Activating T2g orbitals by tetrahedral vacancy in spinel oxides to promote water oxidation

Shen Jingjing

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**ACTIVATING T_{2g} ORBITALS BY TETRAHEDRAL VACANCY IN SPINEL
OXIDES TO PROMOTE WATER OXIDATION**

SHEN JINGJING

SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

2022

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SHEN JINGJING

SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

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

2022

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Abstract

Spinel oxides have been substantially explored as OER catalysts due to their comparable activity compared to the noble electrocatalyst. The octahedral site of the spinel oxide is commonly reported to be more catalytically critical than the tetrahedral site, thus many research groups have focused on modifying the octahedral site to enhance OER performance. Besides octahedral modification, altering the tetrahedral sites also can indirectly influence the octahedron and affect the OER activity. By replacing Zn with a low electronegative metal such as lithium, the electron cloud of oxygen will be more polarized towards the octahedron, thereby introducing higher covalency of Co-O and causing OER performance to be enhanced. Besides, lithium cation does not participate in metal and oxygen hybridization at the energy region near-Fermi-level because the energy of the Li 2s orbitals is very low and far away from the Fermi level. Moreover, lithium metal vacancy can be easily induced by high temperature since it is very light. These results encouraged the investigation of whether an even lower electronegativity can be achieved in the tetrahedral site.

Therefore, theoretical calculation was first employed to investigate the relationship between the loss of metal tetrahedral sites and the Co 3d and O 2p band centers relative to the Fermi level, which concluded that the tetrahedral vacancy in the electrocatalyst could induce t_{2g} orbital activation. To design an electrocatalyst with tetrahedral vacancies, LiCo_2O_4 has been synthesized at different annealing temperatures. Various characterization techniques such as ICP, XPS and XAS techniques were employed to identify the tetrahedral site vacancies. ssNMR, and magnetic analysis have shown the presence of paramagnetic Co^{3+} (intermediate or high spin) in LiCo_2O_4 400 °C, which means that t_{2g} orbital is activated. Moreover, EELS analysis has shown that empty states are induced in the t_{2g} orbital. Electrochemical measurements reveal that OER activity of the LiCo_2O_4 400 °C is superior to that of CoOOH and IrO_2 .

The recommendations have been proposed to conduct theoretical calculations to calculate binding strength of adsorbates to understand the rate determining step in OER. Furthermore, OER performance can be systematically investigated by doping other transition metals in the octahedral site. Further follow-up experiments should also be conducted on the 500 °C sample to study surface reconstruction.

Lay Summary

The global demand for energy is constantly rising, and the associated environmental issues have been a huge global concern. Water electrolysis, which can give rise to hydrogen (clean fuel), seems to be a promising technology. Nevertheless, the slow kinetics of oxygen evolution reaction (OER) at the anode has greatly hindered the efficiency of the electrolyzer, as OER is an intricate four electron-proton transfer process that needs high overpotential to proceed with the reaction. Therefore, an electrocatalyst is required to accelerate the reaction. However, the cost of the noble electrocatalyst used in the industry currently is very high. Thus, the development and search for inexpensive, copious, and efficient electrocatalyst for high OER performance is of high importance.

Spinel oxides have been substantially explored as OER catalysts due to their comparable performance compared to the noble electrocatalyst. The octahedral site of the spinel oxide is commonly reported to be more catalytically critical than the tetrahedral site, thus many research groups have focused on modifying the octahedral site to enhance OER performance. Besides octahedral modification, altering the tetrahedral sites also can indirectly influence the octahedron and affect the OER activity. By replacing Zn with a low electronegative metal such as lithium, the electron cloud of oxygen will be more polarized towards the octahedron, thereby introducing higher covalency of Co-O and causing OER performance to be enhanced. Besides, lithium cation does not participate in metal and oxygen hybridization at the energy region near-Fermi-level because the energy of the Li 2s orbitals is very low and far away from the Fermi level. Moreover, lithium metal vacancy can be easily induced by high temperature since it is very light. These results encouraged the investigation of whether an even lower electronegativity can be achieved in the tetrahedral site.

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Abbreviations

AEM	Adsorbate evolution mechanism
BET	Brunauer–Emmett–Teller
DOS	Density of states
DFT	Density function theory
EXAFS	Extended X-ray absorption fine-structure spectroscopy
LOM	Lattice oxygen mechanism
OER	Oxygen evolution reaction
ORR	Oxygen reduction reaction
RHE	Reversible hydrogen electrode
TGA	Thermogravimetric analysis
XANES	X-ray absorption near-edge spectroscopy
XRD	X-ray Diffraction
XPS	X-ray photoelectron spectroscopy

Chapter 1

Introduction

Water oxidation is crucial to the production of sustainable hydrogen as a clean fuel. However, the electrolyzer efficiency is largely compromised by the slow reaction kinetics of OER occurring at the anode. Spinel oxides are potential catalysts as they are inexpensive, copious and promising in OER performance. This chapter summarizes the prospects of LiCo_2O_4 as an efficient OER catalyst, and how lower electronegativity can be achieved in the tetrahedral site by inducing tetrahedral vacancies. This will cause the electronegativity in the tetrahedron to be minimized, therefore triggering stronger oxygen polarization towards the octahedron. Moreover, the activation of the t_{2g} orbitals is realized with the tetrahedral vacancies, which enhances the OER performance. The hypothesis, objective and the outcomes of this research are as provided.

1.1 Background and Motivation

In 1890, the first water electrolysis unit was set up to produce hydrogen for military applications. However, a more cost-effective alternative, steam reforming, was discovered to generate hydrogen, thus the progression of the water electrolysis technology was hindered. Nevertheless, environmental issue associated with the emission of greenhouse gases during the process of steam reforming has been a matter of concern.[1, 2] Moreover, the fast depletion of fossil fuels urged the need for the development of renewable and sustainable energy resources. Therefore, water electrolysis was once again reinvented to generate clean energy, as oxygen is the only by-product. Yet, challenges including expensive materials, instability of catalysts and limited duration of catalyst lifetime are essential for scientists to overcome to achieve larger scale operations instead of laboratory and minor applications at the moment.

One major obstacle to the mass production of hydrogen is that much of its inefficiency stems from the slow reaction kinetics of the OER process in the anode side due to the complex four-electron transfer.[3, 4] In order to overcome energy barrier at the anode, high overpotential is generally required. Therefore, much effort has been devoted by researchers to elucidate and discover the underlying oxidation reaction mechanism to boost the performance of OER and minimize the energy loss during water splitting. To date, in acidic electrolytes, the noble metal Iridium is still utilized extensively during the OER because is it the sole metal that is able to withstand the harsh acidic environment.[5] Meanwhile, in alkaline electrolytes, 3d transition metal OER catalysts are shown to possess high activity and stability.[6-9]

To date, spinel oxides have attracted much research attention because they are promising OER catalysts. In a spinel oxide, the metal cation can occupy two distinct interstices, specifically the tetrahedral and octahedral sites. To resolve the ambiguity that tetrahedral or octahedral metal takes part in a more important role in boosting the OER activity, our previous work has demonstrated that the six-fold cobalt has a higher OER activity than the four-fold cobalt, ascribing to the stronger oxygen orbital polarization towards the

octahedral metal.[10] Kim et al. has also rationalized that tetrahedral sites are not critical for OER activity by the replacement of cobalt by zinc based on the observation that ZnCo_2O_4 has a slightly higher OER activity than Co_3O_4 . [11] Consequently, the modification of octahedral sites was intensively reported according to the e_g filling number, metal-oxygen covalency, conductivity and the formation of amorphous layers.[12, 13] By utilizing various transition metals such as Cr, Fe and Ni to substitute the octahedron cobalt, the OER activity was improved drastically. Several approaches include Fe substitution promoting the OER activity due to the increase in Co-O valency,[14] high Ni substitution facilitating the amorphous formation and thus the metastable phase improved the OER activity,[13] and Cr substitution enhancing the OER activity driven by the increase in metal-oxygen hybridization.[12] Nevertheless, the incorporation of Mn into octahedron cobalt appears to lower the OER activity due to limited spin channels, as the spin polarization sets hurdles for the transfer of electrons between octahedral cations and oxygen.[15]

Besides octahedral modification, altering the tetrahedral sites also can indirectly influence the octahedron and affect the OER activity. By replacing Zn with a low electronegative metal such as lithium, the electron cloud of oxygen will be more polarized towards the octahedron, thereby introducing higher Co-O covalency and causing OER activity to be enhanced.[10] These results encouraged the investigation of whether an even lower electronegativity can be achieved in the tetrahedral site. By inducing tetrahedral vacancies, electronegativity in the tetrahedron can be minimized, therefore reducing its tendency to attract electrons from oxygen, and triggering stronger oxygen polarization towards the octahedron.[16] Since lithium can be easily released at high temperature, tetrahedral vacancies can be fabricated. Therefore, we proposed that the fabrication of spinel oxide LiCo_2O_4 via simple thermal decomposition method at three heat treatment temperatures 300 °C, 400 °C and 500 °C.

Technically, for LiCo_2O_4 , the oxidation state of cobalt should be +3.5 (provided without any vacancies). In a cobalt-based spinel oxide, the cobalt cations in the octahedral site usually adopts a low spin state (i.e. ZnCo_2O_4 , $t_{2g}^6 e_g^0$). [17] The fully occupied t_{2g} orbitals

are regarded as non-bonding orbitals,[10] where the interaction with the 2p orbitals of oxygen ligands does not take place. The lower energy d-orbitals are unavailable for the transferring of electrons, therefore not contributing to the activity of OER. On the contrary, e_g orbitals are antibonding orbitals responsible for the adsorption properties of oxygen species.[7, 18] Nevertheless, utilizing the t_{2g} orbitals effectively by creating empty t_{2g} orbitals to provide additional pathway for the transport of electrons within the oxide can facilitate the OER process. To activate the cobalt t_{2g} orbital, the presence of partially filled t_{2g} orbitals is essential i.e. $t_{2g}^4 e_g^2$ or $t_{2g}^5 e_g^1$. This will generate spin channels in the t_{2g} orbitals to enable electron hopping between Co-O-Co.[19] In the diagram of density of states (DOS), orbitals above the Fermi level are unoccupied, mostly comprising metal orbitals (i.e. e_g orbital). Orbitals below Fermi level are occupied and mainly consist of the metal and oxygen. It is worth noting that these t_{2g} orbitals are located at the highest occupied molecular orbital (HOMO), which is close to the Fermi level. The electrons close to the Fermi level are more active than those that are away from the Fermi level.[20] The energy states close to the Fermi level are commonly associated with physical and chemical roles[21], such as the conductivity and charge transfer. It suggests that the highly efficient utilization of t_{2g} orbitals can facilitate the OER activity of the cobalt-based oxides. Besides, lithium cation does not participate in metal and oxygen hybridization at the energy region near-Fermi-level because the energy of the Li 2s orbitals is very low and far away from the Fermi level.[22] This further encouraged the exploration of whether temperature-induced vacancy in LiCo_2O_4 can induce t_{2g} orbital activation.

1.2 Hypothesis/Problem Statement

“This thesis tests the hypothesis that temperature-induced tetrahedral vacancy in LiCo_2O_4 can induce t_{2g} orbital activation which results in improved OER performance.”

1.3 Objective and Scope

“The overall objective of this thesis is concerned with the temperature induced tetrahedral

site vacancy in LiCo_2O_4 spinel oxide, leading to the t_{2g} orbital activation, which will provide an additional pathway for electron transfer between the transition metal and oxygen to improve its OER performance. In addition, this thesis will present a greater understanding for application of LiCo_2O_4 as an OER electrocatalyst.”

1.4 Findings and Outcomes

1. Correlating tetrahedral site vacancy and Co-O bond covalency in spinel oxide LiCo_2O_4
2. Demonstrating how tetrahedral site vacancy can lead to t_{2g} orbital activation
3. Identifying the relationship between t_{2g} orbital activation and OER activity

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Chapter 2

Literature Review

This chapter introduces the background of oxygen evolution reaction and how it applies to clean energy storage. Currently, the state-of-the-arts catalyst for OER is too expensive, which causes the practical applications to be very limited. Therefore, transition metal oxide-based catalysts are economical alternatives with comparable or even higher OER activities. Here, the two reaction mechanisms for oxygen evolution reaction are discussed, which includes lattice oxygen mechanism (LOM) and adsorbate evolution mechanism (AEM). Furthermore, the major descriptors of the OER catalytic activity such as e_g orbital occupancy, metal-oxygen covalency and vacancies are also introduced in this chapter.

2.1 Background of OER

Over the decades, the need for the development of sustainable and renewable energy resources has been rising due to the dwindling fossil fuels and increasing greenhouse gas emission. However, the natural resources are usually intermittent, therefore converting and storing the energy is required. For example, storing energy in the form of chemical bond i.e., H_2 , due to H_2 having high energy density, resulting in larger energy per unit volume or weight to be stored. Hydrogen can be produced by electricity-driven water splitting, which is highly efficient and environmentally friendly since the only by-product is oxygen. Besides, recombining hydrogen and oxygen can produce clean electrical energy and water will be the only by-product.

Figure 2.1: (a) Energy storage and conversion diagram consisting of the hydrogen and oxygen cycle. (b) Illustration of electricity-driven water splitting.

The following is the equation representing the overall reaction of water splitting driven by electricity:

The overall reaction is made up of two half redox reactions. One is the reduction process, hydrogen evolution reaction (HER), occurring at the cathode with the standard equilibrium potential $E^0_{H_2/H^+} = 0V$:

The other is the oxidation process, oxygen evolution reaction (OER), occurring at the anode with the standard equilibrium potential $E^0_{\text{O}_2/\text{H}_2\text{O}} = 1.23 \text{ V}$ (vs. SHE):

In comparison to the HER, the OER requires four electrons stepwise transfer, therefore it is more complex and results in the slow kinetics of water electrolysis. More importantly, the overpotential at the anode decreased the efficiency of the overall energy conversion reaction at a large extent. [1] Currently, IrO_2 and RuO_2 are OER catalysts used industrially, but the precious metals are too expensive for them to be used in applications extensively. Therefore, it is crucial to discover economical and stable electrocatalysts for the OER to minimize the overpotential and maximize the overall efficiency.

2.2 Mechanisms of OER

2.2.1 AEM

Figure 2.2: Schematic diagram of the AEM for OER.

There are typically two OER mechanisms that are widely accepted, namely AEM and LOM. As shown in Figure 2.2, the AEM has four concerted proton–electron transfer reactions in the alkaline medium, centered on the metal oxide catalyst

surface, according to the following equations:

Firstly, OH^- is adsorbed on the surface-active site of the catalyst. Following that, the adsorbed OH^- will undergo deprotonation to form O^* . Subsequently, another OH^- will react with O^* to form the HOO^* intermediate. Finally, HOO^* will undergo deprotonation and O_2 will be evolved, and the active site will be regenerated.

Figure 2.3: Gibbs free energy diagram at $U=0$ depicting ideal and real catalysts.

As shown in Figure 2.3, for an ideal catalyst, overpotential will not be present because of the absence of thermodynamic hindrance without the consideration of the kinetic limitation. However, for a real catalyst, the ΔG between the reaction steps related to HOO^* and O^* intermediates are the largest, which indicates that ΔG_3 is the potential-determining step. Therefore, by focusing on the reduction of the energy barrier for this step, enhancement of the electrochemical activity of the catalyst can be achieved.

2.2.2 LOM

Figure 2.4: Schematic illustration of the LOM for OER.

LOM is an OER mechanism that involves the activation of lattice oxygen and provides new reaction pathway (non-concerted proton-electron transfer).[2] Furthermore, this mechanism also successfully explains the PH-dependent OER phenomenon. Compared to AEM, whereby the reaction starts on a single metal site, the reaction of LOM starts on two neighboring metal sites. As shown in Figure 2.4, firstly, deprotonation occurs on the two HO^* on the metal sites, which forms two metal–oxo species. Secondly, the two neighboring oxo species will not combine with OH^- or water to produce HOO^* . Instead, they will couple directly to create the O–O bond. Lastly, oxygen is released, leaving the two metal centers vacant, which are then subsequently occupied by OH^- .

2.3 Major descriptors of OER

2.3.1 eg Orbital Occupancy

Figure 2.5: (a) The Madelung potential of ions causing the shift of ions energy in the crystal structure. (b) Illustration of M 3d and O 2p orbitals, depicting the t_{2g} and e_g orbitals. (c) Schematic band diagram of O 2p and M 3d.

The metal d orbitals and oxygen 2p orbitals will undergo hybridization because they have spatial overlap, and their electronic states are similar in energy. As shown in perovskite oxide in Figure 2.5b, under the octahedral environment, the transition metal 3d and oxygen 2p orbitals hybridized to form σ orbitals and π orbitals. The σ orbitals containing $d_{x^2-y^2}$ and $d_{z^2-r^2}$ lobes overlap strongly with the adjacent O 2p orbitals spatially, while the π orbitals containing d_{xy} , d_{xz} and d_{yz} lobes overlap weakly with adjacent O 2p orbitals. The antibonding states of σ orbitals and π orbitals are known as e_g and t_{2g} orbitals, respectively.

Figure 2.6: Plot of overpotential (OER) against e_g electron occupancy of numerous perovskites in alkaline solution.

Figure 2.7: Plot of activity (OER) on numerous spinel oxides against e_g occupancy based on the octahedral site with active element.

The strength of metal-oxygen bond can be determined by the e_g -occupancy activity descriptor, which is controlled by the number of electrons in the antibonding σ states. [3] According to the Sabatier principle, the bonding strength between the metal and oxygen needs to be neither too weak nor too strong to reach an optimal OER performance. Metal oxides that bind to oxygen too strongly will have an e_g occupancy less than one, while

metal oxides that bind to oxygen too weakly will have an e_g occupancy more than one. Consequently, after thorough investigation on perovskites by Shao-Horn and co-workers, they demonstrated that when the e_g occupancy of the perovskite is close to unity, the optimal OER activity can be achieved (Figure 2.6). Subsequently, the e_g descriptor can also be used to explain the OER for spinel oxides after correcting the geometric occupation (Figure 2.7).[4]

2.3.2 Covalency of Metal and Oxygen

However, some metal oxides with similar e_g orbital occupancy may possess different OER activities. Therefore, e_g orbital occupancy may not be a predominant descriptor, but it requires other activity descriptors to explain the variances in activity. The e_g orbital occupancy descriptor is based on the ionic model and does not reflect the covalent bond between metal and oxygen. For instance, the metal-oxygen bonds in perovskites have mixed ionic-covalent character due to the metal 3d orbitals and O 2p states having spatial overlap (hybridization) and energetic similarity (covalency).[5] As a result, metal-oxygen covalency can also be used as an activity descriptor to better describe the ionic-covalent character of the metal oxides.

Figure 2.8: The OER activity based on the octahedral site metal and oxygen covalency of perovskite oxides.

Shao-Horn's group have shown that increasing the covalent mixing between BO in perovskites, with constant e_g filling of 1, can greatly enhance the OER activity (Figure 2.8).[6] With greater covalency, the active redox couple of the B-site ion has a larger O-2p character, which facilitates the charge transfer between adsorbates and active sites in the rate-determining steps of OER.

Figure 2.9: (a) Diagrams illustrating the molecular orbitals, which depict the Co-OH bonding. (b) Evaluating the potentials of the OER activity at a current density of 25 $\mu\text{A cm}^{-2}_{\text{ox}}$, with N - V parameter as the x-axis. Project density of states (pDOS) of (c) ZnCo₂O₄ and (d) Zn_V-Fe-ZnCo₂O₄.

Figure 2.10: OER activity as a function of the computed oxygen charges for various spinel oxides.

Our group has also discovered that the incorporation of 10-30 at% of Fe into the spinel ZnCo_2O_4 can increase the Co 3d and O 2p covalency. This will allow electrons to inject or extract at a higher rate from oxygen, which result in enhanced OER performance.[7] Furthermore, from the DFT calculations, the pDOS show that the incorporation of iron shrinks the metal 3d and O 2p-band centers in terms of energy, which shows higher covalency in metal-oxygen bond, as shown in Figures 2.9c and 2.9d. Subsequently, a more recent work has shown that the octahedral site in spinel oxide is more catalytically active, as compared to the tetrahedral site.[8] Consequently, the work demonstrated that the six-fold cobalt has a higher OER activity than the four-fold cobalt, ascribing to the stronger oxygen orbital polarization towards the octahedral metal. As a result, among CoAl_2O_4 , ZnCo_2O_4 and Co_3O_4 , Co_3O_4 has the highest specific activity, while CoAl_2O_4 has the lowest. Moreover, since Li has a higher electronegativity than Zn, by replacing Zn with Li partially, the oxygen charges will be more shifted to the active octahedral transition metal center, which leads to enlarged metal–oxygen covalency, thus improving the OER performance (Figure 2.10).

2.3.3 Vacancies

Inducing cation and anion vacancies in metal oxides can affect the surface charge distribution of materials, which can also promote OER. For example, Dai's group reported that by generating oxygen vacancies with Ar plasma treatment on Co_3O_4 caused the surface area to increase and resulted in increasing OER active sites and enhancement in conductivity (Figure 2.11).[9]

Figure 2.11: Schematic diagram showing the preparation of the Ar-plasma-engraved Co_3O_4 , whereby surface area increased with more oxygen vacancies.

Moreover, Qiao *et al.* researched that by introducing oxygen vacancies on 1-D single-crystal CoO can facilitate charge transfer and optimize energetics for OER.[10] Furthermore, introducing cation vacancies allows the decrease of coordination numbers of the active sites, which can promote charge transfer and allow easier adsorption of reactants, which can result in higher OER performance.[11]

2.4 Electrocatalytic Performance Indicators

The purpose of an electrocatalyst is to enable faster charge transfer from the electrode to the reactants, and facilitate adsorption and desorption of reactants and products, respectively. To evaluate the catalytic performance of a catalyst, several parameters are considered, such as overpotential, Tafel slope, turnover frequency, and stability.

2.4.1 Overpotential

In an ideal case, there should not be a difference between the potential applied at equilibrium and the potential required to initiate a reaction. Nevertheless, in fact, an activation energy, which is an energy barrier, is required to be overcome and initiate the reaction. Consequently, the activation energy resulted in an overpotential. The onset potential of the reaction, which has been standardized at the value when current is 10 mA cm^{-2} , is usually used to quantify overpotential. Subsequently, the overpotential is then the difference between the equilibrium potential of OER at 1.23V and the onset potential. Currently, most of the good electrocatalysts possess an overpotential of about 300~400 mV. Thus, much research with the aim to lower overpotential is essential for attaining effective and efficient electrocatalysts.

2.4.2 Tafel Slope

The definition of Tafel slope (b) is the magnitude of current response as regards to potential increase. The Tafel slope is shown according to the following equation:

$$\eta = b \cdot \log (j/j_0)$$

where η is the overpotential, j_0 is the exchange current density and j is the current density. A Tafel slope with a smaller magnitude corresponds to a higher reaction rate because the increase in current density is proportional to the increase in potential. The Tafel slope provides information associated with the rate determining steps.

2.4.3 Turnover frequency

The definition of turnover frequency (TOF) is number of electrons transferred per active site per second. TOF can be used to determine the intrinsic activity of the electrocatalysts.

$$TOF = \frac{\text{rate of reaction}}{\text{number of active sites}} = \frac{\text{moles}}{\text{volume} \cdot \text{time}} \times \frac{\text{volume}}{\text{moles}} = \text{time}^{-1}$$

2.4.4 Stability

The stability of electrocatalysts is of crucial importance for practical applications due to economic and lifetime reasons. For laboratory experiments, chronoamperometry (CA) is usually used by holding constant potential for several hours to study the current response over time. On the other hand, chronopotentiometry (CP) can be carried out by holding the current output constant and measure the potential response.

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Chapter 3

Experimental Methodology

The method of material synthesis, materials characterization techniques and electrochemical measurement methods for this project are mainly discussed in this chapter. X-ray diffraction (XRD) is used to characterize the material crystal structure and phase. Brunauer-Emmett-Teller (BET) adsorption isotherm technique is used to measure the specific surface area of the materials. X-ray absorption spectroscopy (XAS) is employed to determine the oxidation state and local structure. X-ray photoelectron spectroscopy (XPS) is used to analyze the surface chemistry of the material. Solid-state nuclear magnetic resonance (ssNMR) was utilized to obtain the electronic and structural information of the material at the atomic level. Lastly, three-electrode electrochemical testing is used to analyze the electrochemical performance.

3.1 Material Synthesis

Spinel-type lithium cobalt oxides were prepared by a thermal decomposition procedure. All the chemicals were purchased from Sigma-Aldrich. 30 mmol of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 15 mmol of LiNO_3 were mixed and dissolved in 200 mL of DI water to form an aqueous solution, followed by continuous stirring at 90 °C for a period of time to form a viscous gel formed. Then it was transferred to oven at 200 °C for 12 hours to obtain resultant resin. Subsequently, the resultant resin was annealed at different temperatures of 300 °C, 400 °C and 500 °C at a heating rate of 5 °C/min for 6 hours to obtain lithium cobalt oxides.

3.2 Material Characterization Techniques

X-ray diffraction (Panalytical XRD) with $\text{Cu-K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) was used to characterize the crystal structures of the spinel oxide samples. The Brunauer-Emmett-Teller (BET) (by ASAP Tristar II 3020) measured the specific surface area of the samples. X-ray photoelectron spectroscopy (XPS) was employed to measure the cobalt and oxygen contents for all the samples. The valency of cobalt was determined by X-ray absorption near-edge spectroscopy (XANES), and the site distribution of cations was tested by the Fourier transform (FT) of extended X-ray absorption fine-structure spectroscopy (EXAFS). Vienna Ab initio Simulation Package (VASP) was used to conduct all the DFT simulations.

3.2.1 X-ray Diffraction

X-ray diffraction is used to investigate the crystal structure and phase purity of the crystalline sample. The principle of XRD is illustrated in Figure. When the crystalline sample, which composed of regular array of atoms, is irradiated with the incident X-ray beam, the X-ray beams will interact with the atoms and diffract into many directions. As a result, interference patterns will be generated. Constructive interference will occur when the diffraction angle θ satisfies the Bragg Equation:

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

where θ denotes the angle between the incident x-ray beams and diffraction plane; n is the integer number; λ represents the wavelength of the X-ray beam (1.5418 Å for Cu radiation);

d refers to the d -spacing of the crystal plane.

Figure 3.1: Illustration of the X-ray beams interacting with the crystal lattice of the material.

An X-ray detector is used to record the scattered X-ray signals and quantify the signals. By scanning the crystalline sample within the angle range of 2θ , all the constructive interferences will be produced and an XRD pattern will be obtained in terms of diffraction peaks as a function of 2θ . Since different crystal structures will result in a unique set of diffraction pattern, an XRD database will be utilized to match the obtained patterns to identify the phase and crystal structure.

3.2.2 Brunauer-Emmett-Teller

The BET theory strives to explain the physical adsorption of gas molecules on the solid surface and it is an essential analysis technique to measure the specific surface area of materials. The BET theory can be applied to systems of multilayer adsorption and usually utilizes probing gases that do not chemically react with material surfaces as adsorbates to quantify specific surface area. Due to the weak interaction between most gases and solids, the solid material must be cooled, and usually a cryogenic liquid such as nitrogen is used for gas adsorbate. The adsorption and desorption process allow the equilibrium and saturation pressure of adsorbate to be measured. Therefore, the relationship between the amount of adsorbed gas molecules and the relative pressure can be obtained, which is known as the BET adsorption isotherm.

3.2.3 X-ray Absorption Spectroscopy

XAS is used to determine the oxidation states, electronic structure, and local coordination environment of a sample. It measures the response of the sample to an X-ray beam, of which the energy is adjusted. According to Beer's law, the X-ray beams intensity will be reduced when it passes through the sample as shown in Figure, whereby the reduction is characterized by the absorption coefficient (μ):

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

where I_0 is the intensity of incident X-ray, I_t is the intensity of transmitted X-ray, μ is the absorption coefficient, and t is the thickness of the measured sample.

Figure 3.2: Schematic diagram of transmitted and incident X-ray beam.

On a K-edge XAS spectrum, there are mainly three regions as shown in Figure that represent different spectroscopic techniques.

1. Pre-edge peak: These peaks appear when there is electron transition to the lowest unoccupied states. It occurs when binding energy of the electrons in the element's orbitals is higher than the incident X-ray energy.
2. XANES: These peaks occur when the incident X-ray energy is high enough to cause excitation of the core electrons to the unoccupied state. In the process, the sharp increase of μ in the spectrum is due to the strongly absorbed X-ray. As the element of different valence states has different binding energies, the XANES edge is used to measure the valence state of the detected element.

3. EXAFS: With further increase of the X-ray energy, it resulted the core electrons to excite to continuum state that forms the scattering and outgoing wave interference with neighboring atoms. [1] The oscillation of the μ signal is formed by the deconstructive or constructive interferences of the scattering and outgoing waves in the EXAFS region. The EXAFS edge reflects the local atomic structure, whereby the coordination number and bond distance can be determined.

Figure 3.3: Schematic drawing of XAS including pre-edge, EXAFS and XANES regions.

3.2.4 X-ray Photoelectron Spectroscopy

XPS is a technique for surface analysis to determine the element composition, whereby X-rays will irradiate the sample and electrons will be ejected from the sample. Al $K\alpha$ X-rays (1486.6 eV) and Mg $K\alpha$ X-rays (1253.6 eV) are commonly used as the sources due to their high energy and small line width. Subsequently, the interaction between the X-rays and the atoms at the top 10nm of the sample by the photoelectric effect causes the emission of the electrons. The emitted photoelectrons have kinetic energy by the following equation:

$$KE = h\nu - BE - \phi_{\text{sam}}$$

whereby $h\nu$ is the X-ray photon energy, BE is the energy required to remove an electron from each core atomic orbital of each element and ϕ_{sam} represents the work function of the

material. The photoemission process is shown in Figure.

Figure 3.4: Photoemission Process

By measuring the kinetic energy of the emitted photoelectrons, some possible information of the sample can be determined including the elements present near the sample surface, its chemical states, and the binding energy of the electrons.

3.2.5 Solid-state nuclear magnetic resonance (ssNMR)

NMR spectroscopy is a technique to study the nuclear energy levels directly. The energy levels originate from the angular momentum of the nucleus. Thus, the effect of NMR is contingent on the property of the nuclear. Most nuclei have an angular momentum P , which is proportional to spin ($ZUMI$). The proportionality constant is Planck's constant h , and P and I (spin quantum number) are quantum mechanical operators. Table 1 shows the different type of nuclei and their related information applicable to NMR spectroscopy.

Table 1: The type of nuclei and their respective NMR properties.

isotope	spin	nat. abundance (%)	quadrupole moment ^a	rel. sensitivity ^b	ν_0 (MHz) at 2.3488 T	chemical shift range (ppm)	chemical shift reference
¹ H	1/2	99.98	—	1.0	100.000	20 to -1	SiMe ₄
² H	1	1.5×10^{-2}	0.002875	9.65×10^{-3}	15.351	2 to 0	—
⁷ Li	3/2	92.58	-0.040	0.29	38.863	50 to -10	1MLiCl
¹¹ B	3/2	80.42	0.040	0.17	32.084	100 to -120	BF ₃ OEt ₃
¹³ C	1/2	1.108	—	1.59×10^{-2}	25.144	240 to -10	SiMe ₄
¹⁵ N	1/2	0.37	—	1.04×10^{-3}	10.133	1200 to -500	MeNO ₂
¹⁷ O	5/2	3.7×10^{-2}	-0.026	2.91×10^{-2}	13.557	1400 to -100	H ₂ O
¹⁹ F	1/2	100	—	0.83	94.077	800 to -450	CFCC ₃
²³ Na	3/2	100	0.108	9.25×10^{-2}	26.451	10 to -60	1MNaCl
²⁷ Al	5/2	100	0.150	0.21	26.057	200 to -200	[Al(H ₂ O) ₆] ³⁺
²⁹ Si	1/2	4.7	—	7.84×10^{-3}	19.865	100 to -400	SiMe ₄
³¹ P	1/2	100	—	6.63×10^{-2}	40.481	230 to -200	H ₃ PO ₄

^aelectric quadrupole moment Q in multiplies of $|e| 10^{-24} \text{ cm}^2$.

^bat constant field and equal number of nuclei

In ssNMR, the line broadening is mainly due to interactions like dipolar coupling and chemical shift anisotropy (CSA). Therefore, the method of narrowing line is important. To acquire ssNMR spectra with high resolution, proton decoupling and magic angle spinning (MAS) are frequently employed. Moreover, in ssNMR, the interactions of the nuclei are orientation-dependent, which will result in powder pattern, which are the broad peaks. In solids, the molecular tumbling is not present, MAS (spinning the sample at an angle of 54.74° , called magic angle with respect to the axis of B_0 field, shown in Figure 3.5) is used to reduce the anisotropic nuclear spin interactions[2].

Figure 3.5: MAS in an external magnetic field

3.3 Electrochemical Measurements

3.3.1 Preparation of electrode

To prepare the catalyst ink, the as-synthesized LiCo_2O_4 was mixed with acetylene black with a 5:1 mass ratio. The powder mixture was then dispersed into a solvent mixture comprising deionized water, isopropanol (IPA) and Nafion perfluorinated resin. The volume ratios of water: IPA: Nafion solution were maintained at 4: 1: 0.125. The mixture was sonicated to achieve a homogeneous ink with the concentration of $5 \text{ mg}_{\text{ox}} \text{ mL}^{-1}$. A glassy carbon electrode with surface area of 0.196 cm^2 was used as the working electrode in three-electrode cell. The polished glassy carbon electrode was drop-casted with $10 \text{ }\mu\text{L}$ of ink, with a mass loading of $255.10 \text{ }\mu\text{g}_{\text{ox}} \text{ cm}^{-2}$ disk. To dry the ink on the electrode, it was left to evaporate the IPA and water at room temperature.

3.3.2 Three-Electrode electrochemical testing

The electrochemical measurements were performed via Bio-Logic SP150 potentiostat. Oxide-modified glassy carbon electrode, platinum plate and Hg/HgO (1.0 M KOH) electrode were used as the working, counter and reference electrodes, respectively. The measurements were conducted in 1.0 M of KOH at room temperature. Cyclic voltammetry (CV) measurements were carried out in the potential range from -0.02 to 0.70 V (vs Hg/HgO) at a scan rate of 10 mV s^{-1} to examine the OER performances of the lithium cobalt oxides. The resistance of the electrolyte was determined by electrochemical impedance spectra, which gave a value of $\sim 5 \text{ }\Omega$.

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Chapter 4

Results and Discussion

This chapter mainly discussed the theoretical calculations and experimental results which revealed that inducing lithium vacancies in the LiCo_2O_4 spinel oxide can activate the t_{2g} orbital in the electrocatalyst, which will enhance the electron transfer from the reactants to the electrocatalyst due to presence of spin channels. Various materials characterization techniques such as XRD, XAFS and XPS were employed to measure the oxidation state of cobalt and confirmed the tetrahedral vacancies. ssNMR and magnetic analysis were used to determine the electronic structure and spin of the electrocatalyst. The electrochemical performance of the LiCo_2O_4 spinel oxides was also discussed in detail.

4.1 Theoretical Calculation

Figure 4.1: (a) PDOS $T_vCo_2O_4$ and $LiCo_2O_4$ in the x-y plane (T_v denotes the tetrahedral vacancy). (b) Plots of charge and spin distribution along (001) plane of Li vacancy of $LiCo_2O_4$.

In Figure 4.1a, hybridization between O 2p and Co 3d orbitals can be observed through the overlap of energy positions between O 2p and Co 3d states. As illustrated for $LiCo_2O_4$, the energy states below the Fermi level mainly consists of cobalt d_{xy} orbital and oxygen p_x and p_y orbitals, in which d_{xy} orbitals are the majority. Above the Fermi level, the cobalt ions contribute the d_{xy} orbital in spin-down channel and the $d_{x^2-y^2}$ orbital in spin-up channel. Meanwhile, it is observed that O $2p_x$ and O $2p_y$ orbitals in the spin-up channel show partial covalence with $d_{x^2-y^2}$ orbital, while it is unnoticed in the spin-down channel with d_{xy} orbital. When all the lithium cations are removed from the tetrahedral sites, a significant feature is observed in the vicinity of the Fermi level — the d_{xy} orbital crosses the Fermi level and it only exists in the spin-down channel. This orbital symmetry is crucial in allowing electrons to transfer from the Co t_{2g} orbital to the O 2p orbital below the Fermi level, whereby the increased electron density at the Fermi level will facilitate electron transfer from the reactants to the electrocatalyst due to presence of spin channels. Since the initial step of OER involves the electron transfer from the adsorbed oxygen species to the reactive metal

center, then to the lattice oxygen, the orbital crossing will enhance charge transfer from the metal center to lattice oxygen by inducing tetrahedron vacancies.

The charge density and spin distribution are further explored on the (001) principal plane. No distinct change can be observed from the charge distribution of cobalt and oxygen among the three models, as shown in Figure 4.1b. This indicates that the charge does not change dramatically due to the Li vacancies. In contrast, a significant change in spin distribution is noticed. For LiCo_2O_4 , the weak spin polarization exists in the cobalt element while it does not in the oxygen element. The spin polarization in cobalt can be explained by the oxidation state of cobalt (+3.5) in LiCo_2O_4 , whereby electrons in $\text{Co}^{3+}\text{-O-Co}^{4+}$ are not fully paired. In $\text{T}_v\text{Co}_2\text{O}_4$, the cobalt spin polarization becomes stronger compared to that in LiCo_2O_4 , and meanwhile, oxygen spin polarization appears in this sample, represented by the weak yellow dot. These phenomena indicate that the spin polarization of cobalt and oxygen can be induced after removing lithium in the tetrahedral site.

4.2 Materials Characterization

Figure 4.2: XRD patterns of as-synthesized LiCo₂O₄ samples, and ZnCo₂O₄ as the reference pattern.

The XRD diffraction patterns of the as-synthesized LiCo₂O₄ based on different annealing temperatures are in accordance with that of the standard spinel oxide ZnCo₂O₄, verifying that the LiCo₂O₄ samples indeed have spinel crystal structures. Another feature of the pattern demonstrates that as the annealing temperature increased, the crystallinity of the LiCo₂O₄ spinel oxides improved, as illustrated by the increased intensities of the diffraction peaks. Further analysis of the peak intensities revealed an interesting trend — a gain in the (111)/(220) peak ratio from 0.97 (300 °C), 2.88 (400 °C), to 3.29 (500 °C). The intensity ratio of these two peaks reflects the lithium vacancy, whereby a higher ratio indicates more vacancies.[1] This suggests that more tetrahedral sites were emptied by increasing the annealing temperature, implying that the synthesizing method is successful in inducing tetrahedron vacancies.

Table 1: BET analysis of specific surface area of LiCo_2O_4 .

Samples	Specific surface area (m^2/g)
LiCo_2O_4 300 °C	5.2184
LiCo_2O_4 400 °C	0.5087
LiCo_2O_4 500 °C	0.3820

Table 2: ICP-OES (Inductively coupled plasma-optical emission spectrometry) analysis results of LiCo_2O_4 samples.

Sample	Solution Volume (mL)	Elements	Concentration in Solution (ppm, $\mu\text{g}/\text{mL}$)	Dilution Factor	Total Weight in Solution (μg)	Li/Co Atomic Ratio
LiCo_2O_4 300 °C	10	Co	2.51	100	2507.1	0.42
	10	Li	0.12	100	124.0	
LiCo_2O_4 400 °C	10	Co	15.81	20	3161.2	0.26
	10	Li	0.49	20	97.0	
LiCo_2O_4 500 °C	10	Co	21.64	100	661801.2	0.04
	10	Li	0.11	100	3500.7	

4.3 Solid-state Nuclear Magnetic Resonance (ssNMR) Analysis

Figure 4.3: (a) Solid state ^7Li MAS NMR data with vertical expansions of the broader resonances influenced by the paramagnetic interaction. (b) FWHM (dotted lines) and integrated intensity (solid lines) of the ^7Li MAS NMR resonances as a function of thermal decomposition temperature. (c) The Curie-Weiss dependence of each ^7Li chemical shift as a function of $1/T$.

^7Li MAS NMR data is obtained to investigate the change in the local environments of lithium in the synthesized samples. The ^7Li MAS NMR spectra shown in Figure 4.3a demonstrates two distinct Li positions existing within the LiCo_2O_4 spinel framework, as indicated by a narrower upfield resonance at ~ 0.5 ppm and a broader downfield resonance at ~ 8 ppm. At 300 °C, the ~ 8 ppm resonance is shown to be dominant. However, upon increasing heat treatment temperature, the intensity of this ^7Li resonance drops markedly relative to the ~ 0.5 ppm resonance (see the integrated peak areas in Figure 4.3b, downfield resonance/solid lines). This behaviour suggests that the ~ 8 ppm resonance can be attributed to Li occupying the LiCo_2O_4 tetrahedral positions. However, this value differs from the other reports, which claimed that it should be in the range of ~ 15 – 26 ppm.[2, 3] Another

observation of the spectra is that the ~8 ppm resonance is narrowing with increasing heat treatment temperatures (see FWHM of the NMR resonances, downfield resonance/full lines). This observation suggests that the homonuclear ^7Li - ^7Li dipolar interaction broadening these resonances is associated with increasing average ^7Li - ^7Li distance upon Li depletion. Both findings are in good agreement with the ICP data. Furthermore, Figure 4.3c portrays the small paramagnetic contribution to the ^7Li chemical shifts and temperature coefficients, which shows that the residual Li in the tetrahedral positions is influenced by a weak paramagnetic interaction, suggesting the presence of paramagnetic Co^{3+} (high spin or intermediate spin).

4.4 Magnetization Analysis

Figure 4.4: (a) Reciprocal of magnetic susceptibility vs temperature of LiCo_2O_4 samples. (b) Weiss constants of the LiCo_2O_4 samples. (c) The relationship between effective magnetic moments and Weiss constants of LiCo_2O_4 samples, calculated from the paramagnetic region in χ^{-1} vs T plot.

Field-cooled magnetic susceptibility χ_{FC} was measured at an external magnetic field of 1000 Oe. The reciprocal of magnetic susceptibility vs temperature of LiCo_2O_4 samples is plotted in Figure 4.4a. With the decrease of temperature, the magnetization increased significantly and arrived at the highest with 0.046 emu g^{-1} and decreased. A linear relationship is observed from the $1/\chi$ -T curve in the high temperature region, which demonstrates that the oxide is paramagnetic. By analysing the $1/\chi$ -T relation using Curie-Weiss law, Figure 4.4b depicts the Weiss constants of these oxides. The decreasing Weiss constants from -89.70 K (300 °C) to -108.09 K (400 °C) to -113.51 K (500 °C) reflected that a magnetic coupling change has occurred, resulting in more dominant antiferromagnetic properties. As shown in Figure 4.4c, the effective magnetic moments gradually increased from $1.50 \mu_{\text{B}}/\text{Co}$ (300 °C) to $1.56 \mu_{\text{B}}/\text{Co}$ (400 °C) and to $1.60 \mu_{\text{B}}/\text{Co}$ (500 °C). indicating that the spin state of the catalyst is getting higher with increasing temperature. This suggests that the spin state of neighbouring Co bridged by oxygen will be more polarized in the opposite direction. The Co^{3+} cations in ZnCo_2O_4 and Co_3O_4 are

usually in a low spin state with $t_{2g}^6e_g^0$ [4]. If the Co^{3+} cations were to show spin polarized state, it suggests that electrons in t_{2g} orbital are depolarized, either to e_g orbital or to form more covalent bonds.

4.5 X-ray Absorption Spectroscopy

Figure 4.5: (a) Normalized Co K-edge XANES spectra of LiCo₂O₄ samples, Co₃O₄ and ZnCo₂O₄. (b) Fourier transforms (FT) of Co K-edge EXAFS spectra of LiCo₂O₄ samples.

The valency of cobalt was determined by the XANES. As shown in the K-edge spectra (Figure 4.5a), the edge energies of cobalt moved higher as the temperature increased from 300 °C to 400 °C, and dropped to lower values as the temperature raised to 500 °C. The K-edge energy shift is correlated to the oxidation state of the cobalt atom.[5] By using the integral method[6], the oxidation states of cobalt were estimated to increase from +2.63 to +2.85 when the temperature reached 400 °C, and decreased to +2.67 at 500 °C. The increase in oxidation states of cobalt implies that cations in the tetrahedral sites are progressively removed, while the decrease of oxidation state from 400 °C to 500 °C indicates the increase of oxygen vacancies. Figure 4.5b portrays the FT of EXAFS spectra at Co K-edge of LiCo₂O₄ spinel oxides, whereby information on site distribution of cations can be obtained. The first and second main peaks at approximately 1.42 Å and 2.45 Å correspond to Co-O bond and Co-Co_{OH}, respectively. The weak peak at 3 Å represents the Co-M (Td, Li) bond.[7, 8] It is noted that the interatomic distances measured experimentally are approximately 0.5 Å shorter compared to the actual values because of the scattering phase-shift.[9] The effect of heat treatment does not affect the Co-O and Co-

COOH bonds significantly. In contrast, the increasing-temperature heat treatment causes the peak Co-M (Td, Li) to become weaker, suggesting that more vacancies in tetrahedral sites are formed with the increasing heat treatment temperature.

4.6 X-ray Photoelectron Spectroscopy

Figure 4.6: (a) XPS spectra of Co 2p of the LiCo_2O_4 samples. (b) XPS spectra of O 1s of the LiCo_2O_4 samples. (c) The calculated valence state of cobalt at Co $2p_{3/2}$. (d) The calculated valence state of cobalt at Co $2p_{1/2}$. (e) An analysis of the XPS spectra in (b) displaying the ratio of oxygen species, whereby LO, DO and H_2O represent lattice oxygen, defected oxygen and adsorbed water molecule, respectively.

Table 3: Parameters for Co 2p XPS spectra of LiCo_2O_4 samples 300 °C to 500 °C.

	BE of Co $2p_{3/2}$ /eV	Area	BE of Satellite peak/eV	Area	BE of Co $2p_{1/2}$ /eV	Area	BE of Satellite peak/eV	Area	BE of Co $2p_{1/2}$
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									- Co 2p _{3/2} /eV
LiCo ₂ O ₄ 300 °C	779.83	20924	789.48	8308	794.88	1749	804.38	1724	15.05
LiCo ₂ O ₄ 400 °C	779.54	73715	789.49	30595	794.64	8375	804.69	7871	15.1
LiCo ₂ O ₄ 500 °C	780.01	63720	789.76	27020	794.91	8184	804.71	9276	14.9

Table 4: Parameters for O 1s XPS spectra of LiCo₂O₄ 300 °C to 500 °C.

	BE of LO/eV	Area	BE of DO/eV	Area	BE of H ₂ O/eV	Area
LiCo ₂ O ₄ 300 °C	530.15	16026.21	0	0	532.85	172959.1
LiCo ₂ O ₄ 400 °C	529.8	42663.1	531.5	20803.05	532.9	11540.76
LiCo ₂ O ₄ 500 °C	529.85	41918.17	531.55	29385.44	532.8	15988.47

The XPS spectra of Co 2p_{3/2} and 2p_{1/2} orbitals of the LiCo₂O₄ samples were shown in Figure 4.6a. The spin orbit splitting between 2p_{3/2} and 2p_{1/2} orbitals of the three samples are relatively consistent, with a value of ~15 eV, which is in agreement with the reports by Oku's group and Huang's group (see Table 3)[10, 11]. The oxidation states of cobalt at different temperatures are calculated from the ratio shown in Figure 4.6c and 4.6d, and the trend of the cobalt valence states is in agreement with that of the Co K edge XANES, whereby the cobalt cation of 400 °C sample possesses the highest valence state. As shown in Figure 4.6b, the peaks of the XPS spectra of the O 1s are fitted accordingly, namely 529.8 eV, 531.5 eV and 532.9 eV, representing lattice oxygen, adsorbed oxygen species onto the surface vacancy and adsorbed water molecule on the sample surface, respectively (see detailed fitting parameters in Table 4)[12, 13]. From Figure 4.6e, the ratio of oxygen species clearly depicts the increment of defective oxygen as temperature increased, suggesting the rise in oxygen vacancies, which is in accordance with TGA and ICP results.

4.7 XAS Analysis

Figure 4.7: (a) Schematic description of XAS spectra displaying the electronic transition of Co L₂ and L₃ edges. (b) XAS profile of O K-edge of the LiCo_2O_4 samples.

Figure 4.7a displays the X-ray absorption spectra near the Co L_{2,3} edge of the LiCo_2O_4 samples. The two main peaks in the figure, denoted by L₃ and L₂ edges, are a result of spin-orbit coupling.[14] The Co L₃ and L₂ edges represent the electronic transition from Co 2p_{1/2} to 3d and Co 2p_{3/2} to 3d, respectively. The spectra shows that the corresponding main peaks L₃ and L₂ at about 780 and 795 eV, respectively.[15] At 300 °C, a shoulder on the low-energy side of the L₃ peak is observed, suggesting the presence of Co²⁺. [16] Subsequently, a shift towards the higher absorption energy region is observed in the spectra, from 780.4 eV (300 °C) to 780.7 eV (400 °C) near the L₃ edge and from 794.7 eV (300 °C) to 795 eV (400 °C) near the L₂ edge, indicating that there is a promotion in the oxidation state of cobalt. As the temperature is increased to 500 °C, both L₃ and L₂ edges show a reduction in absorption energy, indicating that the oxidation state of cobalt is decreased, which is in good agreement with the Co K edge XANES results.[15, 17, 18] The activation of cobalt t_{2g} orbital can be reflected by analyzing the overlapping of the Co- t_{2g} and O-2p orbitals shown in Figure 4.7b. XAS spectra near O K edge can further verify the

analysis. In Figure 4.7b, peaks A to C illustrate the electronic transitions from O 1s core level to unoccupied partially hybridized Co 3d and O 2p states, while peaks D and E represent the electronic transition from O 1s core level to the unoccupied hybridized Co 4sp and O 2p states.[18-20] For LiCo_2O_4 300 °C, peak A is almost not observable, revealing that Co t_{2g} orbital has no empty states for electrons to occupy. As the heat treatment temperature increased to 400 °C and 500 °C, peak A becomes more apparent, reflecting that empty states are induced in the t_{2g} orbital, resulting in the activation of the cobalt t_{2g} orbital. The decreased intensity of peaks B and C also suggest that there are more electrons in the e_g orbital.

4.8 in-situ XAS

Figure 4.8: (a) Fourier transforms (FT) of Co K-edge in-situ EXAFS of LiCo_2O_4 300 °C-500 °C at 1.52 V vs RHE compared with ex-situ EXAFS of the respective samples. (b) Schematic figures displaying before and after oxygen vacancies are introduced.

To analyse real-time surface reactions with electrochemical kinetics, in-situ EXAFS measurements on the samples are investigated. Figure 4.8a illustrates the in-situ EXAFS spectra of the samples. Apparently, for all three samples of LiCo_2O_4 at 1.52 V vs RHE, the Co-O peak shifts to shorter distance relative to those as-prepared samples. It suggests that there is more orbital overlap and stronger Co-O covalency during the OER process. A broadening of M-M (M-M_{oct} and M-M_{tet}) peaks is also observed, indicating the occurrence of surface reconstruction and the metal in the low coordination converts into that in high coordination environment, which causes the disappearance of M-M_{tet} . More importantly, comparing the intensity ratio of Co-O/Co-Co, it increases with increasing heat treatment temperature. Yet, as for the as-prepared oxides, the intensity of Co-O peak is weaker than that of Co-Co peak, which can also be noticed in Co_3O_4 and ZnCo_2O_4 . [21, 22] Interestingly,

the 500 °C sample has a contrasting trend at the applied potential, which indicates that more Co-O bonds form. It reflects that there is an increasing amount of oxygen vacancies as the heat treatment temperature increased, as more oxygen intermediates can be adsorbed onto the cobalt atom to fill up the oxygen vacancies as shown in Figure 4.8b to reach the coordination number of six.

4.9 Electrochemical Characterization

Figure 4.9: (a) The OER CV curves performed in 1 M KOH (scan rate: 10 mV s⁻¹) after background correction and iR correction[23]. (b) The CV curves measured in 1.0 M KOH without the OER region. (c) Tafel plots of the LiCo₂O₄ samples in comparison with IrO₂[24] and CoOOH[25]. (d) Turnover frequency (TOF) of the LiCo₂O₄ samples, CoOOH[25], IrO₂[26] and Co₃O₄[26] at an overpotential (η) of 350 mV. The number of active sites for TOF calculation is estimated via the Coulombic charge under the Co redox peak (TOF_{redox}). (e) Chronopotentiometry measurements of 24 hours for LiCo₂O₄ 400 °C.

The electrocatalytic OER performance of the LiCo₂O₄ spinel oxides was examined in 1.0 M KOH. As shown in the CV curves (Figure 4.9a), when the annealing temperature was increased from 300 °C to 500 °C, the BET-normalized specific OER current density of the spinel oxides exhibits an increase-then-decrease trend, with the 400 °C sample having the highest current density. Interestingly, these three samples have apparent differences in the non-OER region as displayed in Figure 4.9b. The redox peak at about 1.00~1.15 V, which is attributed to Co²⁺/Co³⁺ transition[27, 28], begins to appear as the heat treatment temperature goes higher, but the redox peak is not noticeable for the 300 °C sample. As typical Co²⁺/Co³⁺ transition occurs on the low coordination of cobalt cations, it indicates that the coordination number of cobalt ions decrease with increasing heat treatment temperature. Considering all the cobalt ions exist in octahedral sites, the reduction in the coordination number demonstrates the increment of oxygen vacancies from 300 °C to 500 °C. Different from other reports, it should be noted that the existence of two peaks for the 500 °C sample suggests that the cobalt ions have two coordination environments. Tafel plots shown in Figure 4.9c confirmed that the OER activity of the 400 °C sample is the most outstanding, even outperforming the activity of CoOOH and the benchmark IrO₂. The 400 °C catalyst also exhibits the highest TOF_{redox} among the three, and it is superior to CoOOH, which is the oxyhydroxide under OER condition (Figure 4.9d). To evaluate the durability of LiCo₂O₄ 400 °C in an alkaline environment, chronopotentiometry test was performed in 1 M KOH solution for 24 hours, at a constant current of 1 mA. Figure 4.9e shows that the overpotential decreased by 19 mV after 12 hours operation, and it maintained stable behaviour over the next 12 hours, suggesting good stability of the

catalyst. Therefore, all the above results indicate that the 400 °C catalyst possess superior electrocatalytic activity and stability.

4.10 Discussion

Figure 4.10: Schematic illustration of the t_{2g} activation, whereby charge transfer from the adsorbed oxygen intermediates to the t_{2g} orbital is forbidden for low spin cobalt cation, while it is allowed for intermediate and high spin cobalt cation.

The OER performances of the three LiCo_2O_4 spinel oxides were compared with IrO_2 . IrO_2 was chosen because it is the commercial OER benchmark catalyst. All the current density is normalized by the metal oxide BET surface area to ensure accurate estimation of specific activity. Electrochemical measurements reflect that the sample synthesized at 400 °C has the smallest overpotential among the LiCo_2O_4 catalysts. Furthermore, TOF was measured for the three LiCo_2O_4 catalysts, and compared with Co_3O_4 and IrO_2 . Among all the samples, LiCo_2O_4 -400 °C exhibits the highest TOF.

OER is a four-electrons charge transfer, and it is important to facilitate the charge transfer at the spinel oxide/electrolyte interface to yield highly efficient OER electrodes. The charge transfer process is illustrated in terms of their electronic structures (Figure 4.10). For low spin cobalt cation, the t_{2g} orbital is fully occupied, which causes the charge transfer from the oxygen to the t_{2g} orbital of the cobalt cation to be forbidden. In contrast, the partially filled t_{2g} orbital in intermediate and high spin cobalt cations provides an additional pathway for the electron to move from the oxygen to the metal center. The participation of the t_{2g} orbital in the charge transfer exhibits the activation of the t_{2g} orbital. Moreover, the non-bonding t_{2g} orbitals have transformed to antibonding t_{2g}^* orbitals due to the π -interaction

occurring from the overlap between the cobalt orbital and oxygen orbital. The higher energy antibonding t_{2g}^* orbitals are closer to the Fermi level, and they can now play a role in promoting charge transfer between oxygen and cobalt. As illustrated in the pDOS plots of the LiCo_2O_4 with tetrahedral site vacancy, at the near-Fermi-level energy region, the orbital crossing of the Co $3d_{xy}$ orbital in the spin down channel reveals the presence of spin channel. This spin channel existing in the t_{2g} orbital allows the activated orbital to transfer electrons within the catalyst more efficiently, which can be reflected in the OER activity of the 400 °C electrocatalyst. Further experimental study such as the Co L-edge measurement has demonstrated the existence of empty states in the t_{2g} orbital. In addition, ssNMR analysis and magnetic results have shown the presence of paramagnetic Co^{3+} (intermediate or high spin) in LiCo_2O_4 400 °C, which results in the 400 °C sample to possess the highest OER performance.

4.11 Conclusion

In summary, the combination of theoretical calculations and experiments have revealed the possibility of inducing tetrahedral vacancies in spinel oxide LiCo_2O_4 by increment of annealing temperature, which generated spin channels in the t_{2g} orbitals to provide an additional pathway for the electron to move from the oxygen to the metal center. This can be reflected in the catalytic activity of the 400 °C sample, whereby the t_{2g} orbital activation has resulted the sample to possess the highest TOF and relative stable activity after 24h of CP at 1 mA. Therefore, this work demonstrated that t_{2g} orbital activation is one of the strategies to enhance OER electrocatalysts for LiCo_2O_4 spinel oxide.

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Chapter 5

Conclusions and Recommendations

This final chapter summarizes the conclusions and recommendations of this work. The hypothesis has shown to be validated by the theoretical and experimental design. For future recommendations, DFT simulations can be used to calculate the binding strength of adsorbates, which is important to understand the rate determining step in OER. Secondly, the octahedral site in spinel oxide is commonly reported as the active site for catalytic activity. By partially substituting Co, which occupies the octahedral site in LiCo_2O_4 , with other transition metals such as Mn, Cr, Ni and Fe in varying amounts, we can study whether doping can affect the DOS and energy gap, and the amount of oxygen vacancies introduced in the spinel oxide. Lastly, further experiments can be conducted on the 500 °C sample to study surface reconstruction.

5.1 Implications

The motivation of this thesis is to design an electrocatalyst which can activate t_{2g} orbitals by inducing tetrahedral vacancies in spinel oxide LiCo_2O_4 . In a typical spinel oxide, there are two geometric sites, namely the tetrahedral site and the octahedral site. Our previous work has shown that the octahedral site plays a more important role in oxygen electrolysis, ascribing to the stronger oxygen orbital polarization towards the octahedral metal in ZnCo_2O_4 . By replacing Zn with a low electronegative metal such as lithium, the electron cloud of oxygen will be more polarized towards the octahedron, thereby introducing higher Co-O covalency and causing OER activity to be enhanced. Besides, lithium cation does not participate in metal and oxygen hybridization near-Fermi-level energy region because the energy of the Li 2s orbitals is very low and far away from the Fermi level. These results encouraged the investigation of whether an even lower electronegativity can be achieved in the tetrahedral site. By inducing tetrahedral vacancies, electronegativity in the tetrahedron can be minimized, therefore reducing its tendency to attract electrons from oxygen, and triggering stronger oxygen polarization towards the octahedron.

Therefore, theoretical calculation (DFT) was first employed to investigate the relationship between the loss of metal tetrahedral sites and the Co 3d and O 2p band centers relative to the Fermi level. When LiCo_2O_4 with tetrahedral site vacancy was modelled, it was noticed the d_{xy} orbital crosses the Fermi level and it only exists in the spin-down channel. This orbital symmetry is crucial in allowing electrons to transfer from the Co t_{2g} orbital to the O 2p orbital below the Fermi level, whereby the increased electron density at the Fermi level will facilitate electron transfer from the reactants to the electrocatalyst due to presence of spin channels.

In view of the aforementioned theoretical outcomes, it is worthwhile to validate and further explore the relationship between tetrahedral vacancies and OER activity, and other possible findings by designing and performing a series of experimental studies.

LiCo_2O_4 was fabricated via simple thermal decomposition method at three different temperatures 300, 400, and 500 °C. XRD was first conducted to ensure that the crystal structures of the as-synthesized LiCo_2O_4 are spinel oxides. XRD analysis has also shown that the increase in the (111)/(220) peak ratio from 0.95 (300 °C), 3.17 (400 °C), to 3.69 (500 °C) reflects the increase in tetrahedral site vacancies as heat treatment temperature increased. Secondly, ICP-MS was conducted to confirm that tetrahedral site vacancies were induced. In addition, EXAFS data has shown that the peak at 3 Å, which represents the Co-M (Td, Li) peak, decreased in intensity with increased heat treatment temperature, suggesting that more vacancies in tetrahedral sites are formed.

XPS and XAFS have reflected that the oxidation state of the 400 °C is the highest among the three samples. The high valency of Co will result in a shorter Co-O bond, which shows that the Co-O bond covalency is higher. This will result in higher OER performance.

Since DFT calculations have shown that tetrahedral vacancies can result in spin channel, it is essential to understand the spin mechanism behind the electrocatalyst. In a cobalt-based spinel oxide, the trivalent cobalt cations in the octahedral site usually adopts a low spin state (i.e. ZnCo_2O_4 , $t_{2g}^6e_g^0$). [1] The fully occupied t_{2g} orbitals are regarded as non-bonding orbitals. [2] The lower energy d-orbitals are unavailable for the transferring of electrons, therefore not contributing to the activity of OER. Nevertheless, utilizing the t_{2g} orbitals effectively by creating empty t_{2g} orbitals to provide additional pathway for the transport of electrons within the oxide can facilitate the OER process. To activate the cobalt t_{2g} orbital, the presence of partially filled t_{2g} orbitals is essential i.e. $t_{2g}^4e_g^2$ or $t_{2g}^5e_g^1$. This will generate spin channels in the t_{2g} orbitals to enable electron hopping between Co-O-Co. [5]. Therefore, ssNMR analysis and magnetic results have shown the presence of paramagnetic Co^{3+} (intermediate or high spin) in LiCo_2O_4 400 °C, which means that t_{2g} orbital is activated. Moreover, XAS analysis has shown that empty states are induced in the t_{2g} orbital when the heat treatment temperature increased to 400 °C and 500 °C, which can result in the activation of the cobalt t_{2g} orbital.

Next, it is important to identify the connection between activation of the cobalt t_{2g} orbital and OER activity. OER is a four-electrons charge transfer, and it is important to facilitate the charge transfer at the spinel oxide/electrolyte interface to yield highly efficient OER electrodes. For low spin cobalt cation, the t_{2g} orbital is fully occupied, which causes the charge transfer from the oxygen to the t_{2g} orbital of the cobalt cation to be forbidden. In contrast, the partially filled t_{2g} orbital in intermediate and high spin cobalt cations provides an additional pathway for the electron to move from the oxygen to the metal center. The participation of the t_{2g} orbital in the charge transfer exhibits the activation of the t_{2g} orbital. Moreover, the non-bonding t_{2g} orbitals have transformed to antibonding t_{2g}^* orbitals due to the π -interaction occurring from the overlap between the cobalt orbital and oxygen orbital. The higher energy antibonding t_{2g}^* orbitals are closer to the Fermi level, and they can now play a role in promoting charge transfer between oxygen and cobalt. As illustrated in the pDOS plots of the LiCo_2O_4 with tetrahedral site vacancy, at the near-Fermi-level energy region, the orbital crossing of the Co $3d_{xy}$ orbital in the spin down channel reveals the presence of spin channel. This spin channel existing in the t_{2g} orbital allows the activated orbital to transfer electrons within the catalyst more efficiently, which can be reflected in the OER activity and TOF of the 400 °C electrocatalyst. It is worth noting that even though the 500 °C electrocatalyst also has tetrahedral site vacancies which resulted in the activation of the t_{2g} orbital, its lower OER activity is due to the lower oxidation state of the cobalt cation in comparison to that of the 400 °C electrocatalyst.

5.2 Recommendations

5.2.1 DFT simulation for surface adsorbates

OER is a four-electrons charge transfer process with different reaction intermediates, thus it is important to study the binding energies of the surface adsorbates and understand the electron transfer process at the electrolyte/spinel oxide interface to yield highly efficient OER electrodes. DFT simulation of surface adsorbates can obtain the free energy and binding strength of adsorbates on different crystal facets. Typically, an electrochemical reaction involves the adsorption/desorption of reactants, adsorption/desorption of reaction

intermediates, and electron transfer at the surface. Therefore, the adsorption strength of surface adsorbates is essential to investigate the rate limiting step to comprehend the OER mechanism. For instance, Norskov's group has reported that the OER rate limiting steps by simulating the free energy of reaction intermediates on Pt and Au (shown in figure 5.1)[6].

Figure 5.1: Depicting the oxidized Au (black line) and oxidized Pt (blue line) free energy diagram, whereby potential is zero.

5.2.2 Doping the octahedral site with transition metals

The octahedral site is commonly reported to be more catalytically critical, as the oxygen charge has a larger tendency to flow into the octahedral transition metal as compared to the tetrahedral transition metal[2]. The shifting of the oxygen charge will result in stronger orbital interaction between the octahedral metal and oxygen, which can bring about better OER performance. Consequently, the octahedral site can be extensively investigated by partially substituting Co, which occupies the octahedral site in LiCo_2O_4 , with other transition metals such as Mn, Cr, Ni and Fe in varying amounts. This will allow the change the electronic structure of the spinel oxides, and study whether doping of other transition metals will result in higher catalytic activity.

5.2.3 Determination of surface reconstruction

Interestingly, by comparing the 2nd and 500th cycle of 500 °C LiCo₂O₄ as shown in Figure 5.2, there is a significant increase in the OER current after further cycling, which may be ascribed to surface reconstruction. This increase in current density with continuous cycling was not observed in 300 °C and 400 °C LiCo₂O₄ samples. Further characterization of the 500 °C sample is necessary. HRTEM can be conducted on the electrocatalyst to reveal the morphological change and surface elemental changes. Many Co-based oxides have been reported to undergo surface reconstruction of Co sites to Co oxyhydroxides, which will result in higher OER activity. Notably, most of the electrocatalysts that underwent surface reconstruction, such as BSCF, will have amorphous surface[7], but some electrocatalyst, such as CoFeAlO₄, exhibited crystalline surface after reconstruction[8]. To distinguish the crystallinity of the reconstructed surface, in-situ TEM can be utilized. Scanning transmission electron microscopy coupled with electron energy loss spectroscopy (STEM-EELS) can help to determine the elemental ratio of Co at the surface, whereby a reconstructed surface will have a higher ratio of Co due to the formation of Co oxyhydroxide. Moreover, the oxygen concentration can be detected to study the mechanism of OER.

Figure 5.2: Cyclic voltammograms (10 mV/s) of the LiCo₂O₄ 500 °C sample over 500 cycles in 1M KOH.

5.3 Conclusion

In conclusion, this thesis has adequately illustrated that the hypothesis was proven by the fact that temperature-induced tetrahedral vacancies in spinel oxide LiCo_2O_4 can result in the activation of t_{2g} orbital, and how the activation relates to the high activity of OER. Moreover, the outcomes in this thesis were adequately reflected in the original hypothesis. For future work and recommendations, DFT simulations can be used to calculate the binding strength of adsorbates, which is important to understand the rate determining step in OER. OER performance can be systematically investigated by doping other transition metals in the octahedral site. Further follow-up experiments should also be conducted on the 500 °C sample to study surface reconstruction.

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