Electrochemically activated surface reconstruction of OER catalyst by Cr leaching

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**ELECTROCHEMICALLY ACTIVATED SURFACE
RECONSTRUCTION OF OER CATALYST BY Cr
LEACHING**

LEE JUN YAN

SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

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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

2019

Statement of Originality

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

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Date

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Lee Jun Yan

Abstract

Global demand for energy consumption has been on the rise over the years with globalization and population growth. However, the current usage of fossil fuel as our main energy source raised concerns over the impact on our environment. Hydrogen appears to be the ideal replacement with scalable water electrolysis from renewable energy sources. However, the sluggish kinetics of oxygen evolution reaction (OER) cause it to be expensive and hindered its usage. Therefore it is important to develop an efficient OER catalyst based on first row transition metals to make water oxidation economical.

For many years, different transition metal based oxides OER catalyst like perovskite, spinels, layered hydroxides and amorphous oxides/hydroxides have been explored. Recently, surface amorphisation and reconstruction of the catalyst during electrochemical cycling through OER was discovered to boost the OER performance. To engineer and advance our understanding on in-situ surface reconstruction, Cr leaching phenomenon from CoCr_2O_4 was investigated. Various characterization techniques like CV, CA, ICP, XPS, XAS and TEM techniques were employed to study the active species of OER. The leaching of Cr created vacancies and defects and allowed the formation of CoOOH surface species and improved the OER performance.

The future works have been proposed on defect and vacancy studies on a series of $\text{Co}_{(3-x)}\text{Cr}_x\text{O}_4$ nanoparticle or nanosheets through controlled leaching of Cr. DFT computation have suggested that there is a possibility of large oxygen vacancies that exist in the CoCr_2O_4 structure and contributed to surface reconstruction. To identify Cr leaching mechanism during OER, isotopic investigation of the O_2 and Cr complexes by OLEMS was proposed as well. Overall, this work have recommended a bottom up approach to design and develop more efficient OER catalyst through surface reconstruction.

Lay Summary

Global demand for energy consumption has been on the rise over the years with globalization and population growth. However, the current usage of fossil fuel as our main energy source raised concerns over the impact on our environment. Hydrogen appears to be the ideal replacement with scalable water electrolysis from renewable energy sources. However, the slow kinetics of water electrolysis cause it to be expensive and hindered its usage. Therefore it is important to develop an efficient catalyst based on first row transition metals to make water oxidation economical.

For many years, different transition metal based oxides have been explored. Recently, surface modification of the catalyst during water electrolysis was discovered to boost catalytic performance. To engineer and advance our understanding on in-situ surface reconstruction, chromium leaching phenomenon from CoCr_2O_4 was investigated. Various characterization techniques were employed to study the active species of water oxidation. Chromium leaching has created vacancies and defects that allowed a layer of newly formed surface which boost the efficiency of the catalyst.

The future works have been proposed on defect studies on a modified series of CoCr_2O_4 materials through controlled leaching of Cr. Computational studies have suggested that there is a possibility of many defects in the CoCr_2O_4 structure and contributed to surface modification during water electrolysis. To identify Cr leaching mechanism during water electrolysis, a sophisticated experiment was proposed as well. Overall, this work have recommended a bottom up approach to design and develop more efficient catalyst for water electrolysis through surface modification.

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Abbreviations

BET	Brunauerr-Emmett-Teller
BSCF	$\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$
CA	Chronoamperometry
CV	Cyclic Voltammetry
EDS	Energy Dispersive X-ray Spectroscopy
RHE	Reversible Hydrogen Electrode
SHE	Standard Hydrogen Electrode
TEM	Transmission Electron Microscopy
TMO	Transition Metal Oxide
XRD	X-ray Diffraction
XAS	X-ray absorption Spectroscopy
XPS	X-ray Photoelectron Spectroscopy

Chapter 1

Introduction

First row transition metals oxides have been tremendously explored the past decades in search for much efficient oxygen evolution reaction (OER) electrocatalyst. This chapter summaries on the prospects of CoCr_2O_4 as an efficient OER catalysts and the importance in understanding the requirements for surface reconstruction. Leaching of Cr is proposed as a strategy in promoting surface construction and thus improvement in OER performance. The hypothesis, objective and expected outcomes of this research are as provided.

1.1 Introduction

Ever since the industrial revolution in the 19th century, fossil fuels like oil, natural gas and coal have been the key energy source driving global development. As global population rises along with technological advancement, growth in energy demand has raised concerns over the impact on our environment. There is a need to search for alternative renewable energy production and storage systems. Current renewable energy are harnessed from solar, geothermal heat, wind, hydro-power, tidal waves and biomass and converted to chemical energy in various forms.

Hydrogen appears to be the ideal replacement for fossil fuels as it has high specific energy and is cleanest of all with water as its only byproduct. Among different ways of producing hydrogen like steam reforming, thermal decomposition and electrolysis etc., extracting hydrogen from water electrolysis using renewable energy and production of water from hydrogen fuel cell creates a sustainable energy cycle for the future.¹ However, its realization for commercialization is hindered by its poor efficiency due to the sluggish kinetics of the oxygen evolution reaction (OER).² Therefore a lot of attention has been on designing of OER electrocatalysts to enhance its efficiency. To date, noble metal based oxide, IrO₂ and RuO₂ are still considered as the benchmark OER electrocatalyst in acid and alkali electrolyte.^{3,4} However, they are not a viable solution due to its scarcity and high cost. Therefore, research has been directed towards exploration of oxides of first row transition metal like Ni, Co, Fe and Mn that are abundant and relatively cheaper than the precious metals.⁵⁻⁷ Co-based oxides appear to be one of the most efficient and stable OER catalyst among them.

Different metal oxide families such as perovskite, spinels, layered hydroxides and amorphous oxides/hydroxides are being explored significantly in these years.⁸⁻¹⁰ Besides that, there has been many studies done on identifying the activity descriptors to design more efficient OER catalysts. Recently, there are many reports on Co-based oxides like Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-δ}¹¹, SrCo_{0.8}Fe_{0.2}O_{3-δ}¹², Sr₄Mn₂CoO₉¹³, Co₃(PO₄)₂·8H₂O¹⁴, LiCoO₂¹⁵,

and LiCoPO_4 ¹⁵ that showed surface amorphisation phenomenon with formation of oxyhydroxides under electrochemical conditions with improvement in OER activity. Chen et al. demonstrated that the amorphous CoO_x clusters displayed higher OER current than crystalline CoO_x clusters due to flexibility in the structure.¹⁶ Out of all those that reported, $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF), a Co-based perovskite was discovered to have OER efficiencies higher than the state-of-art IrO_2 .⁸ May et al. discovered that electrochemical cycling resulted in rapid surface amorphisation of BSCF with leaching of Ba^{2+} and Sr^{2+} was caused by high O 2p band centre relative to the fermi level resulting in high oxygen vacancy and lattice oxygen mobility enhancing OER activity.¹¹ Many supported the theory of high O 2p band centre that resulted in the surface reconstruction process during OER.¹⁷⁻¹⁹ There was another suggestion that amorphisation will occur for Co^{2+} containing perovskites like $\text{Sr}_4\text{Mn}_2\text{CoO}$ and $\text{Sr}_6\text{Co}_5\text{O}_{15}$ as compared to Co^{3+} ones due to the distorted prism coordination of Co^{2+} that caused destabilization during OER.¹³ Besides that, Fabbri et al. concluded that large oxygen vacancy in flexible perovskites structures lead to operando surface reconstruction.²⁰ Despite investigations on the cause of surface reconstruction, the role of cation leaching is still overlooked. It is uncertain whether surface reconstruction occurs with leaching of cations regardless of O 2p band centre, metal ion coordination and oxidation or oxygen vacancies.^{11,13,20} Furthermore, most of the reported surface reconstruction happened during electrochemical cycling which raise questions on whether electrochemical cycling process induced a change in structure besides during OER potentials only.^{11,13,17} Xu had also raised a question on the main factors that should be taken into account when designing a pre-catalyst for surface reconstruction.²¹ Therefore, it is important to understand the cation leaching phenomenon for surface reconstruction on crystalline TMO materials.

To design an OER catalyst with surface reconstruction from a bottom up methodology, the material and experimental conditions such as the cation to be leached out, the surface exposure of cations, electrochemical process, redox potential and electrolyte alkalinity. Chromium ions are known to have multiple oxidation states and the two stable forms are the trivalent (Cr^{+3}) or hexavalent (Cr^{+6}) oxidation state.²² Trivalent chromium compounds like oxides and hydroxides are non-reactive and relatively insoluble in water.²² On the other

hand, chromate (CrO_4)⁻² and dichromate (Cr_2O_7)⁻² are common hexavalent chromium oxyanions that are relatively water soluble.²² Therefore, under a high applied potential, Cr^{+3} will likely be oxidized to Cr^{+6} and get leached out. Besides that, Cr^{+3} will be oxidized to Cr^{+6} in the presence of oxygen at pH above 9.²³ Xu et al. has discovered Cr leaching from $\text{Ni}_{0.6}\text{Fe}_{0.3}\text{Cr}_{0.1}\text{O}_x$ oxide/oxyhydroxide during water oxidation.²⁴ Furthermore, given that Cr has a relatively high octahedral stabilization energy, it will reside in the octahedral site of the Spinel structure.²⁵ This will likely result in Cr occupying the surface site based on experimental research²⁶ and DFT studies^{27,28} allowing ease of Cr leaching. Co on the other hand is one of the popularly reported OER active metal apart from Ni and Fe. Considering the respective roles of Co and Cr, Cobalt chromite (CoCr_2O_4) appears to be a suitable OER electrocatalyst to undergo surface reconstruction with leaching under OER potentials in alkaline condition.

CoCr_2O_4 has been widely explored in hydrogenation, combustion catalysis, water gas shift reaction, oxidation of different organic compounds and drew attention recently in OER catalysis.²⁹⁻³² Yet, it has not been thoroughly studied in OER and the role of Cr is still unclear or unexplained in most of the research.³³⁻³⁵

1.2 Hypothesis/Problem Statement

“This thesis tests the hypothesis that when Co in the octahedral site of Co_3O_4 is substituted by chromium to form CoCr_2O_4 , surface reconstruction occurs with leaching of Cr under OER conditions resulting in improved OER performance.

1.3 Objective and Scope

“The present research is concerned with the leaching of Cr from CoCr_2O_4 to expedite surface reconstruction and in turn enhance its OER performance and provide deeper understanding for application as an OER electrocatalyst.”

1.4 Expected Outcomes/Challenges

- i. Chronoamperometry (CA) measurements for long durations may encounter heavy fluctuations due to the accumulated bubbles on the surface of the working electrode. Electrolyte was stirred using a magnetic stirrer to ensure bubbles are constantly removed from the surface of the working electrode.
- ii. In-situ techniques should be used to investigate the *reconstruction* or surface reconstruction of CoCr_2O_4 as the active species or structure of the amorphous surface layer might change or recover when the OER potentials are removed.

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Chapter 2

Literature Review

This chapter will introduce the background and fundamentals of electrocatalytic water splitting. Key performance indicator of OER will be described. Detailed review of the current state of art OER catalyst like IrO₂ and RuO₂ as well as promising TMO will be discussed. The focus of this chapter will be the study on different crystal structures of TMO and the activity descriptors such as e_g occupancy and metal oxygen covalency that correlates to OER performance.

2.1 Background

Hydrogen is considered an ideal fuel as it has high specific energy and is cleanest of all with water as its only byproduct.¹ Extracting hydrogen from water electrolysis (eqn 2.5) using renewable energy and production of water from hydrogen fuel cell creates a sustainable energy cycle for the future. This would greatly reduce the dependency of fossil fuels while meeting the ever growing demand for energy supply.² Among the two important water splitting reactions, hydrogen evolution reaction (HER) (eqn 2.1 and 2.2) and oxygen evolution reaction (OER) (eqn 2.3 and 2.4), OER turns out to be the bottleneck due to its sluggish kinetics and as a result high overpotential is needed to drive the reaction.³ For the past decades, significant efforts have been dedicated to improve the efficiency of OER.^{4,5} So far, RuO₂ and IrO₂ noble metal oxides are the benchmark catalysts for OER.⁶⁻⁸ However, large scale production is hindered due to its scarcity and cost. Thus, interest has been directed towards the abundant first transition metal oxides (TMOs) of Mn, Fe, Co and Ni, as alternatives.⁹⁻¹¹ Besides, water electrolysis, OER has drawn significant attention from applications like photocatalysis and rechargeable metal–air batteries.^{4,12-15}

HER:

OER:

Overall reaction:

OER is a four step mechanism whether the electrolyte medium is acidic or alkaline. Classical OER mechanisms have been proposed by many research groups with OH and OOH intermediates forming on the surface of metal cations as shown in the Figure 2.1.¹⁶

However, an alternative mechanism which involves the lattice oxygen participation (Figure 2.2) has been suggested on some TMOs recently with improvement in OER performance as compared to classical mechanism. This discovery may bring new insights on the TMOs' OER mechanism and strategies to design of efficient OER catalysts.

Figure 2.1: Classical OER mechanism on metal oxides in acid (blue) and alkaline (red) solution. For both alkaline and acid electrolytes, a peroxide (M–OOH) intermediate is formed during oxygen evolution (black line).¹⁶

Figure 2.2: One of the possible lattice oxygen mechanism of OER.¹⁷

The basis of electrocatalysis revolves around the surface chemistry of reactants, intermediates and products. According to Sabatier's principle, the binding strength of the reaction species to the catalyst surface should never be too strong or too weak.¹⁸ Therefore, there should be a volcano shaped relationship between the catalytic performance and binding strength between the catalyst and reaction species theoretically. However, even with a catalyst of optimum binding strength, OER will remain to be a sluggish process ascribed to the multiple intermediates that has strong binding energies which are closely related through scaling relations $\Delta G_{\text{OOH}} = \Delta G_{\text{OH}} + 3.2 \pm 0.2 \text{ eV}$.¹⁹ Nevertheless, efforts have been made to minimize the overpotential of OER to make water electrolysis efficient and economically viable^{20,21}. Many activity descriptors relevant to the electronic properties were proposed to justify for the difference in binding energy of different materials, like the number of d-electrons^{22,23}, oxidation states²⁴, anti-bonding band filling²⁵, transition metal e_g occupancy^{26,27}, metal-oxygen covalency¹¹, metal-oxygen bond length²⁸ and O 2p band centre²⁹.

2.2 Electrocatalytic performance indicators

The basic function of an electrocatalyst is to facilitate charge transfer from electrode to reactants vice versa as well as adsorption and desorption of reactants and products respectively.¹⁶ There are a few parameters that define the performance of a good catalyst: like overpotential(η), Tafel slope, stability and activity.

2.2.1 Overpotential

Ideally, the applied potential to drive a reaction should be the same as the potential required at equilibrium. However, in reality, there is an energy barrier known as activation energy that needs to be overcome to kick start a reaction. As a result the applied potential is higher than that of the equilibrium potential. In order to measure this overpotential, we will have to judge the onset potential for the reaction which has been standardised at the value when current is 10 mAcm^{-2} .³⁰ The overpotential is then calculated to be the difference between the onset potential and the equilibrium potential of OER at 1.23V. Therefore, the target is

to minimise overpotential to make the reaction more energy efficient. Currently, the good OER catalysts achieved overpotential of around 300-400mV. There is still a lot of room for improvement.

2.2.2 Tafel Slope

The Tafel slope (b) is defined as the extent of current response with respect to increase in potential. It can be expressed according to equation 2.6. where η is the overpotential, j_0 is the exchange current density and j is the current density. A smaller Tafel slope will mean a faster rate of reaction as the current density increase higher for every unit of increase in potential. It provide insights to the kinetics and mechanism of the reaction by defining the rate determining step.¹⁶

$$\eta = b \cdot \log (j / j_0) \quad 2.6$$

2.2.3 Activity

There are a few parameters that measure activity like turnover frequency (TOF), mass activity and specific activity. TOF for OER is defined as the total oxygen evolved per active sites (eqn 2.7), where F is the faraday constant, j (mA cm^{-2}) is the current density at a certain overpotential, n is the number of moles of the active materials and A is the the working electrode area.³⁰ However, we have to take note that the TOF calculated may not reflect the actual TOF as some of the active sites may not be electrochemically active. Mass activity is defined as the current density per mass loading on the working electrode and specific activity is the current density per surface area of the catalyst. The activity can also be plot against the overpotential to review its performance similar to Tafel slope.

$$\text{TOF} = (j \times A) / (4 \times F \times n) \quad 2.7$$

In order to increase activity or rate of reaction, there are two key strategies: (i) by increasing the amount of active sites and (ii) by increasing the intrinsic activity of the active

site of the catalyst.⁵ Both of them can be implemented simultaneously to boost activity. However, if the reaction is diffusion controlled, meaning the reactants transportation is slower than the reaction rate, it will reflect the actual performance of the catalyst. Thus, it is important that we take note of the amount of catalyst loaded onto the electrode. Alternatively, we should put more emphasis on the intrinsic activity as the difference between a performing and poor catalyst can be ten folds or more while a highly loaded or large surface area catalyst might maximise activity by one to three times.³¹ There are basically a few catalysts development strategies in that are currently being used as shown in Figure 2.3. Further elaboration will be made in the sections below.

Figure 2.3: Catalyst development strategies⁵

2.2.4 Stability

For practical applications, stability is very important in order for catalyst to be long lasting and economically viable. The compatibility of the catalyst and electrolyte is important as some of the catalysts are unstable at low pH but perform well at higher pH. The loading method of catalyst on electrodes is also equally important as a catalyst integrated electrode

from production makes a big difference from those coated using binding materials.³⁰ Usually, Chronoamperometry (CA) is employed by holding potential constant for several hours to study the current response over time. Alternatively, Chronopotentiometry (CP) can be carried out by holding the current output constant and measure the potential response. Besides that, post electrochemical characterization techniques like XRD, SEM, XPS and TEM can be conducted to study the structure and electronic composition of the catalysts as the structures.

2.3 Electrocatalysts for OER

Due to the high cost of noble metal oxides, a lot of attention has been given to transition metal oxides due to its abundance, low-cost and good corrosion resistance. There are some other approaches like modifying the precious metal oxides by substitution with other metals to achieve better performance at a low cost. OER as a surface reaction means the surface morphology is a critical factor besides identifying the best material to be used. Besides, morphology, other activity descriptors of OER like oxidation state, 3d electron number of transition metal ions, e_g occupancy, surface oxygen binding energy and composition also determine activity of metal oxides.³² This section will focus more on perovskites, spinels and layered metal hydroxides.

2.3.1 Noble Metal Oxides

In general, noble metals like platinum (Pt), palladium (Pd), iridium (Ir) and ruthenium (Ru) are chemically much more stable than the other metals. Their alloys and oxides are heavily studied due to their spectacular performance in OER. Out of all the noble metals, Ir oxide (IrO_2) and Ru oxide (RuO_2) are so far the state of art OER electrocatalyst due to its high activity with low overpotential in both acid and alkaline medium.^{8,33} Both metal oxide has a rutile structure where the octahedral sites are filled with the Ru or Ir with six oxygen joined to it. Each octahedron are connected though corner sharing as shown in Figure 2.4.

Figure 2.4: Crystal structure of rutile type RuO_2 ¹⁶

Comparing RuO_2 with IrO_2 , RuO_2 has better OER performance but with poorer stability under high anodic potential.³⁴ RuO_2 will transform into hydrous $\text{RuO}_2(\text{OH})_2$ and further into an unstable product RuO_4 . Similarly, IrO_2 experience the same but not as bad as compared to RuO_2 .¹⁶ A doped bimetallic oxide $\text{Ru}_x\text{Ir}_{(1-x)}\text{O}_2$ was suggested to improve stability of the system.³⁵ Besides that, a core shell structure $\text{IrO}_2@\text{RuO}_2$ can be made to decrease the overpotential and improve stability.³⁶ But as compared to their metal form, the oxides have far better stability in basic and acidic conditions. Using the similar doping strategy, small amount of Ir could significantly improve stability with slight decrease in activity.⁶ Furthermore, reducing IrO_2 nanoparticle size would increase active sites and therefore increases OER mass activity.⁷

2.3.2 Perovskites

Perovskites have been widely researched on high temperature fuel cell in the past and have attracted attention in OER due to similar reaction kinetics with 4 step mechanism.³⁷ Besides that, they can be easily manipulated by changing their compositions and structure.³⁸ They generally have a formula of ABO_3 , where A is alkaline or rare earth metal, while B is a transition metal. As shown in Figure 2.5, Perovskites generally have a unit cell that contains eight A cations (green) at the corners with a B cation (blue) in the centre and 12 oxygen anions surrounding both cations. The A and B metals can be doped with other metals to form AA'BB'O_3 so as to tune the desired oxidation state of the transition metal. In a study

on $\text{La}_{1-x}\text{Sr}_x\text{Fe}_{1-y}\text{Co}_y\text{O}_3$ system, OER performance increase with increase in Sr and Co. This is due to the higher oxidation state of Co ion and band distribution of d orbitals to e_g and t_{2g} , suggesting correlation between activity and d band electrons.³⁹ Bockris et al. also reported a perovskite structured catalyst, where they established a trend where OER is in the sequence $\text{Ni} > \text{Co} > \text{Mn} > \text{Cr}$ of B transition metals. They proposed that the B-OH bonding strength in perovskite affects the OER activity is correlated to the electron density of the σ^* or e_g which decrease with the trend $\text{Ni} > \text{Co} > \text{Fe}$.^{25,40} Furthermore, under higher potentials the Tafel slope increased showing that the rate determining step may have changed under different voltages.

Figure 2.5: The structure of an ABO_3 perovskite⁴¹

Suntivich et al. suggested that the number of electrons in e_g orbital close to unity for transition metal will give the highest OER performance for the material.⁴ This is being substantiated by $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ having e_g occupancy close to one. The relationship between OER onset potential and e_g occupancy plotted for different transition metal oxide shows a volcano shape further confirm the optimal performance to be at e_g equal to unity with high covalency between the metal and oxygen bonds. According to density function theory calculations by Vojvodic and Norskov, both e_g and t_{2g} contributes to the oxygen adsorption energies.⁴² Based on Sabatier's rule the optimal adsorption cannot be too weak or too strong to facilitate desorption. Another interesting phenomenon has been reported that electrocatalytic cycling of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{2-\delta}$ cause amorphization of surface during OER and increase in activity.⁴³ Grimaud et al. also discovered that besides the metal-

covalency, lattice oxygen oxidation further facilitate OER activity especially at high pH shown by the threefold increase in OER activity of $\text{SrCoO}_{3-\delta}$ compared to $\text{Pr}_{0.5}\text{Ba}_{0.5}\text{CoO}_{3-\delta}$.⁴⁴ This finding showed that lattice oxygen takes part in the OER mechanism which means that there are new reaction pathways different from conventional mechanisms. The activation of lattice oxygen will only be triggered when the fermi level of the metal is below the top of the O 2p band to form high covalent metal and oxide bonds. Furthermore, the strong metal – oxygen covalency with increase alkalinity shows that the OER mechanism for perovskites with lattice oxygen oxidation is a non-concerted proton-electron transfer.⁴⁴ With all these findings on e_g and metal-oxygen covalency activity descriptor, research direction can be placed on synthesizing perovskites made of late transition metals with high oxidation states to increase overlap of O 2p band with the 3d metal.

2.3.3 Spinel

Spinel have the general formula of AB_2O_4 which A and B consists of transition metals, group 2 and group 13 elements. The normal spinel has a configuration where A cations of divalent charge +2, occupy tetrahedral sites (T_d) while B cations of trivalent charge +3 occupy the octahedral sites (O_h) (Figure 2.6). The inverse spinel have the ($\text{A}^{2+}_{\text{O}_h}$) cations occupy the octahedral site, with half of B cations ($\text{B}^{3+}_{\text{O}_h}$) occupy the octahedral site and other half occupying tetrahedral site ($\text{B}^{3+}_{\text{T}_d}$). Having tetrahedral and octahedral coordination, the transition metals can have different extent of d-band splitting.⁴⁵ Spinel are very stable at high anodic voltage in alkaline medium and relatively good electric conductors making them an appropriate candidate for OER.

Figure 2.6: Crystal structure of spinel AB_2O_4 ¹⁶

Normal spinel Co_3O_4 has been studied extensively in OER and ORR due to its promising catalytic performance, low cost and simple preparation. ^{46,47} Tremendous efforts have been made to modify the existing catalyst to further enhance its activity. Bulk Co_3O_4 has been modified through nanocrystal growth on graphene oxide substrate to form a hybrid in order to increase electric conductivity and therefore activity. ⁴⁶ Furthermore, Dai et.al. discovered that using N-doped reduced graphene oxide as a support for Co_3O_4 nanoparticles enhanced the activity significantly. ⁴⁸ Moreover, metallic doping of cobalt and iron based spinel with for example Ni, Mn, Cu etc, were studied for catalytic performance as well. ^{10,49,50} It was reported that for MFe_2O_4 (where $M = Mn, Cu, Ni, Co$) follows a trend of $Co > Cu > Ni > Mn$ for OER activity. ¹⁶ Similarly, for cobalt based spinels, OER performance has increased with doping Ni, Cu, Li except Mn, ⁵¹ Overall, bimetallic spinel oxides proven to have better OER performance than single metal spinel M_3O_4 due to the synergy created using different metals ions as they might have an impact in optimising adsorption energy.

In order to find out the individual role of metal ions in spinel, Wang et.al. had discovered that for Co_3O_4 , the Co^{2+} ions are the active sites responsible for OER as they substituted Co^{2+} with Zn^{2+} , and Co^{3+} with Al^{3+} . ⁵² They concluded specific metal ions will modify electronic structure and optimise the intermediate and reactant binding strength. However, Chao et.al. suggested that the activity descriptor is depends on the cation from the

octahedral site which the optimum OER activity is at e_g occupancy of ~ 1.2 which is correlated to the valence state of the cation.²⁶ This finding demonstrate that besides perovskites, the e_g is applicable to spinel as well.

Different types of substrates used on the spinel may also affect the OER performance. It has been reported that Co_3O_4 grown on (100) Au substrate can help to oxidize Co_3O_4 enhancing OER activity.⁵³ Besides that various groups have reported the increase in OER activity through dispersion of spinel particles on carbon based substrates like carbon nanotube, graphene etc.^{54,55} Furthermore, to improve on electrical conductivity and self-accumulation, nano-structured spinels with morphologies like nanoparticles, nano-rods, nano tubes, nano-sheets etc.⁵⁶⁻⁵⁸ NiCo_2O_4 hollow microcuboids were synthesized by Gao and his team through combining 3D hollow structure and 1D nanowire mesh. This structure display good OER catalytic activity due to smooth penetrate of the electrolyte through the hollow structures to the active sites.⁵⁹ Furthermore, exposing different facets of a similar material will result in different OER performance. Su et al. reported that catalytic activity of single Co_3O_4 nanocrystals were greatest at crystal plane (111) and lowest at (100).⁶⁰ However, there is an issue of phase transformation in spinel during OER under high anodic potential. Many studies have discovered that the spinel metal oxide at the surface transform to produce a metal oxyhydroxide phase.^{61,62} This suggest that the oxyhydroxide phase is the metastable phase at the potential. This has inspired research direction to consider layered-oxide related structures for OER.

2.3.4 Layered Metal Hydroxides

The layered structured oxides also known as layered double hydroxides (LDH) consist of two types: (i) metal hydroxides ($\text{M}(\text{OH})_2$) and (ii) metal oxyhydroxides (MOOH) where M is transition metal.¹⁶ Their 2D crystal structure consists of layers of $[\text{MO}_6]$ subunits stacked together with protons in between as shown in Figure 2.7. The transition metals cations are in the surrounded by six oxygen anions interconnected by the edges. Out of the many hydroxides, the Ni and Co hydroxide and oxyhydroxide are of interest due to their OER performance in metal oxides.¹⁶ There are different crystal phases that exist for both LDH.

Figure 2.7: Layer double hydroxide structure of β -NiOOH and γ -NiOOH¹⁶

Gao and co-workers found that α -Ni(OH)₂ nanocrystals have better OER activity and stability in alkaline than β -Ni(OH)₂.⁶³ In order to find out about the trend of OER activity between different hydro(oxy)xides, Subbaraman et al. has conducted studies on different 3d transition metal hydroxides and discovered the activity trend (Ni>Co>Fe>Mn).²⁵ They suggested that the superb activity of NiOOH is due to the optimal Ni-OH bond strength. Trotochaud et.al. discovered that doping Fe to form bimetal hydro(oxy)oxide Ni_{1-x}Fe_xOOH resulted in a better performance of γ -NiOOH compared to β -NiOOH.⁹ Similar conclusion was drawn by Corrigan and co-workers where 1ppm of Fe impurity in the electrolyte significantly improve the OER performance.⁶⁴ Other metal oxyhydroxides like LiNi_(1-x)Co_xO₂ also experienced the same results after doping Fe in the compounds.⁶⁵ However, Trotochaud et al. also reported that in the absence of Fe impurity OER activity increased after cycling for Ni(OH)₂ due to the aging effect and draw conclusion that β -NiOOH was more superior than γ -NiOOH.⁹ In order to verify the roles of Ni and Fe in OER, DFT calculations were performed on Ni_(1-x)Fe_xOOH.⁶⁶ It discovered that Fe impurities reduce the overpotential and were the active sites responsible for OER.⁶⁶ Conversely, Burke et al. showed that γ -FeOOH is a poor OER catalyst despite significant improvement in activity after overpotential of 450mV. The inferior performance was attributed to its instability

because of the formation of soluble FeO_4^{2-} which dissolved in the electrolyte as well as poor electrical conductivity.⁶⁷

According to Song et al., single NiFe LDHs have better OER performance than bulk LDHs due to the freedom that allowed the water molecules to intercalate creating more active sites as well as better electrical conductivity.⁶⁸ Besides iron dopant, Mn and Cr have been incorporated into Ni based LDHs and found to yield an increase in OER activity as well.⁶⁹ An intriguing observation of decreasing OER performance accompanying an increase in crystallinity of $\text{Co}(\text{OH})_2$ as cycling proceeds were made by Sayeed et al..⁷⁰ The phenomenon was a result of lattice rearrangement on the surface of $\text{Co}(\text{OH})_2$ resulting in a decrease in active sites.⁷⁰ This highlights the superiority in OER performance of amorphous layers as compared to crystalline forms of the metal hydroxides.

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Chapter 3

Experimental Methodology

In this chapter, synthesis and characterization techniques designed to study CoCr_2O_4 were discussed. The rational for the techniques employed were explained as well. Sol-gel method was used to synthesize CoCr_2O_4 and Co_3O_4 due to its simplicity. Electrochemical experiments were conducted to study the OER performance of these materials. Other material characterization techniques like TEM, XRD, XPS and XAS were adopted to study the phase, structure, elemental composition, chemical state as well as local bonds and coordination.

3.1 Rationale for selection

The sol-gel method was adopted to synthesize CoCr_2O_4 as particle morphology and size distribution requirement are not stringent. Electrochemical measurements were conducted to investigate the OER performance of the catalysts. XRD was employed to identify the crystal structures and phase purity of the synthesized samples.

3.2 Material Synthesis

CoCr_2O_4 and Co_3O_4 were synthesized using the sol-gel technique. Firstly, for CoCr_2O_4 , $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were added in stoichiometry amount into a aqueous solution of ammonium hydroxide (NH_4OH) mixed with Ethylenediaminetetraacetic acid (EDTA) and Citric Acid ($\text{C}_6\text{H}_8\text{O}_7$). The solution was stirred to dissolve and heated at 230°C for several hours to dry. After which, a homogenous viscous gel was formed and it was transferred to an oven for further heating at 250°C for 5 hours. Finally, the intermediate product was calcinated in a furnace at 1200°C for 6 hours to obtain the greenish blue CoCr_2O_4 product. Likewise for Co_3O_4 , the methods were similar, however $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was excluded and the final calcination temperature is at 400°C . These method was employed as it was simple and control of morphology was not required.

3.3 Material Characterisation

3.3.1 Electrochemical Technique

Oxygen evolution reaction electrocatalysis were being carried out using a three –electrode cell setup (Figure 3.1). The auxiliary or counter electrode is a platinum plate ($1 \times 2 \text{ cm}^2$), Hg/HgO (1M KOH) as reference electrode, catalyst drop casted on glassy carbon electrode (0.196 cm^2) as the working electrode and O_2 saturated 1M KOH as the electrolyte.

The catalysts ink used for drop casting on the glassy carbon electrode were prepared as follows. 10 mg of catalyst was mixed with 2mg of acetylene black (AB), 400 μl of

isopropanol, 1.55ml of deionized water and 50 μl of Nafion perfluorinated resin solution (5wt% in H_2O). The mixture were ultrasonicated for at least 15 minutes before 10 μl of ink was drop casted on the glassy carbon electrode and left to dry before electrochemical experiments. The glassy carbon electrode were polished with alumina slurry with ultrasonication in ethanol and water repeatedly before drop casting.

The electrochemical measurements were done using Biologic SP 150 potentiostat. The potential manifested in the results are converted to RHE scale by the following equation:

$$E(\text{RHE}) = E(\text{Hg}/\text{HgO}) + E(\text{Hg}/\text{HgO vs SHE}) + 0.059 \times \text{pH}$$

Where $E(\text{RHE})$ is the reversible hydrogen electrode potential, $E(\text{Hg}/\text{HgO})$ is the potential w.r.t Hg/HgO , $E(\text{Hg}/\text{HgO vs SHE})$ is the potential of Hg/HgO w.r.t SHE (0.098V) and pH is the scale of acidity. Cyclic Voltammetry is an electrochemical method which voltage is applied linearly to the working electrode at a certain scan rate from an initial potential to a final potential and reversed, with the current response measured.¹ The applied potential will then be plotted against the current detected. In this report, the CV obtained were from 0.9V to 1.65V (vs. RHE) and potential measurements were ohmic (IR) corrected. Electrochemical impedance spectra (EIS) was used to determine the solution or ohmic resistance for potential correction at 0V (vs.RHE) under AC voltage amplitude of 10mV with frequencies ranging from 10^5 to 10^{-3} .²

The electrochemically active surface area (ECSA) was being estimated by measuring the double layer capacitance (C_{DL}). In this experiment, the CV was recorded from 0.8V to 0.9V vs. RHE at scan rates (10, 20, 30, 40, 50, 75, 100 mVs^{-1}) with no faradic current response.³ The 1M KOH electrolyte was Ar-saturated to ensure no O_2 gas present. From the formula, $i_{\text{c}} = vC_{\text{DL}}$, the double layer capacitive current (i_{c}) is plotted against scan rate (v) and the double layer capacitance can be determined. With specific capacitance ($\mu\text{Fcm}_{\text{oxide}}^{-2}$) of the material known, ECSA can be determined.

Chronoamperometry (CA) is another electrochemical technique that measures the current

response with under fixed potential as a function of time. It is usually performed to determine the stability of the catalyst. In this report, a series of CA with varying potential is conducted with time to study the surface reconstruction of CoCr_2O_4 . For this experiment CA is conducted at different potential of 1.5V, 1.6V and 1.64V for 7 hours.

Figure 3.1: Three electrode system setup comprising of working, reference and auxiliary (counter) electrode for electrochemical experiment.

3.3.2 X-ray Diffraction

X-ray diffraction is a characterization technique used to analyse and identify different phases of a crystalline material. It can also give information about the unit cell dimensions and phase compositions. When an X-ray beam hits the sample, it interacts with the electrons and results in some elastic scattering. The elastically scattered X-rays will interact with each other to form diffraction when constructive interference happens. The criteria for constructive interference to occur is when the conditions fulfil Bragg's law. Bragg's law is defined as below:

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

where n is an integer, d is the lattice spacing between the diffracting planes, λ represents the wavelength of the x-ray and θ denotes the incident angle. Since the wavelength for a

specific X-ray source (CuK α $\lambda = 1.5418\text{\AA}$) and distance between diffracting planes are inherent values, there are only specific incident angles that could for diffraction to occur. Scanning the X-ray from a range of incident angles will result in a spectrum of characteristic X-ray pattern which the phase of the material can be identified through cross-reference with a database. Only crystalline materials with regularly arranged particles and long range periodicity experience X-ray diffraction. Materials with amorphous structure or poor crystallinity will cause X-ray to scatter randomly resulting in a broad peak with low intensity. The XRD patterns of the samples in this report is measured by Panalytical diffractometer with Cu K α radiation ($\lambda = 1.5418\text{\AA}$) scanning at $2^\circ/\text{min}$.

Figure 3.2: Bragg's law condition for constructive interference to occur

3.3.3 X-ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy is a surface analytical technique that measures elemental composition, empirical formula, valence state as well as the chemical bonding a few nanometers into the material.⁴ It is able to detect every element except Hydrogen and Helium. Basically, when a sample is irradiated with X-ray of sufficient energy, some electrons will be knocked out from the inner core shell of the element. Those photoelectrons that are elastically scattered without energy loss will escape to the surface into the vacuum and get collected by the detector, contributing to the characteristic peak. While those that

are inelastically scattered by neighboring electrons or nucleus will contribute to the background spectrum. The kinetic energy of the emitted photoelectrons are measured and analyzed by an electron spectrometer. By conservation of energy, the spectrum of data are obtained based on the expression below:⁴

$$BE = h\nu - KE - W$$

where KE is the kinetic energy, $h\nu$ is the photon or X-ray energy, BE is the binding energy and W is the spectrometer work function. With this equation, the binding energy can be calculated and the number of photoelectrons can be plotted against the binding energy of the photoelectrons. The energy peak would inherently correspond to a specific element and the intensity of the peaks will determine the ratio of each element. In this report, XPS analysis is conducted on CoCr_2O_4 before and after CA at 1.5V, 1.6V and 1.64V.

Figure 3.3: Schematic illustration of XPS process

3.3.4 X-ray Absorption Spectroscopy (XAS)

X-ray Absorption Spectroscopy is an inner shell spectroscopy where by interacts with core electrons in inner shell instead of valence electrons.⁵ It is a characterisation tool that gives insight on the local geometrical and electronic structures. XAS can be split into two regions: X-ray Absorption Near Edge Structure (XANES) and Extended X-ray Absorption Fine Structure (EXAFS) (Figure 3.4). XANES gives information about valence state while EXAFS yields information about coordination number of the element, average bond distance as well as lattice dynamics.⁶ XAS was conducted at Singapore Synchrotron Light Source under transmission mode.

Basically, XAS measures the X-ray response when a beam of X-ray is transmitted through a sample with certain thickness. The absorption coefficient will then be plotted against energy of the X-ray based on Lambert and Beer's equation:

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

where I and I_0 is the intensity of the incident and transmitted X-rays, μ is the absorption coefficient and t is the thickness of the sample. Usually, the X-rays will become more penetrating when energy increases and resulting in decrease in μ . However, when the energy of the X-rays are greater than the binding energy of the electrons in the core shell, the electrons get promoted to the unoccupied levels or get knocks out to form photoelectrons. This results in a sharp increase in μ and produces the edge of the XANES region.

When the energy of the X-ray are very high, most of the core shell electron are able to escape its bound states and get ejected as photoelectrons. In the process, the photoelectrons interact with the electrons of the atoms in the local chemical environment and produces secondary source of X-rays through the scattering. The interference between the backscattered and outgoing scattered X-ray waves produces a low frequency oscillation in the EXAFS regions above the absorption edge. Higher frequency oscillation would represent a longer interatomic distance vice versa. Fourier transformation of the data is

required to extract useful information on the coordination number and bond distance. In this report, XAS analysis is conducted on CoCr_2O_4 before and after CA at 1.5V, 1.6V and 1.64V.

Figure 3.4: Absorption spectra of La_2CuO_4 as a function of energy. XANES and EXAFS regions are illustrated.⁶

Figure 3.5: Diagram of X-ray absorption under transmission mode.⁵

3.3.5 Transmission Electron Microscopy (TEM)

TEM is a microscopy technique that magnifies the image of an object just like normal optical microscopes. However, TEM is able to capture objects or details that are extremely small at nano scale. The reason for such high resolution is due to the small wavelength of the electrons. The resolution of TEM can be increased by increasing the operating voltage of the electron beam. TEM images are produced when a beam of electrons are transmitted through the sample and followed by focusing the transmitted beam on the camera using the objective lens. Therefore, the samples prepared must be thin to allow the electron beams to transmit through. In this report, TEM JEOL 2100F with 200kV accelerating voltage was used to identify the amorphous layer of the samples before and after the CA experiments. TEM EDS line scan was employed to study the change in the elemental profile from surface to core of the material before and after electrochemical experiments.

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Chapter 4

Results and Discussion

Surface reconstruction and amorphisation are desired phenomena that was discovered to boost the performance for oxygen evolution reaction (OER) electrocatalysts in the recent years. While there are many strategies designed for surface reconstruction to occur, the leaching occurrences were overlooked and unexplained. After employing various characterization techniques, it was discovered that Cr leaching created vacancies and defects favorable for the formation of CoOOH layer on the CoCr_2O_4 surface forming a core shell structure. OER performance of CoCr_2O_4 was discussed in details and compared against Co_3O_4 and IrO_2 .

4.1 Introduction

The exploration of efficient and cost effective OER catalyst for energy conversion and storage devices has been of great priority in recent years.¹ Significant effort has been focused on developing TMO OER catalysts and understanding the fundamental properties relating to the OER performance.² Different activity descriptors have been identified and employed for designing efficient OER catalyst such as transition metal e_g occupancy^{3,4}, metal-oxygen covalency⁵, metal-oxygen bond length^{6,7} and O 2p band centre⁸.

However, catalysis occurs on the surface and the activity descriptors discovered were all based on bulk geometry and electronic structures which give rise to ambiguity in the accuracy of the descriptors. Amorphisation was observed after OER in some of the crystalline TMO electrocatalysts with tremendous improvement in OER activity.⁹ Furthermore, many studies have shown that amorphous oxides outperformed their crystalline counterparts.¹⁰ According to Grimaud et al. and May et al., surface reconstruction was accompanied by leaching of cations.^{9,11} However, many research groups have attributed surface reconstruction to explanations like O 2p band centre⁹, metal ion coordination¹¹ and oxidation or oxygen vacancies^{9,12}, the role of leaching is inadequately elucidated.

Cr has been identified to be a suitable cation for leaching due to the solubility of Cr^{+6} that exist as chromates or dichromates.¹³ In this work, relationship between amorphisation and Cr leaching will be addressed through investigation of $CoCr_2O_4$ under electrochemical cycling and CA (constant potential) conditions. A deep understanding of the bulk and surface chemistry will be essential to help design an electrochemical technique for activating surface amorphisation of crystalline metal oxides.

4.2 Material Characterization

CoCr_2O_4 and Co_3O_4 as-synthesized samples are confirmed to be pure cubic spinel structure with Fd-3m space group by XRD characterization shown in Figure 4.1. The surface area of both samples is determined by BET measurements Table 1.

Figure 4.1: Powder X-ray diffraction (XRD) of CoCr_2O_4 and Co_3O_4

Table 1: BET surface area of CoCr_2O_4 and Co_3O_4

Sample	S_{BET} (m^2/g)
CoCr_2O_4	6.3
Co_3O_4	21.4

4.3 Electrochemical Characterization

Cyclic Voltammetry (CV) was conducted on CoCr_2O_4 to test its OER performance under alkaline conditions. The OER activity is defined as current density normalized by geometric area of glass carbon electrode instead of oxide surface area due to changes in surface area with applied potential which would be discussed further in this section. Figure 4.2 shows that both OER current and pseudocapacitance increased steadily with electrochemical cycling, yielding twice the OER current after 400th cycle as compared to first cycle at 1.65V vs RHE. The initial cathodic and anodic peak at 1.3V is assigned to the redox reaction of Chromium species from Cr^{+3} to Cr^{+4} which is also visible for ZnCr_2O_4 (Figure 4.3b).¹⁴ This observation shows that the surface of the as synthesized CoCr_2O_4 is dominated by Cr species with insignificant or absence of Co. When the catalyst is subjected to a series of voltammetry cycles from low to high OER potential (0.9V – 1.65V vs RHE) back and forth, two new redox peak at around 1.1 V and 1.5 V appeared and increased with cycling. This phenomenon is attributed to the increase in electrochemical active surface cobalt which the peak at 1.1V and 1.45V belongs to $\text{Co}^{2+}/\text{Co}^{3+}$ and $\text{Co}^{3+}/\text{Co}^{4+}$ redox reaction respectively.¹⁵⁻¹⁷ However, electrochemical cycling at a range of 0.9 to 1.55V before OER potential did not result in formation of Co redox peaks (Figure 4.2b).

Figure 4.2: Cyclic voltammograms of CoCr_2O_4 showing several cycles from (a) 0.9V to 1.65V and (b) 0.9V to 1.55V vs RHE at scan rate 10 mV/s in O_2 saturated 1M KOH.

Figure 4.3: (a) Cyclic voltammograms of CoCr₂O₄ at first cycle, 400th cycle, after 7h of chronoamperometry at 1.6V vs RHE and (b) ZnCr₂O₄ at first cycle.

A series of chronoamperometry (CA) followed by one cycle of CV was conducted on CoCr₂O₄ and discovered that the OER potential is around 1.56V which coincide with the formation of Co redox peaks after 1.56V applied (Figure 4.4). Furthermore, as the OER potential increases, the potentiostatic current increases rapidly with time (steeper slope). Besides that, the observation was accompanied by an increase in magnitude of the Co redox peaks with increase in OER potential. This finding shows that the intensity of OER is proportional to the Co species on the surface. Co₃O₄ on the other hand did not experience the same phenomenon (Figure 4.5). This showed that OER played a major role in surface reconstruction for CoCr₂O₄ which was supported by May et. al. on their finding for Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3- δ} .⁹ However, comparing the cyclic voltammograms of 400 cycle CV (0.9V to 1.65V) that takes around 16h and CA (at 1.6V) after 7h, the OER current of CoCr₂O₄ that undergone the latter had outperformed the former by about four times at 1.65V with significant formation of Co redox peak (Figure 4.3 and inset). Therefore, electrochemical cycling is not a significant factor contributing to surface reconstruction and improved OER performance for CoCr₂O₄, in contrast to other OER catalysts that have enhanced performance based on electrochemical cycling.^{11,18 19,20}

Figure 4.4: (a) A consecutive series of chronoamperometry (CA) at different potential and (b) cyclic voltammetry after CA for CoCr₂O₄

Figure 4.5: (a) A consecutive series of chronoamperometry (CA) at different potential and (b) cyclic voltammetry after CA for Co₃O₄

4.4 Leaching analysis

Inductively coupled plasma mass spectrometry (ICP-MS) conducted on the electrolyte after consecutive series of CA on CoCr₂O₄ revealed that chromium leaching becomes significant after 1.56V and accelerates with increase in OER potential (Figure 4.6). Together with the

electrochemical analysis, this finding showed that the oxidation intensity of Cr^{+4} to soluble Cr^{+6} species is accelerated by the amount of oxygen produce from OER. Furthermore, this evidence also proved that the increase in surface Co species were due to leaching of Cr and resulted in a change in surface active species and improved OER activity. However, when a longer interval of CA is conducted, leaching of Cr is observed before OER potential at 1.5V (Figure 4.6). This can be ascribed to the unstable surface Cr^{+4} present at 1.5V that further oxidized to Cr^{+6} with O_2 in the alkaline electrolyte ($\text{pH} > 9$) forming soluble chromate $(\text{CrO}_4)^{-2}$ and dichromate $(\text{Cr}_2\text{O}_7)^{-2}$ species. At OER potentials, oxygen is being produced at the surface Cr^{+4} sites which resulted in rapid oxidation to Cr^{+6} species and therefore greater leaching. In addition, Cr^{3+} in CoCr_2O_4 spinel is relatively stable as compared to Cr^{4+} which shows no leaching under oxygen bubbling condition in pH 14 (Figure 4.7). Overall, there was no significant Co leaching from CoCr_2O_4 .

Figure 4.6: (a) Cumulative mass of element leached after consecutive series of CA conducted at 20mins interval. (b) Mass of element leached at different CA for 7h.

Figure 4.7: Mass of elements leached out under various conditions: i) pure KOH, CoCr_2O_4 ii) soaked 5h in KOH, iii) soaked 5h in KOH with O_2 bubbling, iv) after 400 cycles of CV(0.9 – 1.55V), v) after 400 cycles of CV(0.9 – 1.65V) and CA at 1.6V for 7h.

4.5 Electrochemical active surface area analysis

From Figure 4.8, the CA graph for CoCr_2O_4 showed that OER current increases constantly at the start before reaching a steady current. This can be due to the slowdown of Cr leaching as surface reconstruction gets saturated with majority of Co occupying the surface sites. The double layer capacitance (C_{DL}) of CoCr_2O_4 was measured before and after CA interestingly found an increase of around four times under 1.6V and 1.64 vs RHE (Figure 4.9a). As C_{DL} is proportionate to electrochemically active surface area (ECSA), this would also imply that surface reconstruction or amorphisation has occurred during the OER process. In order to ensure the increase in C_{dl} is not due to increase in acetylene black's (AB) ECSA, another set of CA is conducted on pure CoCr_2O_4 without AB as support (Figure 4.9b). It turns out that increase in C_{dl} occurred under OER potentials regardless of the presence of AB. On the other hand, the increase in C_{dl} for CoCr_2O_4 with AB after CA

at 1.5V was due to the increase in surface area of AB after applied potential. The increase in ECSA during OER is due to the increase in unsaturated sites as Cr leached out causing an improvement in the OER activity. Therefore, the results from all the experiments showed that surface reconstruction occurs when Cr leach at OER potential.

Figure 4.8: Chronoamperometry at different potential for CoCr₂O₄ with (a) acetylene black and (b) without acetylene black.

Figure 4.9: Double layer capacitance (C_{DL}) measurement before and after CA at different potential for CoCr₂O₄ with (a) acetylene black and (b) without acetylene black.

4.6 X-ray photoelectron spectroscopy analysis

XPS analysis was carried out to investigate the surface elemental composition, oxidation state and adsorbed species of pristine CoCr_2O_4 and after CA at different potential of 1.5V, 1.6V and 1.64V for 7h. The sample were named p- CoCr_2O_4 , $\text{CoCr}_2\text{O}_4@1.5\text{V}$, $\text{CoCr}_2\text{O}_4@1.6\text{V}$ and $\text{CoCr}_2\text{O}_4@1.64\text{V}$ respectively. The XPS spectra were corrected based on the offset between the C 1s of the samples and standard C 1s reference line (284.6eV) before analysis. By using Lorentz-Gaussian fitting method, the XPS spectra of O 1s, Co $2p_{3/2}$ and Cr $2p_{3/2}$ have been deconvoluted into smaller contributions as shown in Figure 4.10, Figure 4.12 and Figure 4.13 respectively. Figure 4.10 shows three main peaks fitted for the O 1s spectra of different CoCr_2O_4 samples. The signal at around 530 eV and 531.5 eV reflected the presence of lattice oxygen and hydroxide ions respectively.^{6,21} While the component at 532.9 eV was ascribed to the presence of adsorbed water.¹⁷ The additional deconvoluted O 1s peak at ~536 eV for CoCr_2O_4 samples after CA belonged to oxygen of Nafion® perfluorinated solution which contains $(-\text{CF}_2-\text{O}-\text{CF}_2-)$ that was added to the catalyst ink during drop casting.²² Based on the area of the three main deconvoluted O 1s peaks, a distribution pie chart was constructed (Figure 4.11). The surface of the p- CoCr_2O_4 and $\text{CoCr}_2\text{O}_4@1.5\text{V}$ contains majority lattice oxygen (~50%) while after CA at 1.6V the lattice oxygen (29.5%) detected has reduced with an increased in adsorbed hydroxide ions (29.5%) and water (41%). This can be explained by OER that took place above 1.56V. CA at higher potential (1.64V) resulted in more adsorbed hydroxide ions (50.1%) and further justified that OER plays apart in modifying the surface chemistry of the catalyst.

The Co $2p_{3/2}$ XPS spectrum for all samples had an overall peak at around 780.5eV which resembles the characteristic of CoCr_2O_4 .²³ All samples showed deconvoluted BE signals at around 780.4eV and 782.4eV however both $\text{CoCr}_2\text{O}_4@1.6\text{V}$ and $\text{CoCr}_2\text{O}_4@1.64\text{V}$ had an additional peak at around 781.3eV. According to Yang et al., two peaks at 780.7 eV and 782.5 eV were observed for $\text{Co}(\text{OH})_2$ while CoOOH had two peaks at 780.4 eV and 781.7 eV in the Co $2p_{3/2}$ XPS spectra.²¹ Based on these observations, p- CoCr_2O_4 and $\text{CoCr}_2\text{O}_4@1.5\text{V}$ contained Co^{2+} species only which belonged to the contribution of Co from CoCr_2O_4 while there were presence of both Co^{2+} and Co^{3+} species in $\text{CoCr}_2\text{O}_4@1.6\text{V}$ and

CoCr₂O₄@1.64V. The presence of Co³⁺ could be verified by the weak satellite signal at 786.3 eV for CoCr₂O₄@1.6V and CoCr₂O₄@1.64V indicating the large presence of Co³⁺ as pure Co(III) oxides do not have multielectron excitation satellites.^{21,24} The formation of CoOOH species during OER could have resulted in the detection of Co³⁺ at the surface which has been reported for many Co based catalyst^{25,26}.

Figure 4.10: O 1s XPS spectra of (a) p-CoCr₂O₄, (b) CoCr₂O₄@1.5V, (c) CoCr₂O₄@1.6V and (d) CoCr₂O₄@1.64V.

Figure 4.11: Distribution of different oxygen species on surface of (a) p-CoCr₂O₄, (b) CoCr₂O₄@1.5V, (c) CoCr₂O₄@1.6V and (d) CoCr₂O₄@1.64V.

The Cr 2p_{3/2} XPS spectrum for all the CoCr₂O₄ samples peaked at 576.4eV indicated the presence of Cr³⁺ in octahedral sites of the spinel (Figure 4.13).^{17,27,28} The peak can be further resolved into four smaller peaks due to multiplet splitting for unpaired electrons in Cr³⁺.^{28,29} However, there might be some Cr³⁺ that exist in all samples as CrOOH peak at 577.3eV may be overlapped by the peaks of Cr³⁺ belonging to CoCr₂O₄ lattice. The absence of a peak at around 578.2eV suggested that there were no Cr⁶⁺ species present on the surface.^{17,27}

Based on the species per spectrum area constant derived and the deconvoluted area Co and Cr peaks excluding the satellite region, the ratio of Co and Cr was calculated in Figure 4.14. Initially, p-CoCr₂O₄ contained nearly 70% of Cr which is close to the ratio 1:2 of Co to Cr in CoCr₂O₄. This observation showed that the XPS technique penetrates a few monolayer

into the sample as Co was detected while CV could only detect the surface Cr only. After applying 1.5V for 7h, slightly more Co was exposed probably due to the Cr leaching at 1.5V as Cr is oxidized from Cr^{3+} to Cr^{4+} which is an unstable species. $\text{CoCr}_2\text{O}_4@1.6\text{V}$ and $\text{CoCr}_2\text{O}_4@1.64\text{V}$ samples experience significant Cr leaching and exposed more than 50% of surface Co species. This phenomenon was further supported by the ICP leaching data from Figure 4.6b. It is clear that OER had caused substantial Cr leaching as the oxygen produced from OER could further oxidize the Cr^{4+} to forming soluble chromate $(\text{CrO}_4)^{-2}$ and dichromate $(\text{Cr}_2\text{O}_7)^{-2}$ species as mention in the leaching analysis section.

Figure 4.12: Co 2p XPS spectra of (a) p- CoCr_2O_4 , (b) $\text{CoCr}_2\text{O}_4@1.5\text{V}$, (c) $\text{CoCr}_2\text{O}_4@1.6\text{V}$ and (d) $\text{CoCr}_2\text{O}_4@1.64\text{V}$.

Figure 4.13: Cr 2p XPS spectra of (a) p-CoCr₂O₄, (b) CoCr₂O₄@1.5V, (c) CoCr₂O₄-1.6V and (d) CoCr₂O₄@1.64V.

Figure 4.14: Distribution of Co and Cr species on surface of (a) p-CoCr₂O₄, (b) CoCr₂O₄@1.5V, (c) CoCr₂O₄-1.6V and (d) CoCr₂O₄@1.64V.

4.7 X-ray absorption spectroscopy analysis

In order to understand and further verify the oxidation states of the surface species as well as the atomic structure, XAS was conducted on CoCr_2O_4 before and after CA. For CoCr_2O_4 after OER potentials (1.6V and 1.64V) displayed a slight increase in Co K-edge (Figure 4.15a inset) while Cr K-edge remained relatively constant for all samples (Figure 4.15b). This phenomenon showed that some Co^{2+} was oxidized at OER potentials with no change in Cr oxidation state. In order to quantify the oxidation state of Co, the integral method was adopted to determine the edge position.³⁰ Using Co^{2+} in p- CoCr_2O_4 as reference, the Co valence state of $\text{CoCr}_2\text{O}_4@1.5\text{V}$ remains almost unchanged at around +2 while it have increased for $\text{CoCr}_2\text{O}_4@1.6\text{V}$ and $\text{CoCr}_2\text{O}_4@1.64\text{V}$ from +2 to +2.03 and +2.04 respectively (Figure 4.16). One plausible explanation for such a little increase in oxidation state could be caused by the formation of surface Co^{3+} species like CoOOH species during OER with leaching of Cr.

The local atomic structure changes of the samples are determined before and after CA. Generally, the EXAFS graph can be categorized into two regions which radial distance between 1 Å to 2 Å reflects the presence of metal-oxygen bonds while 2 Å to 3.5 Å is ascribed to the metal-metal bonds.^{31,32} Depending on the cation sites, the metal-metal bonds will have varying length. For spinels, the metal – metal distance between two occupation tetrahedral sites is around 3 Å while the metal – metal distance involving octahedral sites is around 2.5 Å.^{3,33} As seen from Figure 4.15c and d, the pristine CoCr_2O_4 is clearly a normal spinel with Co and Cr fully occupying the tetrahedral site and octahedral site respectively. Furthermore, a sharp Co K pre-edge peak of the XANES spectra indicates tetrahedral occupation of Co.³ These findings is consistent with many reported CoCr_2O_4 literatures.^{34,35} After CA at OER potentials of 1.6 V and 1.64V, there was a slight reduction in the Co-O bonds as compared to pristine CoCr_2O_4 . The higher valence state implied that there is a little increase in oxidation state³² probably due to the formation of CoOOH species on the surface with Cr leaching. This assertion can be supported by the increase in peak intensity of Co-O and Co-Co bonds around 1.5 Å and 2.5 Å respectively for $\text{CoCr}_2\text{O}_4@1.6\text{V}$ and $\text{CoCr}_2\text{O}_4@1.64\text{V}$ which correspond to the appearance of edge sharing

CoO₆ octahedra indicative of CoOOH formation^{36,37} and increase in number of Co-O bonds^{37,38} (Figure 4.15c inset). This was accompanied with a decrease in tetrahedral Co occupation represented by the peak around 3 Å.³

Figure 4.15: Normalized XANES spectra of (a) Co and (b) Cr K edge and EXAFS spectra of (c) Co and (d) Cr K edge for p-CoCr₂O₄, CoCr₂O₄@1.5V, CoCr₂O₄@1.6V and CoCr₂O₄@1.64V.

Figure 4.16: Co valence state of p-CoCr₂O₄, CoCr₂O₄@1.5V, CoCr₂O₄@1.6V and CoCr₂O₄@1.64V determined using integral method.³⁰

4.7 Transmission Electron Microscopy (TEM) Analysis

In order to reveal the morphological change and surface elemental changes, transmission electron microscopy measurements were employed. From the TEM images shown in Figure 4.17, it is clear that initially p-CoCr₂O₄ is a crystalline particle with a few nanometers of amorphous surface layer. At OER potential above 1.6V, surface reconstruction occurs causing an increase in the amorphous surface region. However, recrystallization of Co₃O₄ ($d_{(201)} = 2.06\text{\AA}$) was observed at the surface for the CoCr₂O₄@1.64V which could be due to the prolonged exposure of the sample under the TEM electron beam. Surface reconstruction was observed by the TEM user while operating. Thus, the TEM images taken may not be an accurate representation of the surface condition after the electrochemical experiments.

Nevertheless, the EDX line scan of the samples have shown signs of surface reconstruction at OER potential. Initially, the Co and Cr species are proportionate on the surface of p-CoCr₂O₄ as shown by the slope of Co and Cr intensity (Figure 4.17c). After applying potential at 1.5V for 7h, there was an increase in Cr content on the surface represented by an increase in the slope of Cr intensity as compared to Co (Figure 4.17f). This phenomenon can be ascribed to the surface reconstruction when the Cr ions underwent redox reaction from Cr³⁺ to Cr⁴⁺ at 1.3V vs RHE which resulted Cr ions being drawn towards the surface due to the electric field and redox driving force. CoCr₂O₄@1.6V showed a slightly higher Co intensity with a gentler intensity profile of Cr for a depth of around 15 nm from the surface after which Cr and Co intensity profile revert back to the ratio similar to CoCr₂O₄@1.5V (Figure 4.17i). This is undoubtedly caused by leaching of Cr ions at OER potential. Interestingly, the overall O intensity has increased relative to Co and Cr and traced the Cr's intensity profile for a depth of 15 nm from the surface. One possible explanation could be that surface reconstruction during OER resulted in the adsorption of hydroxide ions to form a new surface layer of oxyhydroxide with a decrease in Cr content. As for the reason for the profile from surface down 15nm, the Cr ions were likely leached through soluble complexes (ie. CrO₄²⁻ or Cr₂O₇²⁻) with ligands of hydroxides or lattice oxygen resulting in a similar O intensity profile as Cr near the surface (~15 nm) with creation of oxygen vacancies despite adsorption of new hydroxide ions. This suggestion is further supported by the findings from XPS results. Finally, after CoCr₂O₄ was subjected to a higher OER potential of 1.64V, the surface profile showed a depletion of Cr together with a significant decline in O for ~20 nm from the surface comparing to CoCr₂O₄@1.6V (Figure 4.17l). This observation has proved that Cr leaching increases with potential and could be aided by the OER process. The decline in O species supports the theory that lattice oxygen are loss along with Cr during leaching and the loss of lattice oxygen outweighs the gain in OH⁻ ions. This further suggested that OER occurred under the adsorption evolution mechanism (AEM) rather than lattice oxygen mechanism (LOM) in order to form soluble complexes (ie. CrO₄²⁻ or Cr₂O₇²⁻) to be leached out.

Figure 4.17: (a and b) TEM image of p-CoCr₂O₄ with indication of line scan position. (c) EDX line scan of p-CoCr₂O₄. (d and e) TEM image of CoCr₂O₄@1.5V with indication of line scan position. (f) EDX line scan of CoCr₂O₄@1.5V. (g and h) TEM image of

CoCr₂O₄@1.6V with indication of line scan position. (i) EDX line scan of CoCr₂O₄@1.6V. (j and k) TEM image of CoCr₂O₄@1.64V with indication of line scan position. (l) EDX line scan of CoCr₂O₄@1.64V.

4.8 Discussion

From all the above characterization analysis, Cr seems to be a transition metal that will undergo leaching in metal oxide at high potential especially above OER potentials. The ICP data showed that Cr leaching occur as early as 1.5V without OER showing that the Cr⁺⁴ is not stable after oxidation and bound to leach out under alkaline conditions (Figure 4.6b). However, Cr leaching rate increased tremendously with increasing potential at OER potentials (Figure 4.6). This can be ascribed to the OER assisted formation of soluble Cr ion complexes like (CrO₄²⁻ and Cr₂O₇²⁻) that boost the leaching rate. There is also a possibility that some of the OER current was contributed by direct electrochemical oxidation of Cr³⁺ to Cr⁶⁺ at OER potential given that reduction potential of Cr₂O₇²⁻ to Cr³⁺(+1.33V) is near the OER reduction potential (+1.23V). Despite that, it takes only less than a coulomb worth of electrons to fully oxidize all the Cr³⁺ in the sample. Therefore, the corrosive or oxidative current of Cr is negligible as compared to the OER current. The continuous dissolution of Cr ions had left large amount of cation and oxygen vacancies exposing the tetrahedral Co from the surface towards the core. This had created a favorable condition for surface reconstruction to form OER active Co oxyhydroxide layer^{12,39} as the OH⁻ ions from the electrolyte would fill up the vacancies to form an amorphous layer of oxygen pool⁴⁰. The newly formed OER catalyst would be a core shell structure of CoOOH shell with a CoCr₂O₄ core. Overall, the activated CoCr₂O₄ catalyst had achieved at least 8 fold increase in OER activity at 1.64V after 7h of CA at OER potential.

In order to rate the performance of CoCr₂O₄, Co₃O₄ and IrO₂ were chosen as Co₃O₄ is known to form a sub nanometer CoOOH shell⁴¹ during OER process and IrO₂ is the commercially available OER benchmark catalyst. For fair comparison, the current density is normalized by the oxide BET surface area. As for CoCr₂O₄-aftCA, the BET surface area was extrapolated from the double layer capacitance which is proportionate to ECSA. The

pristine CoCr_2O_4 displayed a poor OER performance as compared to Co_3O_4 and IrO_2 before CA (Figure 4.18). The CoCr_2O_4 -befCA had a high OER overpotential of 361 mV as compared to Co_3O_4 -befCA and IrO_2 -befCA at 350 mV and 274 mV respectively. While the Tafel slope of CoCr_2O_4 -befCA is steeper than Co_3O_4 -befCA but gentler than IrO_2 -befCA. After 7h of CA at 1.6V, CoCr_2O_4 -aftCA displayed a much lower overpotential (325 mV) as before and outperforming Co_3O_4 -aftCA and IrO_2 -befCA. However, the Tafel slope of CoCr_2O_4 -aftCA remains almost unchanged from before and is still steeper than Co_3O_4 -aftCA. The decrease in overpotential for CoCr_2O_4 -aftCA can be ascribed to the new CoOOH surface formed despite having an unchanged Tafel slope. The OER current of CoCr_2O_4 remains stable after surface reconstruction under 7h of constant potential at 1.6V vs RHE while the OER current for Co_3O_4 deteriorated slightly (Figure 4.19). The OER current of IrO_2 clearly deteriorated significantly over time showing poor stability. Despite having the CoOOH shell on the surface, the activities of CoCr_2O_4 -aftCA and Co_3O_4 -aftCA differ probably due to a different CoOOH structure as well as core material (Figure 4.20). The difference in amount of vacancies and defects in the CoOOH layer might change OER mechanism⁴² and change the electronic structures like e_g state occupancy⁴³ resulting in different OER activity. Furthermore, the difference in core material would have different inductive effect on the Co active sites affecting the binding energies of intermediates and have an impact on the overpotential and Tafel slope⁵.

Figure 4.18: Overpotential at $25 \mu\text{A cm}^{-2}$ oxide and Tafel slope of CoCr₂O₄, Co₃O₄ and IrO₂ before and after CA at 1.6V for 7h.

Figure 4.19: CA at 1.6V for 7h of CoCr₂O₄, Co₃O₄ and IrO₂.

Figure 4.20: Schematic of CoCr_2O_4 -aftCA and Co_3O_4 during OER

4.9 Conclusion

In a nutshell, CoCr_2O_4 was investigated for its OER performance via surface reconstruction. The OER activity improved by around eight times after CA at 1.6V for 7h and can be attributed to the surface reconstruction caused by Cr leaching. The CoCr_2O_4 also showed relative stable activity under 7h of CA at 1.64V. The electrochemical analysis concluded that the appearance of Co redox peaks were due to an increase in Co surface species at OER potentials instead of cycling process. Cr leaching has created vacancies and defects which allowed the formation of CoOOH layer through the adsorption of OH^- ions from the electrolyte and improvement in the OER activity. The difference between the intrinsic activity of CoCr_2O_4 -aftCA and Co_3O_4 -aftCA can be explained by the vacancies and defect in the surface CoOOH formed as well as inductive effect of different core material on the adsorption energies of OER intermediates. Therefore, Cr leaching is one of the strategy to induce surface reconstruction and enhance OER electrocatalysts.

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Chapter 5

Implications and Future Work

This final chapter sums up the entire dissertation. From the design of the catalyst to the proven hypothesis, the design target is met. After identifying the Cr leaching conditions needed to induce surface reconstruction and the active species of the reconstructed oxyhydroxide layer, the follow up plans of this work are discussed in details. Defect and vacancy studies can be conducted on series of $\text{Co}_{(3-x)}\text{Cr}_x\text{O}_4$ nanoparticle or nanosheets through controlled leaching of Cr. DFT computation have suggested that large oxygen vacancies exist in the CoCr_2O_4 structure could have contributed to surface reconstruction. The identification of Cr leaching mechanism can be investigated thorough isotopic study of the O_2 and Cr complexes by OLEMS. Overall, this work have recommended a bottom up approach to design and develop more efficient OER catalyst through surface reconstruction

5.1 Implications

The purpose of this thesis is to design an OER catalyst that will undergo surface reconstruction with cation leaching. CoCr_2O_4 was selected based on the preliminary research in the individual cation to study the possibility of surface reconstruction due to Cr leaching and its impact on OER activity. It is important to study different experimental results closely in order to discover phenomena and provide an accurate interpretation of the data. The CoCr_2O_4 has been studied by various research group^{1,2} and yet none has mentioned, discovered or take into account of Cr leaching that cause a boost in activity over electrochemical cycling or chronoamperometry.

By understanding the phenomenon of how surface reconstruction occurred from leaching, experiments or appropriate actions can then be made to allow surface reconstruction to occur. CoCr_2O_4 was synthesized via sol-gel method. XRD was conducted to ensure that the CoCr_2O_4 is a spinel phase.

From the different electrochemical experiments conducted, like electrochemical cycling at selected range, CA series and CA stability test to ICP experiments, it can be concluded that the leaching of Cr is likely due to high applied potential assisted by OER process. Unlike many proposed driver of surface reconstruction observed through electrochemical cycling process, surface reconstruction for CoCr_2O_4 was simply driven by redox reaction of Cr^{3+} to Cr^{4+} at high potential accelerated by OER process as shown by an improvement in OER current and emergent of Co species. ICP further support the observation through detection of Cr leaching after the $\text{Cr}^{3+}/\text{Cr}^{4+}$ redox potential and with more significant leaching at OER. This result allow us to activate CoCr_2O_4 through applying constant potential which OER occurs instead of usual cycling. An important note here is that in order for Cr leaching to occur, the surface of the catalyst must be rich in Cr to allow leaching and surface reconstruction thereafter. Therefore, it is important that the cation (Cr) intended to be leach goes to the octahedral site as Spinel is octahedral cations rich on the surface.^{3,4} This was proven by the initial Cr redox peak without Co redox peak during the first cycle on the CV.

After identifying the process needed to activate surface reconstruction on CoCr_2O_4 , the next step was to study the surface reconstruction process and the new active site or species formed that boost the OER performance.

XPS analysis was conducted on CoCr_2O_4 to study the changes in the valence state and species of individual elements before and after surface reconstruction. From the O 1s analysis, massive disappearance of lattice oxygen accompanying the increase on hydroxide and water was observed only for samples after CA at OER potentials proving the removal of lattice oxygen with the built up of oxygen pool or oxyhydroxide layers on the reconstructed surface. The appearance of Co^{3+} further proved the formation CoOOH on the surface after OER. The increase in surface Co to Cr ratio also verified Cr leaching from the surface during surface reconstruction at OER potentials. The ex situ XAS was conducted to study the oxidation states of the surface species and the atomic bonds and structure. From the XANES, we could actually detect presence of higher valence Co which is attributed to the formation of CoOOH species without any changes in Cr valence state. This was consistent with the XPS results. EXAFS results showed that CoCr_2O_4 is a normal spinel with Co and Cr occupying tetrahedral and octahedral sites respectively. Samples subjected to OER potentials had a slight reduction in the Co-O bonds which indicate an increase in oxidation state of Co. The increase in peak intensity of Co-O and octahedral coordinated Co-Co bonds at 1.5 Å and 2.5 Å with a decrease in tetrahedral coordinated Co-Co peak intensity at 3 Å supported the theory of surface reconstruction with the formation of CoOOH . The ex situ TEM and TEM line scan was employed to study the morphological changes and the surface elemental composition changes respectively. The TEM images of the samples were not conclusive of formation of amorphous CoOOH or crystalline CoOOH due to inconsistent results. Some of samples were likely to suffer from beam damage during TEM as the user observe some changes happening at the surface of the sample during TEM. Despite the disappointment, the TEM line scan have provided very important information. The changes in the elemental profile after CA at 1.5V showed that Cr species had been drawn to the surface due to the redox reaction of $\text{Cr}^{3+}/\text{Cr}^{4+}$ induced at the potential. After applying OER potentials, the Cr profile showed a significant decline at the surface with a reduction in ratio compared to Co and O. The Cr profile proved Cr leaching at the surface

which intensified with higher OER potential. One interesting observation was the O to Co ratio has increase for the sample that was subjected to CA at 1.6V while it was back to almost the same ratio as pristine sample after CA at 1.64V. After scrutinizing XAS data and making reference to XPS, there was some relationship between Cr and O profile that can explain for this observation. The increase in O to Co ratio for $\text{CoCr}_2\text{O}_4@1.6\text{V}$ was due to an increase in OH^- adsorbed on the surface with increasing vacancies caused by decrease in Cr. However, with more Cr being leach off from the surface, the loss of lattice oxygen was more than the amount of oxygen from OH^- could replace from the electrolyte which explains for the intensity profile for $\text{CoCr}_2\text{O}_4@1.64\text{V}$ and the near surface (15nm) O profile for $\text{CoCr}_2\text{O}_4@1.6\text{V}$. The TEM linescan results not only prove Cr leaching but also that Cr was likely leached as soluble complex ions which created both cation and oxygen vacancies favorable for surface reconstruction.

From the characterization techniques, Cr substitution can be a good strategy in activating surface reconstruction of CoCr_2O_4 through Cr leaching with the formation of CoOOH surface. The TEM linescan further proven that Cr leaching was through soluble complexes ions and produced both octahedral cation and oxygen vacancies.

After confirming that there is surface reconstruction, the OER performance of CoCr_2O_4 was compared against IrO_2 OER benchmark and Co_3O_4 . Co_3O_4 was chosen because of the similarity in CoOOH shell form during OER with the core material being the only difference. Furthermore, there are differences in the CoOOH structure form from CoCr_2O_4 and Co_3O_4 like number of vacancies and defects which would have an impact on the electronic structure and affect the OER performance. As a result, there will be difference in the adsorption energies of intermediates which affects the overpotential and Tafel slope. There might be difference in OER mechanism as well. Judging from the Tafel plot, the surface reconstructed CoCr_2O_4 have better OER performance having a lower overpotential but with a relatively higher Tafel slope as compared to Co_3O_4 . However, CoCr_2O_4 have a slightly more stable OER current after holding at constant potential for 7h as compared to Co_3O_4 . The preliminary comparison of the OER performance will give a better idea on where surface reconstructed CoCr_2O_4 stands among its peers and shed some light on future

work or modifications that can be done to improve its performance. More will be discussed in the next section.

5.2 Future Work

Hereby, in this thesis most of the effort is devoted in the verification of surface reconstruction through Cr leaching and preliminary study of the surface reconstructed species responsible for OER. Comparing the OER performance of CoCr_2O_4 after surface reconstruction and the Co_3O_4 , the former has a lower overpotential but a steeper Tafel slope than the latter. The difference in OER performance of CoCr_2O_4 and Co_3O_4 was likely attributed to difference in structure of the CoOOH formed. The induction effect⁵ from the core material and the difference in oxygen vacancies or defect of CoOOH formed could affect the adsorption energies of intermediates due to a different e_g occupancy^{6,7}. Furthermore, oxygen vacancies will tune the charge transfer energy or metal oxygen covalency which affect the electrical conductivity and OER activity.⁷ Given that their structure during OER are fairly similar, there is a room for modification to improve the OER performance by lowering the Tafel slope of CoCr_2O_4 .

The proposed follow up work is to design a series of surface reconstructed $\text{Co}_{(3-x)}\text{Cr}_x\text{O}_4$ through activation under a constant OER potential for several hours till a steady current is achieved with no more Cr leaching. With varying Cr content, the number of vacancies and defects in CoOOH during surface reconstruction can be controlled and the core material will be different as well. The thickness of the reconstructed CoOOH will also vary with different Cr content. There was a similar reported work but the author did not consider Cr leaching or wait for surface reconstruction to stabilize before measuring the activity.¹ To identify the cause of the improvement in activity, the effects of the core material can be eliminated by synthesizing a nanoparticle or nano-layered of $\text{Co}_{(3-x)}\text{Cr}_x\text{O}_4$ to allow complete Cr leaching during electrochemical activation. The solo effects of varying vacancies and defects on reconstructed CoOOH can then be investigated. Small angle XRD can be employed to examine the orderliness of the CoOOH layer and determine whether

DFT simulation can be carried out to study the electronic structure. Another set of experiments can be conducted on larger $\text{Co}_{(3-x)}\text{Cr}_x\text{O}_4$ particles that form core shell structure during OER and comparison can be made with purely reconstructed CoOOH . After getting the results, the factor for improvement in activity can then be identified and help design better OER catalyst in future.

5.2 Reconnaissance work not included in main chapter

As mentioned by May et. al., surface reconstruction is likely possible only when O 2p centre is higher than -2.2eV relative to the fermi level.⁸ From the DFT computation, the O 2p band centre of CoCr_2O_4 is at -1.803eV relative to the fermi level, indicating the likelihood of surface reconstruction to occur via lattice oxygen mechanism. Besides that, the material might have higher oxygen vacancies and lattice oxygen mobility due to the high O 2p band centre which facilitated surface reconstruction.⁸ However, lattice oxygen mechanism may not have occurred and cause the leaching of Cr and further investigation on the mechanism will be necessary.

5.3 Outstanding questions

5.31 Mechanism

The OER mechanism of the reconstructed CoOOH layer can only be constructed after the active species and the local structure are determined during OER. In-situ XAS can be employed to determine the oxidation state of the species and the M-O bond coordination at different applied potential. Furthermore, to study the surface species, the electron yield mode should be selected as the XAS detection mode instead of transmission or fluorescence mode which is bulk sensitive.⁹ In this study, the transmission mode was used as the electron yield mode is not available. Many work have also proven that OER catalyst which undergo surface reconstruction during OER are likely to follow the lattice oxygen mechanism.^{8,10} To understand whether the OER follows the adsorbate evolution mechanism (AEM) or lattice oxygen mechanism (LOM)¹¹, isotopic studies can be conducted by using H_2^{18}O to prepare the KOH electrolyte for OER. Using the online electrochemical mass spectroscopy

(OLEMS), CrO_4^{2-} , $\text{Cr}_2\text{O}_7^{2-}$ and O_2 produced with partially or fully ^{16}O and would proof lattice oxygen participation.

5.32 Determining amorphisation

The TEM result in this thesis is not conclusive of whether surface reconstruction forms amorphous CoOOH or crystalline CoOOH . To determine this change, in-situ TEM can be conducted while OER occur. The beam current can be adjusted lower or the magnification of the sample can be reduced to prevent beam damage.

5.4 Conclusion

To sum up, this work has presented the use of Cr as a cation for leaching to incite surface reconstruction with the formation of oxyhydroxide layers. The OER process has facilitated the Cr leaching causing both cation and anion vacancies (Cr and O) to form, creating the condition for hydroxides to adsorb and bond with surface Co. The mechanism of the Cr leaching process has to be verified by isotropic study of the Cr complexes and O_2 with OLEMS. The effects of vacancies on OER performance can be investigated by varying the amount of Cr in the structure in nano $\text{Co}_{(3-x)}\text{Cr}_x\text{O}_4$ particles or sheet synthesized. Optimization of the material can be made after comparison with the performance of larger sized $\text{Co}_{(3-x)}\text{Cr}_x\text{O}_4$ particles to control the amount of vacancies, thickness of oxyhydroxide and the Cr content in the core of the reconstructed coreshell structure of $\text{Co}_{(3-x)}\text{Cr}_x\text{O}_4$.

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