steady state.

Oxygen electrocatalysis characterization. The oxygen electrocatalysis (ORR and OER) measurements were performed using the standard three-electrode system in 0.1 M KOH electrolyte (Figure 3.8a).⁴² Platinum wire was the counter electrode and SCE (saturated calomel electrode) served as the reference electrodes. The potential is regulated between

working electrode and reference electrode (Figure 3.8b). The current signal is measured between working electrode and counter electrode (Figure 3.8b).

Figure 3.8 (a) Schematic illustration of a standard three-electrode electrochemical cell for ORR/OER measurement. (b) Circuit of a standard three-electrode electrochemical cell. Reproduced from ref. 42 with permission by Royal Society of Chemistry.

CV is the only one technique employed to obtain ORR/OER activity. Detailed discussion on data processing and activity extraction is included in section 3.4. Despite the stability is an important property for each catalyst, it is not our interest in this thesis. Therefore, stability test was not provided. As indicated by 3.8a, O_2 gas needs to be continuously supplied in the course of the ORR/OER CV measurement. Because O_2 is the reactant for ORR, it must be continuously supplied during the experiment. Especially for accurate estimation of the O_2 mass transport, the flow rate of O_2 gas must be high enough to give a stable limiting current. Although O_2 is no longer the reactant in OER, it is crucial to purge O_2 into the electrolyte to ensure that the O_2 partial pressure is 1 bar; the reaction should be maintained at the equilibrium state.

Prior to ORR activity measurement, CV scans were firstly performed under Ar saturation without rotating the working electrode. Due to the absence of the reactant, the current signal collected under Ar saturation refers to the capacitive current, which will be further used for background-correction in data processing.⁴² Afterwards, CV scans were conducted in O₂-saturated electrolyte with different rotation speeds (100, 400, 900, 1600, 2500 rpm). The CV curve under 1600 rpm is further processed to extract the intrinsic activity. The O₂ mass transport is varied by different rotation speeds, resulting in different limiting current. The plot of limiting current as a function of rotation speed provides the number of electron transfer and gives insight into the reaction pathway.³⁰ Because alkaline solution causes the leaching of glass constituents into electrolyte and thus giving poor reproducible measurement,^{43,44} data collection was completed within 2 hours since the initial exposure of electrolyte to the glass cell.

Since OER is not a mass transport limited reaction, the CV was only measured with 1600 rpm under O₂-saturation. CV scans under Ar saturation is not needed because the background-correction method in OER is different from ORR. The measurement was finalized within 1 hour to avoid the glass corrosion.

Resistance-correction is necessary to rule out the influence of the electrolyte resistance, which results from the different setup for oxygen electrocatalysis measurement.⁴⁵ For example, a longer distance between the three electrodes normally gives a higher resistance.⁴⁵ In this case, if the electrolyte resistance is not taken into consideration, the measured activity would be lower than the real activity. The electrolyte resistance was determined by EIS (electrochemical impedance spectroscopy) at a constant potential with a 10 mV voltage perturbation applied.⁴⁶ The ac spectra were collected from 200 kHz to 1 Hz, where the real part of the resistance at 1 kHz was used as the solution resistance (45 Ω , the PINE electrochemical cell used in this work).⁴⁶

3.4 Electrochemical data analysis

Supercapacitor. Based on the CV curves, the average mass capacitance of composite (metal oxide + carbon) was calculated by the following formula:

$$C_{oxi+c} = \Delta Q / \Delta V / w = \left(\int IdV \right) / s / \Delta V / w / 2$$

where ΔQ is the total amount of charge accumulated over a potential window ΔV ; w is the mass of the active material (metal oxide and carbon); I is the current; $\int IdV$ is the integrated area under the CV loop and s is the voltage scanning rate.⁴⁷ It should be noted that in the formula, it is finally divided by 2. This is because $\int IdV$ refers to the charge transfer of charge and discharge process, but the energy storage capability is only related to the discharge process. Due to the symmetry feature of pseudocapacitive CV curves,¹³ it is reasonable to consider the coulombic efficiency is 100 % and use “2” to separate the charge and discharge from the CV curves.

The mass capacitance (F/g) of pure metal oxides was calculated by subtracting the maximum contribution from carbon according to the following formula:^{6,47}

$$C_{oxi+c} = C_{oxi} \times wt_{oxi} + C_c \times wt_c$$

where C_{oxi+c} is the mass capacitance of composite (metal oxide + carbon); C_{oxi} is the mass capacitance contributed by pure metal oxide; wt_{oxi} is the weight percentage of metal oxide; C_c is the mass capacitance contributed by pure carbon and wt_c is the weight percentage of carbon. C_c was experimentally determined to be 12.3 F/g.

The specific capacitance ($\mu\text{F}/\text{cm}^2$) of metal oxides was estimated by normalizing the charge to the surface area of metal oxide. The surface area is determined by BET (Brunauer–Emmett–Teller) or TEM image.

Oxygen electrocatalysis characterization. ORR activities of metal oxides were extracted from the 10 mV/s negative-going CV scans in O_2 saturation at 1600 rpm.⁴⁸ First, the negative-going polarization curve was background-corrected by subtracting the capacitive current collected under Ar saturation. The original current (without background-correction) is a combination of the capacitive current from the catalyst itself and the catalysis reaction. It is crucial to eliminate the background current and thus to

obtain the real amount of charge transfer from the catalysis reaction. Second, the mass transport correction was performed employing the well-known Levich equation

$$i_{\text{measured}}^{-1} = i_{\text{k}}^{-1} + i_{\text{D}}^{-1}$$

where i_{measured} is the measured O_2 reduction current density, i_{k} is the mass-transport-corrected kinetic ORR current density, and i_{D} represents the limiting current density at a constant rotation speed.²⁹ As indicated by the Levich equation, the measured current density is actually a combination of the O_2 mass transport and the real kinetic current. Accurate extraction of i_{k} relies on excluding the effect of O_2 mass transport. Third, to eliminate the impact of ohmic drop, the iR-correction was conducted by the following equation:

$$E_{\text{iR-corrected}} = E_{\text{applied}} - iR$$

where $E_{\text{iR-corrected}}$ is the potential after iR-correction, E_{applied} is the applied potential before iR-correction, i is the measured current and R is the resistance determined by EIS (45 Ω , in this thesis).²⁹

The number of electron (n) transferred in ORR was estimated according to the Koutecky-Levich analysis, where the slope of the lines is related to n exchanged in the overall ORR

$$\text{slope} = (0.62nFD_o^{2/3}\omega^{1/6}C_o)^{-1}$$

where F is Faraday's constant, D_o is the diffusivity of O_2 molecule in the electrolyte, ω is the rotation speed, ν is the kinetic viscosity, and C_o is the concentration of O_2 in the electrolyte.¹⁴

OER were measured with the same rotating disk electrode set-up as described in ORR measurement (Figure 3.8). O_2 was bubbled throughout the experiment to ensure O_2/HO^- equilibrium at 1.23 V vs RHE. OER activities were obtained from the 10 mV/s CV scans in O_2 saturation at 1600 rpm. First, the capacitive current was corrected by averaging the positive-going and negative-going CV scans. Second, the ohmic drop was corrected by

the same method as described for ORR. Mass transport correction is not necessary for OER, because OER is not a mass transport limited reaction. It should be noted that oxygen evolution is able to cause structural changes on some oxide catalysts. This is eliminated by taking the third CV cycle to generate OER activity, as the initial scans are still a reflection of the original material physical property.

After a series of correction, the obtained kinetic current density was normalized to the surface area of catalyst to give the intrinsic activity. The best way to estimate the surface area of catalyst is the electrochemical method. For example, in this thesis, the surface area of Pt was assessed from the electrochemical H adsorption/desorption, and giving a specific surface of $40.9 \text{ m}^2 \text{ g}^{-1}$.¹⁵ However, electrochemical method is not applicable to metal oxides, because the electrode composition contains carbon additives. Therefore, the BET surface area was used. Although BET surface area is not equivalent to the real surface area of catalyst, the validity is demonstrated by the fact that the capacitive current trends well with the BET values.

3.5 Material characterization

X-ray diffraction (XRD). In Chapter 6, 7 and 8, we aim to establish a relationship between physical property and the electrochemical performance. XRD is therefore an important tool to confirm the correct phase and phase purity.

The basic principle of XRD is illustrated in Figure 3.9. The X-ray beam is shed onto the crystalline sample, where the regular array of atoms generates interference patterns as a response. The constructive interference takes place when the diffraction angle θ satisfies the Bragg's Law:

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

where n denotes the integer number; λ is the wavelength of the X-ray beam ($1.5418 \text{ \AA}$ for Cu radiation in this dissertation); d refers to the d-spacing of the crystal plane. The signal of the constructive interference X-rays is recorded and quantified. Scanning the sample within the angle range of 2θ produces all possible constructive interferences, and thus

giving the diffraction peaks as a function of 2θ . Each sample has a unique set of XRD pattern, which is considered as the fingerprint for phase identification.

Figure 3.9 Schematic illustration of the interaction between X-ray and the crystal lattices.

Transmission electron microscope (TEM). In this thesis, TEM was mainly used for estimating the size distribution and calculating the specific surface area of as-synthesized electrode materials.

The particle sizes of spinel ferrites in Chapter 6 are less than 10 nm in diameter, thus requiring high-resolution microscopy technique to image the general morphology. The resolution of microscopy is determined by the Abbes Equation:

$$d = \frac{0.61\lambda}{NA}$$

where d is the maximum resolution, λ denotes the wavelength of the incident beam and NA is the numerical aperture. The problem of the traditional light microscopy is that the wavelength of visible light is too large (400 ~ 700 nm). In contrast, the superiority of electron microscopy is the smaller λ of electron beam than light beam. The resolution of electron microscopy can be further enhanced by increasing the operating voltage, which generates high-energy electron beam and the resulting wavelength is decreased. This

explains the preference for TEM rather than SEM (scanning electron microscopy). in this thesis: the operating voltage of TEM (200 kV) is much higher than SEM (around 10 kV). Based on the TEM images, the number-average width W_n , was calculated as follows:

$$dW_n = \frac{\sum_{i=1}^n dW_i}{n}$$

where W_i is the diameter of individual nanoparticle, n is the number of counted nanoparticle. W_i was determined by averaging the length measured at two different directions that are perpendicular to each other. For each material, at least 200 particles were counted.

X-ray absorption spectroscopy (XAS). Since Chapter 6 and 7 focus on the spinel oxides, where metal cations can occupy in the tetrahedral or octahedral coordination sites, the cation distribution should be unambiguously revealed. To date, the most commonly used techniques are Mössbauer spectroscopy, neutron diffraction and extended X-ray absorption fine structure (EXAFS). In this study, EXAFS was used to probe the cation distribution and the occupation was quantified by EXAFS fitting.

Figure 3.10 Schematic illustration of X-ray absorption measurement. An incident beam of X-ray (intensity I_0) passes through the sample (thickness t). After X-ray absorption by the sample, the intensity of the transmitted beam (I) is detected.

X-ray absorption measures the response of the sample to a beam of X-ray, of which the energy is tuned. The primary concern is the absorption coefficient (μ), which is defined by the Beer's Law:

$$I = I_0 e^{-\mu t}$$

where I_o is the intensity of the incident X-ray; t is the thickness of measured sample; I is the intensity of the X-ray after absorption (Figure 3.10). At the initial stage, the XAS data is presented by plotting μ as a function of the energy of X-ray. As the energy of the incident X-ray is gradually increased, it becomes large enough to overcome the binding energy of a core-level electron and to kick out the electron (Figure 3.11). As a result, a sharp increase of μ is observed and this region is defined as the edge of XANES. Since the element of different valence state possesses different binding energy of a core-level electron, the XANES edge is employed to quantify the valence state of the target element.

Figure 3.11 Schematic illustration of the photoelectric effect. The X-ray is absorbed and the core-level electron is kicked out from the atom.

The other application of XAS in this dissertation is to use EXAFS technique to determine the local structure, for example, the cation distribution in Chapter 6 and 7. As the energy of X-ray is further increased beyond the XANES region, EXFAS technique measures the effect of ejected photoelectron on the absorption coefficient μ . Ejected by the incident X-ray beam, the outgoing-photoelectron acts as a wave, which propagates away from the absorbing atom (Figure 3.12). When the outgoing-wave hits the neighboring scattering atoms, the scattered-photoelectron wave is generated (Figure 3.12). The interference between the outgoing wave and the scattering wave would trigger the oscillation of the μ signal, which gives the detailed information of the local structure. By building a model structure and simulating the interference of the photoelectron waves, the local chemistry

information can be quantitatively analyzed. This data processing is called as EXAFS fitting. Since the real sample has different neighboring atoms at different distances, all the interference paths should be covered in the theoretical standard for real-sample analysis.

Figure 3.12 Schematic illustration of the photoelectric effect in EXAFS technique. The X-ray is absorbed and the core-level electron is kicked out from the atom.

For each XFe_2O_4 spinel ferrites in Chapter 6, EXAFS spectra are recorded on both X (X = Mn, Co, Ni) and Fe K edges and each edge has a theoretical standard. It is worth noting that the EXAFS fitting of two elements are conducted simultaneously in order to accurately extract the quantitative information of site occupancy. This method has been employed in previous studies.⁴⁹ Theoretical models in this study were built by *ab initio* calculations on FEFF8.⁴⁹ A cubic spinel crystal frame (space group 227) was used. Considering the tremendous number of scattering paths within the fitting range (from 1 Å to ~4 Å), we made several constraints and approximation by referencing a landmark work.⁴⁹

A theoretical standard was calculated for the tetrahedral and octahedral environments for each of the two elements, giving four standards in total. The site occupancy can be described by one variable, $x_A(\text{X})$, i.e., the number of X (X = Mn, Co, Ni) at tetrahedral sites. According to the stoichiometry, $x_B(\text{X}) = 1 - x_A(\text{X})$, $x_A(\text{Fe}) = 1 - x_A(\text{X})$, $x_B(\text{Fe}) = 1 + x_A(\text{X})$. The coordination number was obtained by setting S_0^2 to the value determined from the standard reference sample. For example, bulk Fe_3O_4 serves as the reference sample for all Fe edges; Mn_3O_4 for Mn; Co_3O_4 for Co and NiO for Ni. The model validity was

confirmed by two commonly used parameters: R factor and χ^2_v .^{19,49,50} It should be noted that the values of R and χ^2_v in this work are much smaller than the landmark reports,^{19,49,51} validating the rationality of our model.

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Chapter 4

Nano-engineering MnO_6 Octahedrons: Achieving High Mass Activity for Oxygen Reduction Reaction

Manganese dioxide nanoflakes were synthesized by the reduction of KMnO_4 , of which the morphology was controlled by cationic surfactant cetrimonium bromide. The surfactant/precursor ratio, the heating rate and surfactant type are critical factors for producing such nanoflakes. Our approach here demonstrates a facile nano-chemical method of packing MnO_6 octahedrons into small-sized MnO_2 nanoparticle, thus achieving high mass activity towards oxygen reduction reaction.

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4.1 Introduction

Oxygen reduction reaction (ORR) dominates the major energy loss in fuel cell technologies.¹⁻³ Inventing efficient and low-cost catalysts for ORR has been attracting tremendous efforts in the past decades due to the scarcity of the state-of-art noble-metal-based catalysts. Transition metal oxides,⁴⁻⁷ perovskites,^{8,9} doped carbons,¹⁰⁻¹³ etc. have contributed significant progress on catalyst development. Recent studies have discovered that manganese dioxides (MnO₂), which consists of MnO₆ octahedron as the basic unit, is one of the most promising candidate because of its natural abundance in the earth, low cost, non-toxicity, and most importantly, the relatively high activity towards ORR.¹⁴⁻¹⁷

MnO₂ is an electrode material that has been most intensively investigated for supercapacitors.¹⁸⁻²⁰ Motivated by the supercapacitor research, the basic strategy in enhancing the electrochemical performance of MnO₂-based electrode material has been devoted to develop chemical methods of synthesizing nano-MnO₂ with various morphologies and specific surface area. To date, numerous methods have been discovered for the synthesis of nanostructured MnO₂, including co-precipitation,^{21,22} sol-gel,²³ electrochemical deposition,^{24,25} hydrothermal in aqueous solution,¹⁶ microwave synthesis,²⁶ direct growth on carbon material,¹⁵ etc. These methods can shape nanostructured MnO₂ into flakes,^{27,28} needles,^{24,29} spherical particles,^{22,30} flowers,^{27,31} wires,³²⁻³⁴ ribbons,³⁵ tubes,²⁷ and other morphologies grown on carbon supports.^{15,19} It should be noted that these methods are able to well control the morphology of nano-MnO₂, but the resulting nanoparticle sizes are mostly too large, ranging from 100 nm to micrometers. Challenges remain in successful synthesis of free-standing nano-MnO₂ with uniform size distribution. A small and uniform MnO₂ nanoparticle is expected to give more electrochemically active sites and effectively decrease the mass loading of MnO₂ in ORR catalysis.

Chapter 4 presents the high ORR mass activity of MnO₂, which results from the synthesis of MnO₂ nanoflake with uniform size distribution (~47 nm). To the best of our knowledge, these are the smallest free-standing MnO₂ nanoflakes that have been published. The critical factor for successful synthesis of these uniform-distributed MnO₂ nanoflakes is the utilization of CTAB as the surfactant. Compared with previously

reported MnO₂, Mn-containing perovskite and carbon-based catalysts, a very high ORR mass activity (21 ± 1.2 mA/mg at 0.75 V vs. RHE) in alkaline electrolyte is thus achieved by nanoengineering MnO₆ octahedrons into small and ultrathin flakes.

4.2 Experimental details

Synthesis of MnO₂ nanoflakes. MnO₂ nanoflakes were synthesized in aqueous solution through a typical hot-injection method: pre-dissolved potassium permanganate (KMnO₄) solution was quickly added into hexadecyltrimethylammonium bromide (CTAB) solution at 140 °C, giving a mixture containing 0.05 M CTAB and 0.01 M KMnO₄. Temperature of oil bath was maintained at 140 °C. MnO₂ was collected by adding acetone and following centrifugation. The molar ratio of CTAB/KMnO₄ was varied as control experiments.

Carbon loading. A suspension solution of carbon nanotube (~0.5 mg/ml) was prepared by sonicating the carbon nanotube in ethanol for 3 hours. Afterwards, a solution of as-synthesized MnO₂ NPs (dispersed in ethanol) was added drop-wise into the carbon solution and the mixture was further sonicated for 2 hours. The MnO₂/C precipitation was collected by centrifuging for 10 min at 9500 rpm and was subsequently dried at 80 °C for further use. In order to ensure the mass loading of MnO₂ to be 20 wt%, the concentration of MnO₂ NPs solution used in carbon loading was determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES).

Electrode preparation. Typically, as-prepared C/MnO₂ was dispersed in a mixture of solvents containing water, isopropanol and Nafion® perfluorinated resin solution (5 wt% in water) (v/v/v = 4/1/0.05) by sonication for 30 min to form a 2 mg/mL suspension. 15 µL of this ink was then dropped onto the rotating disk electrode (RDE, 0.196 cm², PINE) and dried at room temperature, yielding a MnO₂ mass loading of 6 µg (30.6 µg cm⁻²_{disk}). As a control experiment, commercial Pt/C (50 wt%) was dispersed in the same mixture solvents to form a 0.8 mg/mL suspension. 15 µL of this ink was then dropped onto the RDE and dried at room temperature, yielding a Pt mass loading of 6 µg (30.6 µg cm⁻²_{disk}).

Electrochemical characterization (ORR). Electrochemical measurements were conducted with a rotating-disk electrode (Pine) using a PINE WaveDriver 20

bipotentiostat. The 0.1 M KOH electrolyte was prepared from Milli-Q water ($18 \text{ M}\Omega\cdot\text{cm}$) and KOH pellets (99.99% weight, Sigma-Aldrich). All electrochemical results were collected in a three-electrode glass cell and potentials were referenced to RHE scale.

4.3 Results and discussion

Figure 4.1 (a) A representative TEM image of as-synthesized MnO_2 nanoflakes. (b) TEM image of a folded MnO_2 nanoflake. The insets are SAED pattern and the size distribution histogram of thickness measured from 150 nanoflakes. (c) TEM image of an unfolded nanoflake. (d) XRD patterns of as-prepared nanoflakes (top) and 500°C heat-treated nanoflakes (middle). Bottom is the standard $\alpha\text{-MnO}_2$ (PDF#00-044-0141) pattern.

MnO_2 nanoflakes were prepared by the hot injection method. At the temperature of 140°C , the KMnO_4 solution was quickly injected into the CTAB solution with magnetic stirring. Immediately after injection, the color changed from purple to brown, indicating

the decomposition of KMnO₄ into MnO₂. The flake morphology is confirmed by the TEM image in Figure 4.1a. By measuring more than 200 unfolded nanoflakes, the average diameter is determined to be 47 ± 4 nm. The average thickness of the as-synthesized nanoflakes is 1.5 ± 0.4 nm, calculated after measuring the edge thickness of more than 150 folded nanoflakes (inset, Figure 4.1b). In the HRTEM image (Figure 4.1c), those small crystal grains indicated the nanoflakes are polycrystalline. The two dominant lattice distances of 2.5 Å and 4.8 Å are attributed to the (400) and (200) in α -MnO₂.²⁷ According to the very weak SAED (selected area electron diffraction) pattern (inset, Figure 4.1b) and the two broad peaks in XRD pattern, we conclude the nanoflakes are amorphous in nature. The arrangement of MnO₆ octahedrons in those small crystal grains was further confirmed to be α -MnO₂ by annealing the nanoflakes. The resulting XRD pattern perfectly fit the standard pattern of α -MnO₂, indicating the nanoflakes are indeed MnO₂, rather than other manganese oxides such as MnO, Mn₂O₃, or Mn₃O₄.¹⁸ According to the XPS fitting of O_{1s}, Mn_{2p} and Mn_{3s} spectra, the oxidation valence state of Mn is determined to be +3.5 ~ +3.6. The Mn valency is not +4 because of the presence of K⁺ in the 2×2 channels of α -MnO₂.¹⁶

To reveal the chemistry origin underlying the formation of such MnO₂ nanoflakes, the synthesis recipe was modified. First, we control the molar ratio of CTAB/KMnO₄ by varying the concentration of KMnO₄ from 0.005 to 0.05 M and fixing the CTAB at 0.05 M. Consequently, the molar ratio of CTAB/KMnO₄, which is the only one variable, was varied from 0.5 to 10. The morphology given by each recipe was probed by TEM (Figure 4.2 and Table 4.1). It can be seen that when the ratio is 2.5, 5, or 10, the nanoflake morphology can be achieved without apparent difference in size. In the cases of 1 and 0.5, the flake morphology was generally kept but the size was totally out of control: particles were too large and some tubular wires were observed. This set of results indicates that the formation of nanoflakes with uniform size distribution is dependent on the molar ratio of CTAB/KMnO₄, which should be maintained higher than 2.5.

Figure 4.2 The representative TEM images of a series of control experiments. The corresponding recipes are indicated in Table 4.1.

Table 4.1 The detailed recipes of a series of control experiments. The corresponding morphologies are shown in Figure 4.2.

Panel in Figure 4.2	KMnO_4	CTAB	Method
a	0.1 M	0.05 M	Hot-injection
b	0.05 M	0.05 M	Hot-injection
c	0.02 M	0.05 M	Hot-injection
d	0.01 M	0.05 M	Hot-injection
e	0.005 M	0.05 M	Hot-injection
f	0.01 M	0.05 M	Heating-up
g		0.05 M (CTAC)	Hot-injection
h		0.05 M (KBr)	Hot-injection
i		0.05 M (SDS)	Hot-injection

Second, the surfactant was varied to reveal the role of CTAB in morphology control. CTAB has made great contribution in the quest of shape control for gold nanoparticles. The soft template model, proposed by C. J. Murphy's group,^{36,37} has used double-layered

CTAB micelles to direct the growth of gold nanoparticles. The basic mechanism is the positive charge of the CTA⁺ attracts AuCl₄⁻ anion and encloses them in the CTAB micelle to control the particle growth. Considering the ionic similarity of AuCl₄⁻ and MnO₄⁻, it is proposed that this chemistry also fits the interaction between KMnO₄ and CTAB. To demonstrate this hypothesis, the cationic surfactant CTAB was replaced by the anionic surfactant SDS (sodium dodecyl sulfate). The resulting morphology of MnO₂ is quite irregular (Figure 4.2).

Third, the heating rate was varied in order to feature the importance of hot injection. When the CTAB and KMnO₄ were pre-mixed at room temperature and heated up slowly (< 5 °C/min), the resulting MnO₂ particles did not exhibit nanoflake morphology, but agglomerated sheet-particles (Figure 4.2f). In contrast, the formation of nanoflakes was observed under a fast heating rate. This explains the prerequisite of the successful synthesis of nanoflakes is the fast reduction rate of KMnO₄, which possibly favors a homogeneous burst of nucleation and maintains the size uniformity. To maximize the heating rate, a hot injection method was developed for large-scale production of MnO₂ nanoflakes.

The ORR activity of these MnO₂ nanoflakes was then estimated in alkaline electrolyte. The electrode was prepared by the traditional drop-and-cast method. In order to remove the CTAB surfactant attached on the nanoflakes, each electrode underwent 100 cycles between 0 ~ 1.0 V vs. RHE in Ar-saturated 0.1 M KOH. After updating a new batch of electrolyte, the activity was evaluated by CV (cyclic voltammograms) under O₂-saturated condition with a scan rate of 10 mV/s. Figure 4.3a shows the ORR polarization curves of MnO₂ nanoflakes under various rotation speeds. The polarization curves can be categorized into 3 regions: the diffusion-controlled region between 0 V and 0.45 V vs. RHE, the diffusion-kinetic combined region between 0.45 V and 0.7 V vs. RHE, and the kinetic-controlled region at > 0.7 V vs. RHE. To further unveil the reaction pathway, the number of electrons transferred was determined by Koutecky-Levich plots (inset, Figure 4.3a), where the slope, $B^{-1}C_0^{-1}$, of the linear relation between the limiting current and $\omega^{-1/2}$, was extracted.⁴ The Bc_0 parameters at 0 V and 0.4 V vs. RHE are 0.150 mA cm⁻²_{disk} rpm^{-1/2} and 0.148 mA cm⁻²_{disk} rpm^{-1/2}, respectively. Similar to Pt/C, the obtained electron

transfer number is ~ 4 , indicating the ORR on the MnO₂ nanoflakes proceeds through a $4e^-$ reaction pathway.

Figure 4.3 (a) The background-corrected polarization curves of ORR on MnO₂ nanoflakes collected with a scan rate of 10 mV/s at room temperature in O₂-saturated 0.1 M KOH. The rotation speeds are 100, 400, 900, 1600, and 2500 rpm. Solid lines represent forward scans and the dotted line represents the backward scan at 1600 rpm. The inset shows the Koutecky-Levich plots at 0, 0.1, 0.2, 0.3, and 0.4 V (vs. RHE). (b) The background-corrected polarization curves of ORR on MnO₂ nanoflakes (solid line) and large particles (dash line) with a scan rate of 10 mV/s at 1600 rpm in O₂-saturated 0.1 M KOH. The inset shows the Tafel plots of these two samples obtained from the normalized polarization curves in the forward scans at 1600 rpm. The two samples have the same MnO₂ mass loading of 30.6 $\mu\text{g}/\text{cm}^2$ on glassy carbon electrodes. The BET surface areas of MnO₂ nanoflakes and large particles are 74.6 m²/g and 42.8 m²/g, respectively. They were used as oxide surface area to normalize the current density in the Tafel plots.

Figure 4.4 Specific activities of MnO₂ nanoflakes, large particles, and commercial Pt/C. For comparison, α -MnO₂ nanorods, CaMnO₃, LaMnO₃, and LaMnO_{3+ δ} are calculated and read from reported literatures. Error bar represents for at least three independent experiments.

In the control experiment, the ORR activity of large MnO₂ particles prepared by a CTAB/KMnO₄ ratio of 5:1 was measured for comparison. The polarization curves are basically similar to that of MnO₂ nanoflakes (Figure 4.3b) and those reported previously.¹⁷ The reaction pathway given by large MnO₂ particles is the same as MnO₂ nanoflakes because their electron transfer number are the same (~ 4).^{9,38} Note that the ORR at commercial Pt/C (50 wt %) was also measured to demonstrate the reliability of our electrochemistry measurement. In accordance with the previous landmark works in 0.1 M KOH electrolyte,⁹ the limiting current density of Pt/C is $\sim 5.7 \text{ mA/cm}^2_{\text{disk}}$ and the mass activity after the background-, mass transport-, iR-correction is $133 \text{ mA/mg}_{\text{Pt}}@0.9$ vs. RHE. In the comparison of MnO₂ nanoflakes and large MnO₂ particles, the specific activities after background-, mass transport-, iR-correction are shown in the inset of Figure 4.3b. The current densities of the Tafel plots were normalized to the surface area of catalyst, which was determined by the BET measurement. It can be seen that the locations of these two Tafel plots almost overlap with each other, indicating these two MnO₂ catalysts possess the same intrinsic ORR activity. At the given potential of 0.75 V

vs. RHE, the difference of specific current densities are negligible; they are 28 ± 2 mA/cm² and 23 ± 1 mA/cm², respectively. Hereby, the different morphologies of α -MnO₂ give the same specific activity, which is consistent with the findings of other metal oxides.^{8,16,39} This proves that as long as we do not touch the intrinsic property of MnO₆ octahedron, the packing size of MnO₆ octahedrons cannot alter the intrinsic ORR activity. Of notable interest is that our α -MnO₂ materials exhibit the same specific activity as α -MnO₂ nanorods in previous reports (Figure 4.4),¹⁶ which further supports our conclusion that the same crystal structure of MnO₂ should have the same electrochemical performance. This is different from the Pt catalyst studies, where the particle size tunes the specific activity.⁴⁰⁻⁴²

In terms of the mass activity, nanoflakes are significantly superior to the large particles. As shown in the Tafel plots where the current densities are normalized by the loading mass of oxides (Figure 4.5a), MnO₂ nanoflakes are almost two times higher than MnO₂ particles. At the given potential of 0.75 V vs. RHE, the mass current densities of MnO₂ nanoflakes and large MnO₂ particles are 21 ± 1.2 mA/mg and 9.2 ± 0.1 mA/mg. Such an enhancement on MnO₂ nanoflakes is due to the smaller size, which results in more electrochemically active sites. To compare with literature results, both the specific and mass activity of Tafel plots of α -MnO₂ nanorods,¹⁶ LaMnO₃,⁸ and LaMnO_{3+ δ} ⁸ were extracted and put together (Figure 4.4 and 4.5). Although the specific activity of our MnO₂ nanoflakes is not prominent among various Mn-based oxides, the mass activity can be drastically improved by nanoengineering MnO₆ octahedrons into smaller size. At the given potential of 0.75 V vs. RHE, the activity of our MnO₂ nanoflakes is four, ten and six times higher than other MnO₂ catalysts;^{16,43,44} and 18, 4 and 7 times higher than LaMnO₃ perovskite,⁸ B-doped CNTs,¹⁰ and N-doped graphene.¹¹ Along with enhanced ORR mass activity, the MnO₂ catalyst is also capable of resisting the methanol poison, which is another disadvantage of the noble metal-based catalysts but another advantage of the MnO₆ octahedron-based catalysts (Figure 4.6).

Figure 4.5 (a) Mass activities of MnO₂ nanoflakes, large particles, and commercial Pt/C. For comparison, α -MnO₂ nanorods, LaMnO₃, and LaMnO_{3+ δ} are calculated and read from landmark literatures. (b) Mass-normalized current densities at 0.75 V (vs. RHE) of MnO₂ nanoflakes and large particles in this work, compared with those reported in landmark literatures: α -MnO₂ nanorods, β -MnO₂, MnO₂, LaMnO₃, B-doped CNT and N-doped graphene.

Figure 4.6 Chronoamperometric response of as-synthesized MnO₂ nanoflakes and Pt/C at 0.6 V vs. RHE with a rotation speed of 1600 rpm. Methanol crossover was tested by injecting 1 ml methanol into 75 ml O₂-saturated 0.1 M KOH electrolyte.

4.4 Conclusion

Uniform-sized MnO₂ nanoflakes have been successfully synthesized by coupling CTAB with MnO₄⁻ and their ORR performance was in depth studied. There are 3 key parameters to obtain MnO₂ nanoflakes: the ratio of surfactant to Mn precursor, the heat rate and the type of surfactant. The as-synthesized MnO₂ nanoflakes do not alter the intrinsic activity of MnO₂, but show enhanced mass activity. Our approach sets an example that nano-engineering the packing size of MnO₆ octahedrons is an efficient method to lower the catalyst loading mass. Changing the intrinsic activity lies in tuning the physical nature of MnO₆ octahedron, rather than the particle size.

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Chapter 5

Interplay Between MnO₆ Octahedron and Different Carbon Supporting Materials

Uniform-sized MnO₂ nanoflakes were employed to study the interplay between various carbon supports (CNTs, rGO and AB) and MnO₆ octahedrons. The pseudocapacitive behaviors of MnO₂/C (C = CNTs, rGO and AB) composites were in depth studied. It was demonstrated that rGO is the best conductive support for MnO₆-based supercapacitor applications at slow scan rates. However, due to the limited charge transport within the MnO₂/rGO composite, CNTs and AB exhibit better energy storage capability than rGO at high scan rates. This chapter presents the rational selection of conductive supports for supercapacitors operated under different scan rates (or current densities).

5.1 Introduction

Supercapacitors are a class of promising energy storage technologies to electrochemically take advantage of renewable energy resources in our daily life.¹⁻³ The major scientific challenge is to develop efficient and low-cost electrode materials for enhanced high energy density and power density.⁴⁻⁶ Because of the earth-abundance, nontoxicity and mostly importantly the high specific capacitance, particular attention has been paid to the manganese dioxide (MnO₂), of which the basic unit to build up the crystal is MnO₆ octahedron.^{7,8} Considering MnO₂ is non-conductive, the conductive additives are indispensable to the smooth charge transport within the supercapacitor application. It is thus highly demanded to understand the interplay between the stacking of MnO₆ octahedrons and the conductive support such as various carbon materials. The traditional MnO₂/carbon composites have exhibited enhanced pseudocapacitance,⁹⁻¹³ but the different chemistry/physics approaches for composite preparation lead to different MnO₂ composition, morphology, mass ratio of MnO₂ to carbon, etc. and consequently, the influence of various conductive supports on interface electron transport still remains unclear.

This Chapter elaborates the interplay between MnO₆ octahedrons and various carbon supports, i.e., AB (acetylene black), rGO (reduced-graphene oxide) and CNTs (carbon nanotubes), which represent 3 typical morphologies of carbon materials. The flexibility of studying the effect of different conductive supports on interface charge transfer could be brought by the successful synthesis of uniform-sized free-standing MnO₂ nanoparticles. The uniform-sized MnO₂ nanoflakes were used as the standard active component to physically mix with various carbon materials and the resulting pseudocapacitive behaviors of various MnO₂/C (C = carbon) composites were compared.

5.2 Experimental details

Synthesis of MnO₂ nanoflakes. MnO₂ nanoflakes were synthesized in aqueous solution through a typical hot-injection method: pre-dissolved potassium permanganate (KMnO₄) solution was quickly added into hexadecyltrimethylammonium bromide (CTAB) solution

at 140 °C, giving a mixture containing 0.05 M CTAB and 0.01 M KMnO₄. Temperature of oil bath was maintained at 140 °C. MnO₂ was collected by adding acetone and following centrifugation. The molar ratio of CTAB/KMnO₄ was varied as control experiments.

Carbon loading. A suspension solution of carbon nanotube (~0.5 mg/ml) was prepared by sonicating the carbon nanotube in ethanol for 3 hours. Afterwards, a solution of as-synthesized MnO₂ NPs (dispersed in ethanol) was added drop-wise into the carbon solution and the mixture was further sonicated for 2 hours. The MnO₂/C precipitation was collected by centrifuging for 10 min at 9500 rpm and was subsequently dried at 80 °C for further use. In order to ensure the mass loading of MnO₂ to be 20 wt%, the concentration of MnO₂ NPs solution used in carbon loading was determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES).

Electrode fabrication. Working electrode was prepared by a traditional method. Before working electrode fabrication, as-synthesized XFe₂O₄ (X = Fe, Co, Ni) powders were calcinated at 300 °C. To turn the inversion degree, as-synthesized MnFe₂O₄ was calcinated at 200, 300, and 400 °C in air for 6 hours. Nanoparticles were then mixed with Vulcan carbon CX72 with a mass ratio of C:XFe₂O₄ = 40:60. The as-prepared C/XFe₂O₄ (XFe₂O₄ = 60 w%) material and polyvinylidene difluoride (PVDF) were mixed in a mass ratio of 90:10 and dispersed in N-methyl pyrrolidone (NMP). The resulting slurry was pasted onto nickel foam substrate (1 cm × 1 cm) with a spatula. After drying at 80 °C for 12 hours, the electrode was pressed at a 10 MPa pressure.

5.3 Results and discussion

To achieve insights into the influence of various C (C = carbon) on the pseudocapacitive behavior of MnO₂/C, we start with the pure carbon materials. Figure 5.1a is the CV (cyclic voltammogram) curves of pure AB (acetylene black), CNTs (carbon nanotubes) and rGO (reduced-graphene oxide) at the scan rate of 10 mV/s. The CV shapes of these carbons are rectangular, which is the typical characteristic of the double layer

capacitance.¹⁴⁻¹⁶ It is observed that the CV loop of rGO is apparently larger than AB and CNTs, indicating the rGO gives the highest capacitance. This is due to the high specific surface area of rGO, which is the advanced superiority of this two-dimension carbon material.^{7,17,18} By quantitative estimating the area under the CV loop, the mass capacitances of these 3 carbon materials as a function of the scan rate are shown in Figure 5.1b. They all exhibit the typical rate-capability trend: the mass capacitance of these 3 carbons decreases with the increasing scan rate.^{19,20} At each scan rate, the highest mass capacitance is rGO, followed by CNTs and AB.

Figure 5.1 (a) CV curves of acetylene black (AB), carbon nanotubes (CNTs) and graphene (rGO) at the scan rate of 10 mV/s in 1 M Na₂SO₄. (b) Specific capacitance of 3 carbon supports as a function of the scan rate. The inset is the close view for specific capacitance at the scan rate of 2, 10, 20 and 50 mV/s. Each data point and its error bar were obtained from three independent measurements.

The uniform-sized MnO₂ nanoflakes were physically loaded onto AB, CNTs and rGO to form MnO₂/C composite with different MnO₂ weight percentage. The TEM images of as-prepared composites are shown in Figure 5.2 to demonstrate that the MnO₂ nanoflakes are well-dispersed on the carbon supports.

To probe the effect of the MnO₂ wt% (MnO₂ loading mass), the mass capacitances of MnO₂/C were plotted against that. Figure 5.3a includes all the capacitances normalized to the total mass of MnO₂ + carbon at the scan rate of 5 mV/s. The 3 types of composites possess the same overall trend, where the higher MnO₂ wt% gives higher capacitance and the optimum point locates at MnO₂ wt% = 80 wt%. This is because at the slow scan rate

(for example, 5 mV/s), the dominantly active component is MnO₂. Therefore, an increase of the MnO₂ amount generally leads to an enhanced capacitance.²¹ However, the pure MnO₂ is not competitive, which is due to the conductivity limitation (see discussion in literature review). At each mass loading, the MnO₂/rGO is apparently higher than MnO₂/AB and MnO₂/CNTs; while the difference between MnO₂/AB and MnO₂/CNTs is not prominent. The larger capacitance of MnO₂/rGO is mainly due to the larger intrinsic capacitance of rGO itself.¹⁰

Figure 5.2 TEM images of (a) MnO₂ nanoflakes, MnO₂ nanoflakes supported on (b) acetylene black, (c) carbon nanotubes and (d) reduced graphene oxide.

To extract the influence of the carbon supports on MnO₂, the capacitance of carbon materials was subtracted to give the pure capacitance contribution from MnO₂ (Figure 5.3b). As a function of the MnO₂ mass loading, the overall trends of these 3 types of composites are the same. With increasing MnO₂ wt%, the capacitance purely contributed by MnO₂ linearly drops. At the region of slow scan rates, rGO is able to give higher capacitance of supported MnO₂ than AB and CNTs. It indicates the combination of the two-dimensional MnO₂ nanoflakes and two-dimensional carbon has synergy effect.

Figure 5.3 Specific capacitance of MnO₂/C composites normalized by the total mass of MnO₂ and carbon at (a) 5 mV/s, (c) 50 mV/s and (e) 500 mV/s. Specific capacitance of MnO₂ from the contribution of supported MnO₂ at (b) 5 mV/s, (d) 50 mV/s and (f) 500 mV/s. The mass loading of MnO₂ refers to the mass percentage of MnO₂ in the composite. For example, 20 wt% of MnO₂ refers to a composition of MnO₂ : C = 20 : 80 in mass. Each data point and its error bar were obtained from three independent measurements.

The capacitance of MnO₂/C composite as a function of MnO₂ wt% at 50 mV/s is shown in Figure 5.3c. The overall trend is similar to 5 mV/s, but the gap between the dotted line and the other two lines (solid line and dash line) becomes narrower. It implies that at a higher scan rate, the advantage of rGO is no longer as prominent as that at a slower scan rate. The performance degrading of MnO₂/rGO is more apparent if the scan rate is further increased to 500 mV/s. In Figure 5.3e, the trend of MnO₂/rGO (the dotted line) locates below the other two MnO₂/C composites, indicating that MnO₂/rGO gives the worst energy storage capability at the scan rate of 500 mV/s. The poor rate capability of MnO₂/rGO originates from the slower charge transfer within MnO₂/rGO compared with the other two composites. Moreover, the optimum loading mass of MnO₂ is no longer 80 wt%; it shifts towards the direction of lower MnO₂ wt%. This is because a higher scan rate requires higher conductivity, which can be ensured by reducing the MnO₂ wt%.

Attention was further paid to the pure capacitance contribution of MnO₂ after subtracting the double layer capacitance of carbon from the composite. As the scan rate was increased from 5 mV/s (Figure 5.3b) to 50 mV/s (Figure 5.3d) and to 500 mV/s (Figure 5.3f), the location of the dotted line shifts increasingly lower than the other two, which means that the supported MnO₂ on rGO degrades more significantly than CNTs and AB. The observation on the poor rate capability of supported MnO₂ is consistent with that of the MnO₂/rGO composite. It should be noted that the interaction between MnO₂ and C is purely physical binding without any chemical modification. Carbon supports only serve as conducting additive and substrate. Despite rGO has the largest intrinsic capacitance, its large sheet morphology and high porosity might inhibit the charge transfer,^{10,22} and giving poor rate capability. The above set of results proves that rGO is not always the best conductive support. The selection of the conductive additive for supercapacitor highly depends on the real application circumstances. If the device is operated under a low current density (slow scan rate), rGO is preferred and a higher current density (high scan rate) prefers to CNTs or AB.

To further investigate the capacitance retention versus the scan rate, the capacitances of all MnO₂/C composites at each scan rate were shown in Figure 5.4. In general, they all exhibit the typical capacitance-retention trend: the mass capacitance of these 3 MnO₂/C composites decreases with the increasing scan rate. Across various MnO₂ wt%, the rate

capability of MnO₂/CNTs and MnO₂/AB almost overlaps with each other. However, as shown in the insets of Figure 5.4a and Figure 5.4b, the performance drop of MnO₂/rGO is the most remarkable at relatively lower MnO₂ wt% (20 and 40 wt%). This is consistent with the previous discussion that the charge transportation within MnO₂/rGO possesses higher resistance. At high load mass (60 and 80 wt%), the percentage of capacitance decrease of MnO₂/rGO composite almost overlaps with the other two composites (Figure 5.4c and Figure 5.4d). This is due to the lower mass loading of carbon materials eliminates the influence from the carbon supports and thus the difference among various MnO₂/C becomes negligible. It is worth noting that the rate capability of pure rGO is almost the same as pure CNTs and AB. The poor charge transport is only observed when MnO₂ is loaded onto rGO, which indicates the different carbon supports indeed impose significantly different impacts on the interplay with MnO₂.

Figure 5.4 Specific capacitance of MnO₂/C composites normalized by the total mass of MnO₂ and carbon at different scan rates. The 4 panels refer to the 4 compositions: (a) 20 wt%, (b) 40 wt%, (c) 60 wt% and (d) 80 wt% of MnO₂. The inset in each figure shows the capacitance drop in a percentage scale. The highest capacitance measured at 5 mV/s was defined as 100 %.

Figure 5.5 Specific capacitance of MnO₂ from the contribution of supported MnO₂ at different scan rates. The 4 panels refer to the 4 compositions: (a) 20 wt%, (b) 40 wt%, (c) 60 wt% and (d) 80 wt% of MnO₂. The inset in each figure shows the capacitance drop in a percentage scale. The highest capacitance achieved at 5 mV/s was defined as 100%.

After subtracting the double layer capacitance from carbon, the capacitance purely contributed by MnO₂ is examined against the scan rate (Figure 5.5). Similar to Figure 5.4, across various MnO₂ wt%, the rate capability of supported MnO₂ on CNTs and on AB almost overlaps with each other. The performance decay of MnO₂ supported on rGO is the most prominent at relatively lower MnO₂ wt% (20 and 40 wt%), as shown in the insets of Figure 5.5a and Figure 5.5b; and at high load mass (60 and 80 wt%), the percentage of capacitance decrease of MnO₂ supported on rGO composite almost overlaps with the other two composites (Figure 5.5c and Figure 5.5d). The above set of results again confirms that MnO₂/rGO is good at storing energy at slow scan rate, but at fast scan rate, the MnO₂ supported on rGO cannot be sufficiently utilized and therefore

giving poor rate capability. It is well-published that the energy storage on metal oxides relies on two processes: one is the faradaic reaction which involves the insertion/extraction of the charge carrier; the other one is the non-faradaic reaction which involves the adsorption/desorption of the charge carrier. When the scan rate is slow, MnO₂ has enough time to respond to the changing voltage and the faradaic reaction can make a dominating contribution to the capacitance. At a high scan rate, the energy storage is limited by the transport of charge carrier within the composite and thus dominated by the non-faradaic reaction. The experimental results have clearly pointed out that the carbon supports are able to affect the charge transfer inside the MnO₂/C. The origin of the poor rate capability of MnO₂/rGO may be due to the large size of rGO sheets ($> 1 \mu\text{m}$),^{10,22} which inhibits the charge transfer within the composite interface.

Figure 5.6 Galvanostatic charge/discharge curves of MnO₂/C composites with 20 wt% of MnO₂ at the current density of 3 A/g. Solid lines and dash lines refer to 2nd and 1000th cycles, respectively.

The influence of various carbons on the pseudocapacitive stability of MnO₂/C was investigated by Galvanostatic charge/discharge measurement at a constant current density (3 A/g). The difference between the 2nd and 1000th cycle is shown in Figure 5.5 to present the capacitance fading. It is observed that MnO₂/rGO possesses the highest capacitance at the initial cycle but its capacitance decay is the most apparent among 3 types of MnO₂/C. After quantifying the capacitances during the cycling, the stability curves versus the cycle

number are shown in Figure 5.7. With each mass loading of MnO₂, there is no obvious difference between MnO₂/AB and MnO₂/CNTs; they can maintain > 90 % capacitance retention. In contrast, it is clearly seen that the cyclability of MnO₂/rGO is the worst; its capacitance loss is more than 15 %. During the stability test, a brown color was observed in the electrolyte near the working electrode region. We suspect the poor stability of MnO₂/rGO is due to the hydrophilic oxygenated-species on the rGO sheets,^{10,23} which causes the dissolution of electrode materials. With increasing mass loading of MnO₂, the capacitance drop becomes less significant, which results from the fact that a lower mass loading of rGO eliminates its influence on the cyclability.

Figure 5.7 Cyclability of MnO₂/C composites tested by Galvanostatic charge/discharge method at the current density of 3 A/g. The panels show the specific capacitance by total mass of the composite and the capacitance retention (in gray) as the function of cycles for the composites with the MnO₂ mass loading of (a) 20, (b) 40, (c) 60 and (d) 80 wt%.

5.4 Conclusion

Uniform-sized MnO₂ nanoflakes were loaded onto carbon materials to form various MnO₂/C (C = CNTs, rGO and AB) composites. The resulting pseudocapacitive behaviors of these 3 types of composites were in depth studied to reveal the influence of different carbon supports. It was found that MnO₂ supported on rGO can be fully utilized at slow rate and gives the highest capacitance. However, at high scan rates, CNTs and AB displays better energy storage capability. The as-revealed trend offers rational selection of carbon supports for electrochemical device fabrication.

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Chapter 6

Pseudocapacitive Performance of Spinel Ferrite XFe₂O₄ (X = Mn, Co, Ni, Fe): Revealing the Role of MnO₆ Octahedrons for Energy Storage

Chapter 6 reports a systematic study on the pseudocapacitive behavior of spinel XFe₂O₄ ferrites (X=Mn, Fe, Co, Ni) with the aid of in-situ XAS (X-ray absorption spectroscopy). The comparison among different substituents demonstrates that the ability of metal cations to change their valence state governs the pseudocapacitance. The subsequent investigation on various MnFe₂O₄ with different cation distribution proves the superiority of MnO₆ octahedron in energy storage.

6.1 Introduction

Substantial effort has been devoted to the study on the electrochemical performance of manganese oxides (MnO_x) and Mn-containing perovskites.¹⁻⁵ MnO_x is purely built upon MnO₆ octahedron and in perovskite, the rare-earth metal under cuboctahedral coordination is apparently inactive. Because these two crystal structures do not have the site occupation argument, the role of MnO₆ octahedron has been fairly clear; it is unambiguously the electrochemical activity contributor, which is in charge of the energy storage and conversion.¹⁻⁵ However, in spinel, another one of the largest metal oxide family, the character of MnO₆ octahedron still remains as a puzzle. As the spinel framework can accommodate different metal cations in either the tetrahedral site or the octahedral site,⁶⁻⁸ the mysterious mechanism that how the energy storage/conversion proceeds on the spinel is still undiscovered. Numerous studies have focused on spinel oxides as the energy material.⁹⁻¹³ For example, the ORR (oxygen reduction reaction) activity of MnFe₂O₄ is comparable to commercial Pt/C, while Fe₃O₄, CoFe₂O₄, NiFe₂O₄ are nearly inactive.¹⁴ It was found that the pseudocapacitance of MnFe₂O₄ is significantly higher than other spinel ferrites.⁷ Such evidences strongly imply the substituent metal cation and its occupation govern the electrochemical performance. However, the lack of systematic mechanistic studies hinders the fundamental understanding of the way that spinel oxides contribute to the energy storage and conversion, and most importantly, the role of MnO₆ octahedron in such crystal structure.

With the aid of in-situ XAS (X-ray absorption spectroscopy) technique, Chapter 6 presents a systematic study on the relationship between the physical properties of spinel ferrites XFe₂O₄ (X = Fe, Mn, Co and Ni) and their pseudocapacitive performance. Since the pseudocapacitive behavior is a surface sensitive reaction,¹⁵ where only the atoms at/near the surface regions contribute to the energy storage, XFe₂O₄ nanoparticles with diameters less than 10 nm were used to maximize the X-ray absorption signals from the material surface. If the topmost 2 nm is defined as the surface region, 70 % atoms locate at the surface in our ferrite nanoparticles. We start revealing the role of MnO₆ octahedron from the comparison across the different element X (X = Fe, Mn, Co and Ni), where the capability of changing valence state is demonstrated to be the key parameter that governs

the pseudocapacitance of XFe₂O₄. We further vary the occupation of MnFe₂O₄ and prove that the MnO₄ tetrahedron is inactive, but MnO₆ octahedron is the active site.

6.2 Experimental details

Nanoparticle synthesis. The ferrite nanoparticles were synthesized by modified thermal decomposition method.¹⁶ In a typical synthesis of Fe₃O₄ nanoparticles, 3 mmol of Fe(acac)₃ was dissolved in 15 mL oleylamine. The mixture was firstly maintained at 110 °C for 1 hour, followed by refluxing at 300 °C for 1 hour under Ar atmosphere. Nanoparticle powders were washed with ethanol and hexane by centrifuging at 12000 rpm for 15 minutes. The washing process was repeated for three times to remove the excessive amount of oleylamine. The synthesis of other ferrites (XFe₂O₄, X = Mn, Ni, Co) were identical to the method described above but using a molar ratio of 2:1 when feeding Fe(acac)₃ and X(acac)₂ (X = Mn, Ni, Co) in 15 mL oleylamine. After centrifugation, nanoparticle samples were collected by dispersing in hexane or drying in 80 °C oven for 1 hour.

Electrode fabrication. Working electrode was prepared by a traditional method.^{17,18} Before working electrode fabrication, as-synthesized XFe₂O₄ (X = Fe, Co, Ni) powders were calcinated at 300 °C. To turn the inversion degree, as-synthesized MnFe₂O₄ was calcinated at 200, 300, and 400 °C in air for 6 hours. Nanoparticles were then mixed with Vulcan carbon CX72 with a mass ratio of C:XFe₂O₄ = 40:60. The as-prepared C/XFe₂O₄ (XFe₂O₄ = 60 w%) material and polyvinylidene difluoride (PVDF) were mixed in a mass ratio of 90:10 and dispersed in N-methyl pyrrolidone (NMP). The resulting slurry was pasted onto nickel foam substrate (1 cm × 1 cm) with a spatula. After drying at 80 °C for 12 hours, the electrode was pressed at a 10 MPa pressure.

6.3 Results and discussion

Before pseudocapacitor test, the XFe₂O₄ (X=Fe, Ni, Co, and Mn) nanoparticles were loaded onto Vulcan carbon to exclude the possibility that the conductivity may serve as a

variable.¹⁹ The XFe₂O₄ nanoparticles are well-dispersed on carbon support (Figure 6.1) and thus eliminating the influence of particle aggregation on pseudocapacitive performance. The size distribution extracted from TEM images shows that these nanoparticles range from 7.0 ~ 9.5 nm (Figure 6.2). All the spinel ferrites are pure in phase as confirmed by synchrotron XRD patterns (Figure 6.3).

Figure 6.1 (a) MnFe₂O₄, (b) CoFe₂O₄, (c) NiFe₂O₄, and (d) Fe₃O₄. Their average diameters are 7.0 ± 1.0 , 8.1 ± 2.5 , 9.5 ± 2.0 , and 7.2 ± 0.9 nm, respectively.

Figure 6.2 Synchrotron XRD (X-ray diffraction) patterns of MnFe₂O₄, CoFe₂O₄, NiFe₂O₄ and Fe₃O₄ spinel ferrites.

Figure 6.3 Size distribution of carbon supported ferrite nanoparticles: (a) MnFe₂O₄, (b) CoFe₂O₄, (c) NiFe₂O₄, and (d) Fe₃O₄.

Figure 6.4 (a) CV curves of spinel ferrites in 1 M Na₂SO₄ at a scan rate of 5 mV/s. (b) Specific capacitance of spinel ferrites normalized to the mass of ferrites (black squares) and the surface area of ferrite nanoparticles (red circles). The specific surface area of ferrite nanoparticles is obtained by BET method. The double layer capacitance contribution of Vulcan carbon has been subtracted.

Table 6.1 Summary of specific surface area for XFe₂O₄ (X = Mn, Fe, Co, Ni).

S/N	Sample	Surface area (m ² /g)
1	Fe ₃ O ₄	166.2
2	CoFe ₂ O ₄	130.3
3	NiFe ₂ O ₄	113.5
4	MnFe ₂ O ₄	150.6

The pseudocapacitive CV (cyclic voltammetry) curves were recorded in 1 M Na₂SO₄ electrolyte at 5 mV/s (Figure 6.4a). The MnFe₂O₄ has the largest CV loop, indicating its specific capacitance is the highest. To quantify the real contribution from spinel oxides, the capacitance from carbon was subtracted by the method published previously.²⁰ It can be seen in Figure 6.4b that the either the mass capacitance (capacitance normalized to the mass loading of spinel oxides) or the specific capacitance (capacitance normalized to the surface area of spinel oxides) of MnFe₂O₄ is significantly higher than the others. The surface area of XFe₂O₄ was measured by BET and the results are shown in Table S1. The above results demonstrate that the substituent in spinels indeed has substantial effect on the pseudocapacitance.

To understand the underpinning mechanism of metal cation substitution, the in-situ XAS technique was employed to monitor the structural changes when the pseudocapacitor is running. As the applied potential was gradually increased from 0 to 0.9 V vs Ag/AgCl, only Mn in MnFe₂O₄ displayed apparent edge shift towards the high energy direction (Figure 6.5a), while the Fe remains its edge position unchanged (Figure 6.5b). The in-situ XANES (X-ray absorption near edge structure) spectra indicate the Mn in MnFe₂O₄ is gradually oxidized by the increasing applied potential but Fe does not change. To quantify the oxidation state, the integral method was used to determine the edge position.²¹ The ex-situ oxidation state of Mn in MnFe₂O₄ is +2.6, which is probably due to the partial oxidation by air during the calcination for surfactant removal.^{7,22} The in-situ valence state change of Mn in MnFe₂O₄ is from +2.6 to +2.9. This is similar to the observation of MnO₂, where the Mn undergoes redox reaction between Mn³⁺ and Mn⁴⁺.^{23,24} The smaller valence state variation of MnFe₂O₄ might explain the lower specific capacitance compared with MnO₂. Another possible reason is the inner space for

charge carrier accommodation. MnO₂ crystals have large inner channels,²⁵ while spinel crystal is so densely packed that the void volume is really small. As for the Fe in MnFe₂O₄, the valence state kept unchanged at 2.8+. Since the Mn valence state is the only one variable, it is concluded that the pseudocapacitance of MnFe₂O₄ relies on the redox reaction Mn cations; the Fe cations are inactive and only serve as the building block to construct the spinel structure.

Figure 6.5 In-situ XANES spectra of XFe₂O₄: (a) MnFe₂O₄ (b) CoFe₂O₄; (c) NiFe₂O₄.

Figure 6.6 In-situ XANES spectra of Fe₃O₄.

In the cases of Fe₃O₄, CoFe₂O₄ and NiFe₂O₄, all the edge positions remain unchanged (Figure 6.5 and 6.6). The valence state of Fe kept at 2.7+ in Fe₃O₄; Fe in CoFe₂O₄ and NiFe₂O₄ remained at 2.8+; Co at 2+ and Ni at 3+. The poor capability of changing valence state results in the low capacitance of these spinel ferrites.

The local fine structure change as a function applied potential was further probed by the in-situ EXAFS (extended X-ray absorption fine structure) and the atomic structure information was quantified by the EXAFS fitting. In the typical EXAFS curves of spinel crystals, the 1st shell region ($1 \text{ \AA} < R < 2 \text{ \AA}$) reflects the metal-oxygen bond; the 2nd and 3rd shell region ($2 \text{ \AA} < R < 3.5 \text{ \AA}$) tells the metal cation distribution.^{6,7} For the 1st shell region (Figure 6.7), only the Fourier transformed amplitude of Mn in MnFe₂O₄ increased with increasing applied potential; while others remain unchanged. This means the increasing applied potential increases the coordination number of Mn-oxygen bond but does not touch the others. For the 2nd and 3rd shell region (Figure 6.7), all the curves remained unchanged, indicating the increasing applied potential fails to change metal cation distribution of spinels. Since MnFe₂O₄ is the only one sample that exhibits variation on the EXAFS curves, the spectra were fitted to quantify the atomic information (Figure 6.8 and Table 6.2). Moreover, although the in-situ EXAFS curves of CoFe₂O₄ remained unchanged under the increasing applied potential, they were also fitted for comparison (Figure 6.9 and Table 6.3).

Figure 6.7 In-situ EXAFS spectra of $X\text{Fe}_2\text{O}_4$: (a) MnFe_2O_4 (b) CoFe_2O_4 ; (c) NiFe_2O_4 ; (d) Fe_3O_4 with increasing applied potential.

Figure 6.8 In-situ EXAFS $k^3χ(R)$ spectra and fitting results at MnFe₂O₄ Mn and Fe K edge. (a) 0.084 V; (b) 0.284 V; (c) 0.484 V; (d) 0.684 V; (e) 0.884 V.

Figure 6.9 In-situ EXAFS $k^3\chi(R)$ spectra and fitting results of CoFe₂O₄ at Co and Fe K edge. (a) 0.084 V; (b) 0.284 V; (c) 0.484 V; (d) 0.684 V; (e) 0.884 V.

Table 6.2 Summary of *in situ* EXAFS fitting results for MnFe₂O₄ under different applied potentials.

E _{applied} (V)		0.084	0.284	0.484	0.684	0.884
Tetrahedral site	x _{Mn}	0.513	0.513	0.513	0.513	0.513
	Mn-O (Å)	1.88	1.88	1.89	1.88	1.90
	Mn-O coordination No.	3.0	3.0	3.2	3.5	4.7
	x _{Fe}	0.487	0.487	0.487	0.487	0.487
	Fe-O (Å)	1.92	1.92	1.92	1.92	1.92
	Fe-O coordination No.	3.0	3.0	3.0	3.0	2.9
Octahedral site	y _{Mn}	0.487	0.487	0.487	0.487	0.487
	Mn-O (Å)	2.01	2.01	2.01	2.01	2.03
	Mn-O coordination No.	4.4	4.5	4.6	5.06	6.6
	y _{Fe}	1.513	1.513	1.513	1.513	1.513
	Fe-O (Å)	1.99	1.99	1.99	1.99	1.99
	Fe-O coordination No.	4.5	4.5	4.4	4.5	4.4

Table 6.3 Summary of *in situ* EXAFS fitting results for CoFe₂O₄ under different applied potentials.

E _{applied} (V)		0.084	0.284	0.484	0.684	0.884
Tetrahedral site	x _{Co}	0.109	0.109	0.109	0.109	0.109
	Co-O (Å)	1.81	1.80	1.80	1.81	1.81
	Co-O coordination No.	3.4	3.4	3.5	3.5	3.6
	x _{Fe}	0.891	0.891	0.891	0.891	0.891
	Fe-O (Å)	1.93	1.93	1.92	1.92	1.93
	Fe-O coordination No.	3.0	3.0	3.0	3.0	3.0
Octahedral site	y _{Co}	0.891	0.891	0.891	0.891	0.891
	Co-O (Å)	2.06	2.06	2.07	2.06	2.06
	Co-O coordination No.	5.2	5.1	5.1	5.3	5.4
	y _{Fe}	1.109	1.109	1.109	1.109	1.109
	Fe-O (Å)	1.99	1.99	1.98	1.98	1.99
	Fe-O coordination No.	4.5	4.5	4.5	4.5	4.5

The inactive nature of Fe is again proven by the fact that all the Fe-O bond lengths and coordination numbers almost did not change, which is in accordance with the in-situ

XANES results. It is interesting to observe that the Mn-O bond length did not change, but an apparent increase of the coordination number was listed in Table 6.2. The values for Mn at octahedral and tetrahedral site are smaller than the theoretical number (6 for octahedral site and 4 for tetrahedral site). This is because our nanoparticles are so small that the surface undercoordinated atoms are dominant, which is also proposed as the origins of energy storage at metal oxides.²⁶ The variation of the coordination number is explained by the oxidation state variation of Mn as observed in in-situ XANES. When the Mn is oxidized, it needs more coordination to compensate the charge.

Figure 6.10 XRD patterns of MnFe₂O₄ calcinated at different temperatures.

Figure 6.11 CV scans of MnFe₂O₄ - 200 °C, MnFe₂O₄ - 300 °C and MnFe₂O₄ - 400 °C at the scan rate of 5 mV/s in 1 M Na₂SO₄.

Table 6.4 Summary of specific surface area for various MnFe₂O₄ calcinated at different temperatures.

S/N	Sample	Surface area (m ² /g)
1	MnFe ₂ O ₄ - 200 °C	150.6
2	MnFe ₂ O ₄ - 300 °C	133.8
3	MnFe ₂ O ₄ - 400 °C	114.9

Figure 6.12 (a) Specific capacitance of MnFe₂O₄ heated treated in air at 200, 300 and 400 °C. Black squares and red circles refer to the capacitance normalized to the mass and the surface area of spinel nanoparticles, respectively. The double layer capacitance contribution of Vulcan carbon has been subtracted. (b) Fourier transforms (FT) of Mn K-edge EXAFS spectra of MnFe₂O₄. (c) Occupation of Mn cations in tetrahedral and octahedral sites as a function of temperature. (d) The specific capacitance per surface area of MnFe₂O₄ as a function of Mn in octahedral sites.

To further compare the pseudocapacitance of MnO₄ tetrahedron and MnO₆ octahedron, the cation distribution was tuned by calcinating MnFe₂O₄ in air at 200, 300 and 400 °C. The heat treatment temperature is the key parameter that controls the Mn occupation and the Mn valence state.^{7,27-29} The phase purity was confirmed by the XRD patterns, where no other impurities were found (Figure 6.10). The surface area of various MnFe₂O₄ is shown in Table 6.4. According the area under the CV loops, it is observed that the higher calcination temperature gives higher mass capacitance (Figure 6.11). After subtracting the contribution from carbon support, the real contribution of spinel oxides are show in Figure 6.12a. Either the mass capacitance or the specific capacitance trend indicates the higher heat treatment temperature leads to the better pseudocapacitive performance.

To understand the origin of the pseudocapacitance enhancement, EXAFS fitting was employed to probe the occupation variation resulting from the calcination temperature. It was found that increasing the heat treatment temperature pushes more Mn to the octahedral sites and Fe to the tetrahedral sites (Figure 6.12b and c). In MnFe₂O₄ - 200 °C, 49 % Mn cations locate at the octahedral sites; for MnFe₂O₄ - 300 °C, there are 70 % Mn cations are under octahedral coordination and MnFe₂O₄ - 400 °C has 91 %.^{24,25} When the specific capacitance was correlated with the fraction of Mn occupation at the octahedral sites (Figure 6.12d), the remarkable linear relationship signifies that the MnO₆ octahedron is responsible for the pseudocapacitive energy storage, while MnO₄ tetrahedron is electrochemically dead.

It should be noted that the initial Mn valence state in oxides is considered not to be influential to supercapacitor performance. The successive multiple redox reactions lead to the pseudocapacitive charge storage mechanism.^{23,24} With CV (cyclic voltammetry) scans, Mn is subjected to cycles of oxidation and reduction, and meanwhile the charge/discharge takes place. It does not matter what the starting point (the initial valence state) of Mn is, as long as the CV potential window covers the Mn redox potential, Mn will be oxidized/reduced.^{23,30} The valence state independence of supercapacitor capacitance is also verified by comparing our MnFe₂O₄-300 °C and MnFe₂O₄-400 °C. They have the same Mn valence state (Figure 6.13) but MnFe₂O₄-400 °C (with more Mn at octahedral site) outperforms MnFe₂O₄-300 °C. This again confirmed the importance of MnO₆ octahedron.

Figure 6.13 XANES spectra of (a) Mn and (b) Fe K-edge at MnFe₂O₄ calcinated at different temperatures. Valence state of (c) Mn and (d) Fe K-edge at MnFe₂O₄ calcinated at different temperatures.

6.4 Conclusion

With different metal cations to substitute Fe₃O₄, the comparison of XFe₂O₄ (X = Fe, Mn, Co and Ni) featured the advantage of Mn in electrochemical performance. It was found the superior pseudocapacitance of MnFe₂O₄ originates from the ability of Mn cation to change its valence state. Fixing the nominal formula as MnFe₂O₄ and tuning the cation distribution via heat treatment helped differentiate the pseudocapacitive contribution from MnO₄ tetrahedron and MnO₆ octahedron. Our results proved that MnO₆ octahedron is in charge of storing the energy relying on its capability of changing valence state.

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Chapter 7

Oxygen Electrocatalysis Performance on Spinel: Revealing the Role of MnO₆ Octahedrons for Energy Conversion

This Chapter presents a systematic study on oxygen electrocatalysis (ORR and OER) of spinel oxide catalysts starting with MnCo₂O₄. It was found that MnCo₂O₄ synthesized at different temperatures share the same Mn/Co content in the same crystal playground, but exhibit different ORR/OER catalytic activities. X-ray absorption spectroscopy studies reveal that the different ORR/OER activities are determined by the Mn valence state and the number of MnO₆ octahedrons. Co only serves as a building block to construct spinel crystal framework and has negligible activity contribution. This mechanistic principle is further applied to successfully explain the ORR/OER activities of other transition metal spinels. The e_g occupancy and occupation fraction of the active element at octahedral site is dominant in determining the ORR/OER catalytic activities of transition metal spinels.

7.1 Introduction

Oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) are essential half reactions to drive many energy storage and conversion systems such as fuel cells,^{1,2} meta-air batteries,^{3,4} and water electrolyzers.^{5,6} Due to the sluggish kinetics of oxygen electrocatalysis, the dominant energy loss of those energy applications originates from ORR/OER.⁷ Developing efficient and low-cost catalysts for ORR/OER has attracted significant effort in the past decades. Particular interest has fallen within the family of MnO₆ octahedron-based oxides because of their earth-abundance, nontoxicity and mostly importantly the excellent activities, which are comparable to the state-of-art catalysts.⁸⁻¹⁰ It thus necessitates a fundamental understanding of the physical origin underlying the MnO₆ octahedron. Recent studies have elucidated the relation between the physical properties of MnO₆ octahedron-based perovskites and their oxygen electrocatalysis performance.^{8,10-12} However, when putting MnO₆ octahedron in the crystal structure of spinel oxides, the character of MnO₆ octahedron still remains as a puzzle. Spinel is a more challenging and interesting problem because metal cations in spinel can occupy either the tetrahedral or octahedral site,^{13,14} while there is no site occupation argument in perovskite. Although numerous studies have investigated the oxygen electrocatalysis on spinel oxides,¹⁵⁻¹⁹ most existing reports are based on the mass activity (normalized to the mass loading of active material) discussion, which cannot reflect the real mechanism underlying the surface-sensitive electrochemical process. Unveiling the mysteries of MnO₆ octahedron in spinels has been hindered by the lack of systematic studies base on the intrinsic specific activity (normalized to the real surface area of electrode materials) analysis.

Chapter 7 is devoted to reveal the role of MnO₆ octahedron in spinel oxides. We fix the nominal formula as MnCo₂O₄ and tune the electronic structure via controlling the heat treatment temperature. With the aid of XAS (X-ray absorption spectroscopy), the physical properties (e.g., valence state and cation distribution) of various MnCo₂O₄ is correlated with the electrochemical performance. It is found that the valence state of the Mn in MnO₆ octahedron and the fraction of Mn that occupies in the octahedral site simultaneously govern the ORR/OER activity. The discovered principle is further

demonstrated by extending to elucidate the physical origin of ORR/OER at a broader range of transition metal spinels.

7.2 Experimental details

Material synthesis. Most Mn_xCo_{3-x}O₄ catalysts used in this report were synthesized via a modified conventional solid state reaction.^{13,20} 9 mmol mixture of Mn(NO₃)₂·4H₂O and Co(NO₃)₂·6H₂O was dissolved in 15 mL of DI water, followed by stirring and vaporization in 80 °C oven. The resulting slurry was calcinated at 250 °C for 2 hours in air to completely decompose nitrous. After grinding, the black oxide powders underwent calcination in air for 8 hours. Calcination temperature of 400 °C, 500 °C, 700 °C and 900 °C were used to prepare different MnCo₂O₄ catalysts. MnCo₂O₄-500 °C was also calcinated in form of pellets for a total duration of 24 hours with two intermediate procedures of re-grinding and re-pressing to ensure the formation of a homogeneous phase. Mn_xCo_{3-x}O₄ (0 ≤ x ≤ 1) cubic spinels synthesized at 400 °C were prepared by varying the feeding ratio of Mn to Co. NiCo₂O₄, ZnCo₂O₄ and Co₃O₄ were synthesized with the same method and annealed at 400 °C.

MnCo₂O₄ synthesized at 150 °C were produced by hydrothermal method.¹⁸ 0.533 mL of 0.6 M Co(OAc)₂ (cobalt acetate) and 0.266 mL of 0.6 M Mn(OAc)₂ (manganese acetate) solution were mixed with 0.3 mL DI water and 0.5 mL NH₄OH at room temperature. After ultrasonication, the mixture was transferred to autoclave, where the reaction was maintained at 150 °C for 3 hours. The precipitate was collected by centrifugation. Mn₁Co₂O₄ synthesized at 300 °C were produced by colloidal method. A solution of 1 mmol Mn(acac)₃, 2 mmol Co(acac)₂ (acac = acetylacetonate) and 15 mL oleylamine in a three-necked flask was kept at 120 °C under Ar flow for 30 minutes, followed by refluxing at 300 °C for 2 hours. After centrifugation, the synthesized powder was further annealed at 300 °C for 8 hours in air to remove the excessive surfactant.

The ferrite nanoparticles (XFe₂O₄, X = Ni, Co, Fe) were synthesized by modified thermal decomposition method.²¹ In a typical synthesis of Fe₃O₄ nanoparticles, 3 mmol of Fe(acac)₃ were dissolved in 15 mL oleylamine. The mixture was firstly maintained at 110 °C for 1 hour, followed by refluxing at 300 °C for 1 hour under an Ar atmosphere.

Nanoparticle powders were washed with ethanol and hexane by centrifuging at 12000 rpm for 15 minutes. The washing process was repeated for three times to remove the excessive amount of oleylamine. The synthesis of other ferrites (XFe₂O₄, X = Ni, Co) were identical to the method described above but using a molar ratio of 2:1 when adding Fe(acac)₃ and X(acac)₂ (X = Ni, Co) in 15 mL oleylamine. After centrifugation, nanoparticle samples were collected by dispersing in hexane or drying in 80 °C oven for 1 hour. Before the fabrication of the working electrode, the synthesized XFe₂O₄ (X = Mn, Co, Ni) powders were calcinated at 300 °C for 1 hour. MnFe₂O₄ was further annealed at 500 °C for 6 hr in Ar.

LiMn₂O₄ catalyst was a Sigma-Aldrich product. Li_{0.7}Mn₂O₄ was synthesized by a delithiation reaction with LiMn₂O₄ as the precursor. LiMn₂O₄ was added to a 0.1 M HNO₃ solution to form an aqueous suspension (100 mg/10 mL). After 2 h sonication, powder product was collected by centrifugation, decanting and washing with bicarbonate solution and DI-H₂O. As-obtained powder was dried at 90 °C in oven.

Electrode preparation. Oxide electrode was fabricated by drop-casting catalysts onto glassy carbon (GC) electrode with a modified ink recipe as described elsewhere.²² Catalysts inks were prepared by ultrasonicated spinel oxides, acetylene black (AB) and Na⁺-exchanged Nafion in tetrahydrofuran (THF, purity 99.9%) for 1 hour. The concentrations are 1.8 mg_{Oxide} mL⁻¹, 4.2 mg_{AB}/mL⁻¹ and 1 mg_{Nafion}/mL⁻¹. 10 µL of as-prepared ink was drop-cast onto rotating disk GC electrode (RDE, 0.196 cm², PINE) and dried overnight at room temperature. Prior to ink preparation, the AB (Alfa Aesar, 50% compressed, specific area 80 m² g⁻¹) was pre-treated in concentrated nitric acid at 80 °C overnight. Na⁺-exchanged Nafion was prepared as reported previously.²³ After measurement, GC electrode was polished using alumina slurry for 30 minutes and cleaned by repeated ultrasonication in ethanol and DI water.

Commercial Pt/C (40 wt%, Sigma-Aldrich) electrode was measured as a control experiment. Pt/C was dispersed in a mixture of solvents containing water, isopropanol and Nafion® perfluorinated resin solution (5 wt% in water) (v/v/v = 4/1/0.04) by sonication for 1 hour. 15 µL of this ink was then dropped onto the RDE and dried at room temperature, yielding a Pt mass loading of 2 µg (10.2 µg cm⁻²_{disk}). Surface area of Pt was

assessed from the electrochemical H adsorption/desorption, and giving a specific surface of 40.9 m² g⁻¹.

Electrochemical characterization. Oxygen electrocatalysis tests were conducted with a rotating-disk electrode (Pine) using a PINE WaveDriver 20 bipotentiostat. The 0.1 M KOH electrolyte was prepared from Milli-Q water (18.2 MΩ·cm) and KOH pellets. All electrochemical results were collected in a three-electrode glass cell with a working electrode of glass carbon RDE (rotating disk electrode, 0.196 cm²), a counter electrode of platinum wire, and a saturated calomel reference electrode (SCE). All potentials were referenced to RHE scale (RHE = SCE + 1.0127 V) and iR corrected. The resistance (45 Ω) was determined by impedance measurement.⁹

Determination of e_g occupancy. Co³⁺ (*t*_{2g}⁶*e*_g⁰, LS)^{24,25} at octahedron is catalyzing the reaction in Co₃O₄ and ZnCo₂O₄. In the case of NiCo₂O₄, most Ni cations (~84%) go to octahedral sites and thus Ni^{2.5+} (*t*_{2g}⁶*e*_g^{1.5}, LS)^{24,25} is defined as the active site. The identification of Ni as the active site is also confirmed by the greatly enhanced activity of Ni-substituted Co₃O₄ than Co₃O₄.²⁶ CoFe₂O₄ and NiFe₂O₄ are inverse spinels with Co²⁺/Ni²⁺ predominantly occupying the octahedral position. Because Co²⁺ (*t*_{2g}⁵*e*_g², HS),²⁷⁻²⁹ Ni²⁺ (*t*_{2g}⁶*e*_g², HS),²⁹⁻³¹ Fe²⁺ (*t*_{2g}⁴*e*_g², HS)^{29,30} and Fe³⁺ (*t*_{2g}³*e*_g², HS)^{29,30} have the same e_g occupancy, they are considered to have equivalent activity. Therefore, in CoFe₂O₄, both Co and Fe on the octahedral position are active sites. Similarly, in NiFe₂O₄, both Ni and Fe on the octahedral position are active sites. As Mn₂Co₁O₄, Mn_{2.5}Co_{0.5}O₄, and Mn₃O₄ have octahedral sites fully filled with Mn, the active sites are determined to be Mn^{3.2+} (*t*_{2g}³*e*_g^{0.8}, HS), Mn^{3.1+} (*t*_{2g}³*e*_g^{0.9}, HS), and Mn^{3.0+} (*t*_{2g}³*e*_g¹, HS), respectively.¹³ Similarly, since LiMn₂O₄ and Li_{0.74}Mn₂O₄ have octahedral sites fully occupied by Mn and tetrahedral solely occupied by Li,³² the active sites are Mn^{3.5+} (*t*_{2g}³*e*_g^{0.5}, HS), Mn^{3.7+} (*t*_{2g}³*e*_g^{0.3}, HS).³³ MnFe₂O₄ is Mn^{2.1+} (*t*_{2g}³*e*_g^{1.9}, HS).³⁴ Detailed results are shown in Table 7.2.

7.3 Results and discussion

Figure 7.1 (a) Spinel crystal structure. (b) XRD patterns of MnCo₂O₄ synthesized at 150, 300, 400, 500, 700, 900 °C. (c) BET surface area of various MnCo₂O₄.

The phase purity of various MnCo₂O₄ cubic spinels were confirmed by XRD (X-ray diffraction pattern) patterns (Figure 7.1b), where they all match the standard cubic spinel patterns. The surface area was evaluated by BET (Brunauer-Emmett-Teller) measurement (Figure 7.1c).

The CV curves of ORR and OER at MnCo₂O₄-900 °C, as an example, are shown in Figure 7.2a and b. For ORR, the geometric limiting current density of MnCo₂O₄-900 °C is ~5.5 mA cm⁻²_{disk}. This value falls within 10 % of 5.7 mA cm⁻²_{disk}, which is the theoretical value for 4e⁻ reaction pathway in 0.1 M KOH electrolyte.^{35,36} This validates that Koutecky-Levich is reliably applicable to quantify the electron transfer number.³⁵

The slope of Koutecky-Levich plot at MnCo₂O₄-900 °C is the same as Pt/C (inset, Figure

7.2b), indicating the number of electron transfer is 4.⁹ The ORR/OER Tafel plots of specific activity are shown in Figure 7.2c and 7.2d. The activities of the state-of-art catalysts for ORR and OER were estimated to prove that the electrochemistry experiment in this work is reliable. The limiting current density of commercial Pt/C (40 wt%) is 5.7 mA cm⁻²_{disk} (Figure 7.3a); the Tafel plots normalized to the mass loading of Pt and the surface area of Pt are in accordance with the landmark studies.^{22,37} The OER specific activity is also consistent with the previous work.³⁸

Figure 7.2 (a) ORR CV curves of MnCo₂O₄-900 °C in O₂-saturated 0.1 M KOH with a scan rate of 10 mV/s and rotation speeds of 100, 400, 900, 1600 rpm. The inset is the Koutecky-Levich plots of MnCo₂O₄-900 °C (black) and Pt/C (red) at 0.5 V vs. RHE. (b) The background-correction and iR-correction of OER CV curves on MnCo₂O₄-900 °C in O₂-saturated 0.1 M KOH with a scan rate of 10 mV/s at the rotation speed of 1600 rpm. (c) ORR and (d) OER specific activities, i_s , of various MnCo₂O₄ spinels oxides. ORR Tafel plots were obtained from the capacity-corrected negative-going CV scans at 10 mV/s with a rotation speed of 1600 rpm. Error bars represent at least three independent measurements.

According to either ORR or OER Tafel plots (Figure 7.2c and 7.2d), it generally follows the trend that higher heat treatment temperature gives better oxygen electrocatalysis activity. An exception is MnCo₂O₄-150 °C, which even shows higher specific activity than MnCo₂O₄-500 °C. The confusion will be clarified in the following section. Herein, the results indicate that the heat treatment temperature must have tuned the electronic structure of MnCo₂O₄ cubic spinels, despite they have the same Mn/Co content in the same crystal playground.

Figure 7.3 (a) The positive-going and negative-going CV scans after background-correction. The activity of Pt/C was extracted from the the postive-going scan. (b) OER measurement at IrO₂ catalyst.

To understand the underlying mechanism, identifying the active site is necessary. We noticed that both Mn and Co could be the active site of MnCo₂O₄ cubic spinels because the individual MnO_x and CoO_x have been well-published as good ORR/OER catalysts.^{17,39,40} Although attempts and predictions have been made on MnO_x and CoO_x,^{41,42} direct evidences are still missing. In this work, we experimentally demonstrated that Mn cation serves as the active site. First, XANES (K-edge X-ray near edge spectroscopy, Figure 7.4a and 7.4b) shows that edge position of Mn K-edge changes with different heat treatment temperature. In contrast, the position of Co K-edge remains unchanged. This means that the valence state of Mn is varied, but Co not. By quantifying

the valence state with the integral method,⁴³ it can be seen that Mn valence state is varied between 3.2 and 3.7, while Co maintains at 2.5.

Figure 7.4 (a) Mn and (b) Co K-edge XANES spectra of various MnCo₂O₄ oxides and standard samples. EXAFS $k^3χ(R)$ spectra (gray circles) and fitting results (solid lines) of MnCo₂O₄ oxides at (c) Mn and (d) Co K-edge. (e) Mn and Co valence state as a function of synthesis temperature. Edge position is determined by integral method.⁴³ (f) Mn occupation at tetrahedral and octahedral sites in various MnCo₂O₄ oxides, determined by EXAFS fitting.

Figure 7.5 XANES pre-peaks of various MnCo₂O₄ at (a) Mn and (b) Co K-edge.

Table 7.1 Summary of EXAFS fitting results for MnCo₂O₄ synthesized at different temperatures.

Sample		150 °C	300 °C	400 °C	500 °C	700 °C	900 °C
Tetrahedral site	x_{Mn}	0.509	0.064	0.104	0.195	0.198	0.107
	Mn-O (Å)	1.82	1.92	1.77	1.77	2.14	1.74
	Mn-O coordination No.*	3.6	3.4	3.8	3.8	4.0	4.0
	x_{Co}	0.491	0.936	0.896	0.805	0.802	0.893
	Co-O (Å)	1.90	1.97	1.92	1.92	1.93	1.86
	Co-O coordination No.	3.5	3.4	3.9	3.8	4.0	4.0
Octahedral site	y_{Mn}	0.491	0.936	0.896	0.805	0.802	0.893
	Mn-O (Å)	1.92	1.90	1.89	1.89	1.92	1.91
	Mn-O coordination No.	5.4	5.1	5.7	5.7	6.0	6.0
	y_{Co}	1.509	1.064	1.104	1.195	1.198	1.107
	Co-O (Å)	1.93	1.92	1.92	1.92	1.91	1.97
	Co-O coordination No.	5.3	5.2	5.8	5.8	6.0	6.0

Second, EXAFS (X-ray absorption spectroscopy, Figure 7.4b and 7.4c) technique was employed to quantify the cation distribution, metal-oxygen bond distance and coordination number. Results show that in various MnCo₂O₄ cubic spinels, either the occupation of Mn or Co is generally the same (Figure 7.4f, ~80% Mn cations occupy at

the octahedral site and ~10% Co cations at the tetrahedral site). The unchanged cation distribution is further supported by the shape of pre-edge peaks in XANES (Figure 7.5), which can qualitatively tell the cation occupation. Metal cation at octahedral site results in a broad pre-peak, while tetrahedral-coordinated metal cation has a sharp one.^{44,45} Both the Mn and Co XANES pre-peaks keep their shape unchanged. Therefore the overall cation distribution is the same. Moreover, in each MnCo₂O₄ oxide, the coordination number of Mn-O bond (either at tetrahedral or octahedral site) is nearly the same as that of Co-O bond. It indicates the surface Mn/Co ratio is equal to the bulk Mn/Co ratio and this eliminates the possibility that the different activity results from the formation of a Mn-rich or Co-rich surface. Hereby, as revealed by XAS, heat treatment temperature of MnCo₂O₄ cubic spinels varies the physical property of Mn, but does not change Co and the overall cation occupancy of tetrahedral/octahedral sites. As the single variable, Mn is concluded as the active site which governs the different ORR/OER behaviors of MnCo₂O₄ cubic spinels.

Figure 7.6 (a) ORR activity at 25 $\mu\text{A cm}^{-2}_{\text{Oxi}}$ of various MnCo₂O₄ oxides as a function of nominal Mn valence state. The indicated volcano trend (gray dash line) is the data extracted and adapted from ref 47 (assuming a Tafel slope of 60 mV/decade). (b) OER activity at 25 $\mu\text{A cm}^{-2}_{\text{Oxi}}$ as a function of nominal Mn valence state on various MnCo₂O₄ spinels. The gray dash line is the data extracted and adapted from ref 12 (using a 60 mV/decade Tafel slope and a high spin state of Mn cation). Each data point represents three independent measurements.

It has been established that the e_g filling of octahedral-coordinated B cation is the activity descriptor in governing the ORR and OER activities of perovskite catalysts.^{11,12,46} In our various MnCo₂O₄, since most Mn cations go to octahedral sites and the Mn valence state is relevant to the antibonding orbital occupancy of Mn-O bond, we examine the ORR/OER specific activity as a function of the Mn valence state. The specific activity is defined as the potential to reach a given specific current density ($25 \mu\text{A cm}^{-2}_{\text{Oxi}}$ for ORR and OER). Interestingly, it is found that MnCo₂O₄ spinels generally fit the volcano trend extracted from the landmark work on perovskites,^{12,47} which is a hint that the underlying mechanisms of these two materials (spinel and perovskite) are interlinked. The summit locates at Mn^{3.3+} for ORR and Mn^{2.7+} for OER (Figure 7.6a and 7.6b). This is indicative of Sabatier's principle, where too high Mn valency gives too strong interaction with oxygen and low Mn valency gives too weak binding. ORR/OER activity is optimized by a balanced situation. It also draws our attention that the ORR/OER volcano shape exhibits an asymmetric feature, where the optimum Mn valence states are slightly different. This implies the different energy barrier for the seemingly reversible ORR/OER reaction steps.

Figure 7.7 Tafel plots of (a) ORR and (b) OER specific activity of Co₃O₄ and ZnCo₂O₄.

It is worth noting that these MnCo₂O₄ spinels do not perfectly fit the volcano trend extracted from perovskites (the gray dash line in Figure 4a and 4b). This is ascribed to the influence of Mn cation occupation. Spinel crystal framework gives each metal cation two choices: either to occupy the tetrahedral site or octahedral site. Because in the best

catalyst of this work (MnCo₂O₄-900 °C), where 90 % Mn cations are under octahedral coordination, it is proposed that the octahedral site is in charge of catalyzing ORR/OER for spinel oxide materials. First, to further support this hypothesis, we compared the ORR/OER performance of Co₃O₄ and ZnCo₂O₄. Zn²⁺ cation has a strong preference for tetrahedral site⁴⁸⁻⁵⁰ and is considered to be electrochemical dead because of its d¹⁰ electronic configuration. The comparison between Co₃O₄ and ZnCo₂O₄, therefore, aims to reveal the role of tetrahedral-coordinated Co²⁺. As shown in Figure 7.7, the ORR and OER Tafel plots of these two catalysts overlap with each other, suggesting that blocking the tetrahedral site does not cause any negative impact. The tetrahedral-coordinated Co²⁺ is not the active site, but the octahedral-coordinated Co³⁺ is. Our result is consistent with a previous measurement on electrochemical deposited Co₃O₄ and ZnCo₂O₄ electrodes.⁴⁸ Therefore we tentatively say that the octahedral site of spinel oxides is the active site.

Figure 7.8 Spatial arrangement of oxygen ligands in a metal-oxygen (a) octahedral and (b) tetrahedral coordination with respect to five d-orbitals. (c) The energy levels of the degenerate d-orbitals in octahedral and tetrahedral coordination.

Second, metal cation with tetrahedral coordination has completely different d-orbital degeneracy compared with octahedral coordination.⁵¹ In octahedral coordination (Figure 7.8a and c), the e_g orbital directly points to O and thus has a strong spatial overlap with O-2p orbital. The strong overlap inspires the discovery of e_g as the activity descriptor in perovskite catalysts.¹¹ However, in tetrahedral coordination (Figure 7.8b and c), neither the e nor the t_2 orbital directly points to O. The angle between the e orbital and the ligand is $54^\circ 44'$; for t_2 , the angle is $35^\circ 16'$.⁵¹ The mismatch causes weak spatial overlap with O, which results in a weak interaction between tetrahedral-coordinated metal and O, as supported by Co^{2+} at the tetrahedral site of spinel.⁵²

Figure 7.9 (a) ORR activity at $25 \mu\text{A cm}^{-2}_{\text{ox}}$ of various MnCo_2O_4 oxides as a function of nominal Mn valence state. (b) OER activity at $25 \mu\text{A cm}^{-2}_{\text{ox}}$ as a function of nominal Mn valence state on various MnCo_2O_4 spinels. ORR and OER activity are occupation-corrected. The gray dash lines are the same as Figure 7.6.

Hereafter, we take into account of the occupation influence that ORR/OER activity of MnCo_2O_4 is only contributed by the Mn at octahedral sites. The occupation effect was corrected by further normalizing the specific current density to the fraction of MnO_6 octahedrons and the relationship between ORR/OER activity and Mn valence state was re-examined. With occupation-correction, these spinels fit perfectly to the volcano trend (Figure 7.9), suggesting that the Mn valence state is the major descriptor and the fraction of MnO_6 octahedrons serves as a secondary descriptor for MnCo_2O_4 spinels. The

importance of Mn occupation explains why the ORR and OER activities of MnCo₂O₄-150 °C are lower than the expected ones (below the gray dash line, Figure 7.6) even though the valence state of Mn in it is ~3.2. This is because only ~50 % Mn forms MnO₆ octahedrons and thus less Mn cations are able to contribute. After occupation-correction, MnCo₂O₄-150 °C fits well with the volcano plots (Figure 7.9).

With the as-established knowledge of Mn valency and occupation for ORR/OER at MnCo₂O₄, a general principle is further developed for describing the ORR/OER at other transition metal spinels. The oxidation state is a reflection of electronic structure and partially represents the antibonding filling state. It is therefore postulated that the e_g occupancy of the active element at octahedral site is the activity descriptor for ORR/OER at spinels. For each spinel, the active element and its e_g occupancy was determined by EXAFS and XANES (Figure 7.10 and Figure 7.11). The detailed results are shown in section 7.2 and Table 7.2.

Figure 7.10 EXAFS $k^3\chi(R)$ spectra data and fitting results of MnFe₂O₄, CoFe₂O₄, NiFe₂O₄ and NiCo₂O₄ at K-edge. Detailed results are in Table 7.2.

Figure 7.11 (a) XANES spectra of $\text{Mn}_x\text{Co}_{3-x}\text{O}_4$ tetragonal spinels at Mn K-edge. (b) XANES spectra of $\text{Li}_x\text{Mn}_2\text{O}_4$ cubic spinels at Mn K-edge. (c) XANES spectra of MnFe_2O_4 cubic spinels at Mn K-edge. (d) NiCo_2O_4 cubic spinel at Ni K-edge. For the detailed information about the spinel ferrites, please see our previous results of CoFe_2O_4 and NiFe_2O_4 in Chapter 6.

Table 7.2 Summary of the electron assignment of spinels measured in this work.

S/N	Sampe	Octahedral site	Tetrahedral site
1	MnCo ₂ O ₄ - 150 °C	Mn ^{3.23+} ($t_{2g}^3 e_g^{0.77}$, HS) ¹³ Co ³⁺ ($t_{2g}^6 e_g^0$, LS) ¹³	Co ²⁺ ($e^4 t_2^3$, HS) ^{18,19} Mn ^{3.23+} ($e^2 t_2^{1.77}$, HS)
2	MnCo ₂ O ₄ - 300 °C	Mn ^{3.63+} ($t_{2g}^3 e_g^{0.37}$, HS) ¹³ Co ³⁺ ($t_{2g}^6 e_g^0$, LS) ¹³	Co ²⁺ ($e^4 t_2^3$, HS) ^{18,19} Mn ^{3.63+} ($e^2 t_2^{1.37}$, HS)
3	MnCo ₂ O ₄ - 400 °C	Mn ^{3.60+} ($t_{2g}^3 e_g^{0.40}$, HS) ¹³ Co ³⁺ ($t_{2g}^6 e_g^0$, LS) ¹³	Co ²⁺ ($e^4 t_2^3$, HS) ^{18,19} Mn ^{3.60+} ($e^2 t_2^{1.40}$, HS)
4	MnCo ₂ O ₄ - 500 °C	Mn ^{3.51+} ($t_{2g}^3 e_g^{0.49}$, HS) ¹³ Co ³⁺ ($t_{2g}^6 e_g^0$, LS) ¹³	Co ²⁺ ($e^4 t_2^3$, HS) ^{18,19} Mn ^{3.51+} ($e^2 t_2^{1.49}$, HS)
5	MnCo ₂ O ₄ - 700 °C	Mn ^{3.33+} ($t_{2g}^3 e_g^{0.67}$, HS) ¹³ Co ³⁺ ($t_{2g}^6 e_g^0$, LS) ¹³	Co ²⁺ ($e^4 t_2^3$, HS) ^{18,19} Mn ^{3.33+} ($e^2 t_2^{1.67}$, HS)
6	MnCo ₂ O ₄ - 900 °C	Mn ^{3.33+} ($t_{2g}^3 e_g^{0.67}$, HS) ¹³ Co ³⁺ ($t_{2g}^6 e_g^0$, LS) ¹³	Co ²⁺ ($e^4 t_2^3$, HS) ^{18,19} Mn ^{3.33+} ($e^2 t_2^{1.67}$, HS)
7	NiCo ₂ O ₄	Ni ^{2.48+} ($t_{2g}^6 e_g^{1.52}$, LS) ^{24,25} Co ³⁺ ($t_{2g}^6 e_g^0$, LS) ^{24,25}	Co ²⁺ ($e^4 t_2^3$, HS) ^{18,19} Ni ^{2.48+} ($e^4 t_2^{3.52}$, HS) ^{18,19}
8	ZnCo ₂ O ₄	Co ³⁺ ($t_{2g}^6 e_g^0$, LS) ^{24,25}	Zn ²⁺ ($e^4 t_2^6$, HS)
9	Co ₃ O ₄	Co ³⁺ ($t_{2g}^6 e_g^0$, LS) ^{24,25}	Co ²⁺ ($e^4 t_2^3$, HS) ^{18,19}
10	Mn ₂ Co ₁ O ₄	Mn ^{3.18+} ($t_{2g}^3 e_g^{0.82}$, HS) ¹³ Co ³⁺ ($t_{2g}^6 e_g^0$, LS) ¹³	Co ²⁺ ($e^4 t_2^3$, HS) ^{18,19}
11	Mn _{2.5} Co _{0.5} O ₄	Mn ^{3.08+} ($t_{2g}^3 e_g^{0.92}$, HS) ¹³ Co ³⁺ ($t_{2g}^6 e_g^0$, LS) ¹³	Co ²⁺ ($e^4 t_2^3$, HS) ^{18,19} Mn ^{3.08+} ($e^2 t_2^{1.92}$, HS)
12	Mn ₃ O ₄	Mn ³⁺ ($t_{2g}^3 e_g^1$, HS) ¹³	Mn ²⁺ ($e^4 t_2^1$, LS) ¹³
13	MnFe ₂ O ₄	Fe ²⁺ ($t_{2g}^4 e_g^2$, HS)/Fe ³⁺ ($t_{2g}^3 e_g^2$, HS) Mn ^{2.11+} ($t_{2g}^3 e_g^{1.89}$, HS)	Fe ^{3.0+} ($e^2 t_2^3$, HS) ²⁹ Mn ^{2.11+} ($e^2 t_2^{2.89}$, HS)
14	CoFe ₂ O ₄	Co ^{2.00+} ($t_{2g}^5 e_g^{2.00}$, HS) ²⁹ Fe ²⁺ ($t_{2g}^4 e_g^2$, HS)/Fe ³⁺ ($t_{2g}^3 e_g^2$, HS) ^{29,30}	Fe ^{3.0+} ($e^2 t_2^3$, HS) ²⁹ Co ^{2.00+} ($e^4 t_2^3$, HS) ²⁹
15	NiFe ₂ O ₄	Ni ^{2.00+} ($t_{2g}^6 e_g^{2.00}$, HS) ²⁹⁻³¹ Fe ²⁺ ($t_{2g}^4 e_g^2$, HS)/Fe ³⁺ ($t_{2g}^3 e_g^2$, HS) ^{29,30}	Fe ^{3.0+} ($e^2 t_2^3$, HS) ²⁹ Ni ^{2.00+} ($e^4 t_2^{4.00}$, HS) ²⁹
16	LiMn ₂ O ₄	Mn ^{3.50+} ($t_{2g}^3 e_g^{0.50}$, HS) ^{33,53}	Li ⁺ ($1s^2$)
17	Li _{0.74} Mn ₂ O ₄	Mn ^{3.63+} ($t_{2g}^3 e_g^{0.37}$, HS) ^{33,53}	Li ⁺ ($1s^2$)

Figure 7.12 ORR activity on various spinels as a function of e_g occupancy of the active element at octahedral site. The indicated volcano trend (gray dash line) is the same as Figure 7.6. Each data point represents three independent measurements.

Figure 7.13 OER activity on various spinels as a function of e_g occupancy of the active element at octahedral site. The indicated volcano trend (gray dash line) is the same as Figure 7.6. Each data point represents three independent measurements.

After occupation-correction, the specific ORR/OER activity is plotted against the as-extracted e_g occupancy (Figure 7.12 and 7.13). The remarkable volcano-shaped trend demonstrates the applicability of our principle to unify the ORR/OER activity prediction

of transition metal spinels: the e_g occupancy of the active element at octahedral site and its occupation are activity descriptors for oxygen electrocatalysis performance.

The importance of our principle was further demonstrated by plotting the ORR/OER activities as a function of antibonding filling (e-occupancy) at the tetrahedral site element. The resulting plot (Figure 7.14) does not exhibit a correlatable relationship; the antibonding occupancy at tetrahedral site cannot explain the big activity gap (~ 3 orders of magnitude). Interestingly, the electron assignment of the tetrahedral-coordinated metal cations (Table 7.2) implies a hint on the origin of its inactive nature. The e-orbital is so over-filled (more than 2) that the interaction between the reactant and catalyst is too weak.

Figure 7.14 (a) ORR and (b) OER activity on various spinels as a function of e_g occupancy of the active element at tetrahedral site. Black circle is cubic MnCo_2O_4 spinels with Mn as the active element. Red circle is the Mn of tetragonal spinels ($\text{Mn}_2\text{Co}_1\text{O}_4$, $\text{Mn}_{2.5}\text{Co}_{0.5}\text{O}_4$ and Mn_3O_4). Orange circle is the Mn of ferrite. Green up triangle is the Mn of cubic $\text{Li}_x\text{Mn}_2\text{O}_4$ spinels. Blue diamond is the Co of cubic spinels (Co_3O_4 , ZnCo_2O_4 and CoFe_2O_4). Pink square is the Ni of cubic spinels (NiCo_2O_4 and NiFe_2O_4).

It is well known that spinel crystal can undergo a cubic/tetragonal phase transition,¹³ depending on the type and content of metal cation. Considering the Jahn-Teller effect^{54,55} a different crystal field of the octahedral coordination in tetragonal spinels, it possibly results in a different descriptor from the cubic spinel. However, our results indicate both cubic and tetragonal $\text{Mn}_x\text{Co}_{3-x}\text{O}_4$ spinels follow the e_g theory. Although the Jahn-Teller effect elongates the c lattice parameter and consequently the increases Mn-O bonding

length along z-axis, the overall occupancy of e_g orbital remains unchanged and therefore leading to negligible influence on activity. This is consistent with the discussion about the Jahn-Teller effect in Chapter 2.

The volcano trends in Figure 7.12 and 7.13 are not perfect; they are slightly scattered. For example, the spinels with Co or Ni as the active site (Co₃O₄, ZnCo₂O₄, CoFe₂O₄ and NiCo₂O₄) slightly deviate from the dash line. It should be noted that the e_g theory is a very simplified model that is purely based on counting the number of e_g electrons. It cannot take into account of the covalency of metal-oxygen bond or the influence of tetrahedral-coordinated metal cation on the crystal field of octahedral-coordinated metal cation. For example, with the same e_g fillin, the activity comparison of LaMnO₃, LaCoO₃, and LaNiO₃ shows a ~120 mV deviation from the expected volcano trend;^{7,11} the ionic radius of lanthanide (A^{3+}) in AMnO_{3+ δ} perovskites is able to tune the ORR activity.⁵⁶ It limitation explains why the series of Mn_xCo_{3-x}O₄ perfectly fit the volcano trend but other spinel family shows a deviation.

7.4 Conclusion

The ORR/OER performance of MnCo₂O₄ synthesized at various temperatures has been investigated. It was found that MnO₆ octahedron serves as the active site, while Co is just a building block to construct the spinel crystal. The descriptors for various MnCo₂O₄ are the Mn valence state of MnO₆ octahedron and the fraction of MnO₆ octahedron. The universality of this principle was further proven and extended to explain the ORR/OER activities of other transition metal spinels.

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Chapter 8

Implications and Future Work

Chapter 8 draws together the threads of this dissertation. The hypothesis is adequately proven and the design target is met. Hereby, most efforts have been paid to reveal the role of MnO_6 octahedron in energy application, but the effect of the arrangement of MnO_6 octahedrons is still unknown. It is thus recommended in this chapter to assemble MnO_6 octahedrons into different polymorphs and study their influence on oxygen electrocatalysis. To date, different manganese oxides have been successfully synthesized. The correlation with oxygen electrocatalysis performance will be further investigated.

8.1 Implications

We present in depth studies to understand the relationship between the physical properties of MnO_6 octahedrons in transition metal oxide model and the electrochemical performance, i.e., pseudocapacitor and oxygen electrocatalysis.

We started from tuning the ORR (oxygen reduction reaction) activity by tuning the stacking size of MnO_6 octahedrons to form MnO_2 nanoparticles. In order to achieve a tight control on the nanoparticle size, the classic soft template mechanism was borrowed from the shape control of Au nanoparticles. The successful synthesis of uniform-sized MnO_2 nanoflakes (~47 nm in diameter) has proven that this soft template strategy is also applicable to tune the stacking of MnO_6 octahedrons. The positive-charged CTA⁺ (the polymer chain of cetrimonium bromide) wraps the negative-charged KMnO_4^- into micelles and consequently morphology control is achieved. The as-synthesized MnO_2 nanoflakes were subsequently tested for ORR to correlate the activity with particle size. It was found that the ORR mass activity is drastically enhanced by polymerizing MnO_6 octahedron monomers into smaller MnO_2 nanoparticles. The conjectures that a smaller particle size brings more electrochemical-active sites and leads to higher mass activity were adequately proven by our experimental results. Of notable interest is that the stacking size of MnO_6 octahedrons fail to change the specific (intrinsic) activity of MnO_2 and it was proposed that the underlying origin is the physical nature of MnO_6 octahedron is not varied.

Considering MnO_6 octahedron is non-conductive, the conductive additives are indispensable to ensure the smooth charge transport for fabrication of MnO_6 -based electrochemical devices. It is thus important to understand the interplay between the MnO_6 octahedrons and the conductive support. In *Chapter 5*, the uniform-sized MnO_2 nanoflakes obtained in *Chapter 4* was employed as the model of MnO_6 octahedrons and 3 carbon materials – AB (acetylene black), rGO (reduced-graphene oxide) and CNTs (carbon nanotubes) – were used as the conductive supports. After physical mixing to form composites, it was indeed observed that the pseudocapacitive behaviors of MnO_2/C (C = AB, rGO, CNTs) were varied significantly by different carbon supports, which demonstrates the hypothesis that the different morphology of carbon support influences

the interface charge transfer. By analyzing either the capacitance of composite (MnO_2/C), or the capacitance purely contributed by MnO_2 , rGO was found to serve as the best conductive support to enhance the energy storage capability at the slow scan rate. However, at the fast scan rate, rGO gives the lowest capacitance, which is possibly due to the slow charge transport within the MnO_2/rGO composite.

MnO_6 octahedron was subsequently put into the crystal environment of spinel oxides for further understanding the role of MnO_6 octahedron in pseudocapacitive performance. It is believed that the different cation distribution (i.e., the substituted element and its geometric occupation) in spinel structure can result in different pseudocapacitive performance. First, this hypothesis was testified by the comparison of XFe_2O_4 ($\text{X} = \text{Fe}, \text{Mn}, \text{Co}, \text{Ni}$) spinel ferrites, where the only one variable is the metal element. The resulting intrinsic capacitance followed the trend that $\text{MnFe}_2\text{O}_4 \gg \text{CoFe}_2\text{O}_4 > \text{NiFe}_2\text{O}_4 \approx \text{Fe}_3\text{O}_4$, indicating that the substituted element is able to significantly alter the energy storage capability and fully proving our hypothesis. In order to reveal the origin of the various pseudocapacitive behaviors among XFe_2O_4 ($\text{X} = \text{Fe}, \text{Mn}, \text{Co}, \text{Ni}$), in-situ XAS (X-ray absorption spectroscopy) was employed. It was found that the pseudocapacitance is determined by the valency change capability of transition metal cation and this capability elucidates the great advantage of Mn over the other elements. Second, with the help of EXAFS (extended X-ray absorption fine structure), fixing the nominal formula as MnFe_2O_4 and tuning the cation distribution via heat treatment allow us to differentiate the electrochemical contribution from MnO_4 tetrahedron and MnO_6 octahedron. It was discovered that the pseudocapacitance of various MnFe_2O_4 forms a linearly relationship with the fraction of MnO_6 octahedrons, demonstrating the hypothesis that the geometric occupation is influential to the capacitance and MnO_6 octahedron is superior to MnO_4 tetrahedron.

Following the relation of MnO_6 octahedron and pseudocapacitor, the target was then set to unveil the role of MnO_6 octahedron in oxygen electrocatalysis. We proposed a similar hypothesis that the different physical properties (i.e., the valence state of the substituted element and cation distribution) in spinel structure can result in different oxygen electrocatalysis performance. We started verifying this hypothesis from fixing the nominal formula as MnCo_2O_4 and tuning the electronic structure via controlling the heat

treatment temperature. It was shown that the ORR/OER activity of various MnCo_2O_4 exhibits a volcano-shaped trend as a function of the valence state of Mn in MnO_6 octahedron and the fraction of Mn that occupies in the octahedral site also govern the ORR/OER activity. The as-revealed descriptor of MnCo_2O_4 proved the validity of our hypothesis and the universality of the discovered principle for MnCo_2O_4 was further validated by extending to describe the ORR/OER at transition metal spinels.

8.2 Recommended future work

Hereby, most efforts in this dissertation have been devoted to the role of MnO_6 octahedron itself, for example, the superiority of MnO_6 octahedron to MnO_4 tetrahedron, the valence state of Mn in MnO_6 octahedron, the capability of changing valence state. However, in the case of engineering MnO_6 octahedrons for real oxygen electrocatalysis application, it is necessary to consider another factor, namely the arrangement of MnO_6 octahedrons. It has been reported that with various arrangements of the basic crystal unit – MnO_6 octahedron, MnO_x (manganese oxides) can form 8 polymorphs (as shown in Figure 8.1) in total.¹⁻⁴ Nevertheless, it is unknown that how these arrangements of MnO_6 octahedrons affect the ORR/OER performance. Despite some studies have paid attention to the oxygen electrocatalysis on MnO_x , most existing reports are based on the mass activity (normalized to the mass loading of active material) discussion,^{1,2,5} which cannot reflect the real mechanism underlying the surface-sensitive electrochemical process. Moreover, there is still not a universal descriptor to describe the ORR/OER at various MnO_x . Unveiling the mysteries of MnO_6 octahedron arrangements has been hindered by the lack of systematic studies base on the intrinsic specific activity (normalized to the real surface area of electrode materials) analysis.

Figure 8.1 Illustration of 8 polymorphs of manganese oxides with different MnO₆ octahedron arrangement: (a) β -MnO₂, (b) γ -MnO₂, (c) α -MnO₂, (d) δ -MnO₂, (e) λ -MnO₂, (f) LiMn₂O₄, (g) Mn₂O₃, (h) Mn₃O₄. Reproduced from ref. 6 with permission by American Chemical Society.

This Chapter recommends a systematic study on the correlation between the arrangements of MnO₆ octahedrons and the ORR/OER performance. Various MnO_x were synthesized according to reported recipes^{2,4,6} and the phase purity was confirmed by XRD (X-ray diffraction). The physical properties were probed by XAS technique and related to the oxygen electrocatalysis activity.

8.3 Experimental details

Synthesis of α -MnO₂ (K⁺) and α -MnO₂ (H₃O⁺). α -MnO₂ (K⁺) were synthesized in aqueous solution through a typical hot-injection method: pre-dissolved potassium permanganate (KMnO₄) solution was quickly added into hexadecyltrimethylammonium bromide (CTAB) solution at 140 °C, giving a mixture containing 0.05 M CTAB and 0.01 M KMnO₄. Temperature of oil bath was maintained at 140 °C. MnO₂ was collected by adding acetone and following centrifugation. Alternative synthesis of α -MnO₂ (H₃O⁺) involved taking powdered commercial Mn₂O₃ and heating at 700 °C to remove impurities. The resulting material was then added to a 4 M H₂SO₄ solution to form an aqueous suspension. After heating at 80 °C for 6 hours under stirring, the resulting product was

centrifuged, decanted and washed with deionized H₂O and dried at 90 °C in air to form nanocrystalline α -MnO₂.

Synthesis of β -MnO₂. β -MnO₂ was synthesized by annealing α -MnO₂ (K⁺) at 500 °C in air for 6 hr.

Synthesis of γ -MnO₂. LiMn₂O₄ powder was added to a 3 M H₂SO₄ solution (100 mg: 50 mL) to form an aqueous suspension and refluxed in an oil bath at 120 °C for 28 h. The solution was centrifuged, decanted and washed with bicarbonate solution and deionized H₂O and dried at 90 °C in air to form nanocrystalline γ -MnO₂.

Synthesis of δ -MnO₂. An aqueous solution of 0.38 M KMnO₄ was added to a 1.4 M glucose solution. As the resulting brown gel undergoes syneresis, the water is decanted and the product was dried at 110 °C for 24 h. The resulting xerogel was then calcined at 400 °C, followed by washing with deionized H₂O and drying at 90 °C in air to form nanocrystalline potassium type δ -MnO₂.

Synthesis of λ -MnO₂. Nanocrystalline LiMn₂O₄ powder (f) was added to a 0.1 M HNO₃ solution (100 mg: 10 mL) to form an aqueous suspension. After 2 h of sonication, the solution was centrifuged, decanted and washed with bicarbonate solution and deionized H₂O and dried at 90 °C in air to form nanocrystalline λ -MnO₂.

Synthesis of LiMn₂O₄. LiMn₂O₄ catalyst was a Sigma-Aldrich product. Li_{0.7}Mn₂O₄ was synthesized by a delithiation reaction with LiMn₂O₄ as the precursor. LiMn₂O₄ was added to a 0.1 M HNO₃ solution to form an aqueous suspension (100 mg/10 mL). After 2 h sonication, powder product was collected by centrifugation, decanting and washing with bicarbonate solution and DI-H₂O. As-obtained powder was dried at 90 °C in oven.

Synthesis of Mn₂O₃. Mn₂O₃ was directly purchased from Alfa Aesar.

Synthesis of Mn₃O₄. Mn₃O₄ was synthesized by annealing α -MnO₂ (K⁺) at 1100 °C in air for 8 hr.

8.4 Preliminary result

The phase purity of various polymorphs of manganese oxides were confirmed by the XRD technique. Each manganese oxide matches its standard pattern, indicating that all the MnO_x used in this dissertation are correct in phase. As for α -MnO₂, the formation of 2

$\times 2$ channel needs to be stabilized by cations. In order to know the effect from the different cations in the channel, two kinds of α - MnO_2 were prepared: one is α - MnO_2 (K^+), stabilized by K^+ ; the other one is α - MnO_2 (H_3O^+), stabilized by H_3O^+ .²

Figure 8.2 The XRD patterns of α - MnO_2 (K^+) and the standard pattern.

Figure 8.3 The XRD patterns of α - MnO_2 (H_3O^+) and the standard pattern.

Figure 8.4 The XRD patterns of $\beta\text{-MnO}_2$ and the standard pattern.

Figure 8.5 The XRD patterns of $\beta\text{-MnO}_2$ and the standard pattern.

Figure 8.6 The XRD patterns of $\gamma\text{-MnO}_2$ and the standard pattern.

Figure 8.7 The XRD patterns of Mn_2O_3 and the standard pattern.

Figure 8.8 The XRD patterns of $\delta\text{-MnO}_2$ and the standard pattern.

Figure 8.9 The XRD patterns of Mn_3O_4 and the standard pattern.

Figure 8.10 The XRD patterns of $\lambda\text{-MnO}_2$, LiMn_2O_4 and the standard pattern.

Next, we experimentally estimate the ORR/OER performance and correlate it with the physical properties of various MnO_x .

8.5 Conclusion

In conclusion, the basic strategy of this dissertation is to hypothesize that some material physical properties govern the electrochemical performance. The hypothesis was proven by experimentally tuning those proposed physical properties and correlating them with the resulting electrochemical performance. The outcomes in this thesis were adequately reflected in the original hypothesis.

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List of Publications

Chao Wei, Zhenxing Feng, Guenther G. Scherer, James Barber, Yang Shao-Horn, Zhichuan J. Xu*, "Cations in octahedral sites: a descriptor for oxygen electrocatalysis on transition metal spinels", Submitted.

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Yi Zhao, **Chao Wei**, Shengnan Sun, Luyuan Paul Wang, Zhichuan J. Xu*, "Reserving interior void space for volume change accommodation: an example of cable-like MWNTs@ SnO_2 @C composite for superior lithium and sodium storage", *Advanced Science*, 2015, 2, 1500097 [Link](#)

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