

I. Abstract

Hydrogen is viewed as an energy carrier of the future as it is environmentally friendly, inexhaustible and possesses high energy density. Water electrolysis is an efficient and sustainable way to produce hydrogen. However, the practical application of water electrolysis is limited due to its high cost. This is related to the high overpotential associated with oxygen evolution reaction (OER) at the anode. Cobalt based spinel metal oxides are potential candidates for OER due to their excellent catalytic properties and stability in alkaline medium. We have prepared various spinel oxides, namely $\text{Cu}_x\text{Co}_{3-x}\text{O}_4$ ($0 \leq x \leq 1$), $\text{Ni}_{1-x}\text{Cu}_x\text{Co}_2\text{O}_4$ ($0 \leq x \leq 0.75$), $\text{Fe}_y\text{Cu}_{x-y}\text{Co}_{3-x}\text{O}_4$ and $\text{Fe}_y\text{Ni}_{x-y}\text{Co}_{3-x}\text{O}_4$ ($0 \leq x \leq 1$, $0 \leq y \leq 1$) using thermal decomposition method. The films were analyzed, using several structural, chemical and electrochemical methods such as X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), cyclic voltammetry and X-ray photoelectron spectroscopy (XPS). Electrochemical measurements show that the electrodes exhibit overall good catalytic activity towards OER. However, addition of small amount of Fe to form $\text{Fe}_y\text{Cu}_{x-y}\text{Co}_{3-x}\text{O}_4$ and $\text{Fe}_y\text{Ni}_{x-y}\text{Co}_{3-x}\text{O}_4$ show a significant enhancement, indicating these compositions are potential candidates for OER.

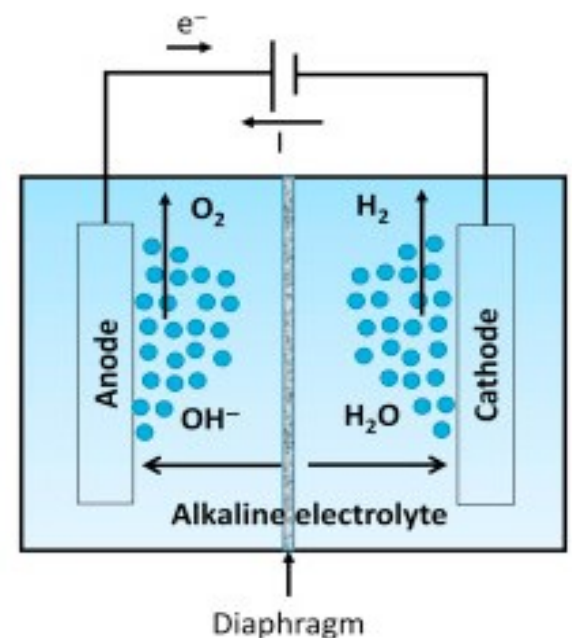
II. Introduction

The increasing energy crisis demands earth-abundant alternative energy supplies and sustainable use of energy sources. Electrochemical technology is a cleaner and promising approach as it offers environmental protection through nonpolluting energy sources. The production of hydrogen gas by water electrolysis is a perfect example of this [1, 2]. Water splitting involves two half-reactions, hydrogen evolution reaction (HER) and oxygen evolution reaction (OER). The OER involves a four-electron transfer and hence requires a larger overpotential than HER. This represents a significant energy loss in the water splitting process [3, 4]. Noble metal oxides like IrO_2 and RuO_2 possess superior catalytic activity for OER. However, these materials are very expensive and less earth-abundant [1, 5]. The goal of our research is to design highly efficient and stable electrocatalysts for OER from earth-abundant transition metals so that the cost of hydrogen production can be reduced significantly, and thus clean and sustainable energy is available to mankind at an affordable price.

Cathode (HER) : $4\text{H}_2\text{O} + 4\text{e}^- \rightarrow 2\text{H}_2 + 4\text{OH}^-$, $E^0(\text{HER}) = -1.071\text{ V vs. SCE}$

Anode (OER) : $4\text{OH}^- \rightarrow 2\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^-$, $E^0(\text{OER}) = +0.159\text{ V vs. SCE}$ [6]

- The minimum voltage required for the water electrolysis at standard conditions is 1.23 V
- High overpotential is associated with OER



III. Objectives

- Prepare various compositions of spinel oxides by thermal decomposition method
 $\text{Cu}_x\text{Co}_{3-x}\text{O}_4$ ($0 \leq x \leq 1$), $\text{Ni}_{1-x}\text{Cu}_x\text{Co}_2\text{O}_4$ ($0 \leq x \leq 0.75$) and $\text{Fe}_y(\text{Ni}/\text{Cu})_{x-y}\text{Co}_{3-x}\text{O}_4$ ($x = 0.5, 1$ and $y = 0.1, 0.15$)
- Study their electrocatalytic properties for OER and correlate their performance to their surface structure.
- Optimize suitable composition for OER

IV. Sample Preparation

Process: Thermal decomposition
Precursor: Metal nitrates
Solvent: Isopropanol-water mixture

Metal nitrate salt solutions are deposited on normal glass for XRD, FTO glass for SEM and electrochemical characterizations. After depositing a minimum of five layers a final annealing was performed. For $\text{Cu}_x\text{Co}_{3-x}\text{O}_4$ and $\text{Ni}_{1-x}\text{Cu}_x\text{Co}_2\text{O}_4$, each layer was heated for 10 mins at 300°C and final annealing carried out at 300°C for 1 hour. While for $\text{Fe}_y\text{Cu}_{x-y}\text{Co}_{3-x}\text{O}_4$ and $\text{Fe}_y\text{Ni}_{x-y}\text{Co}_{3-x}\text{O}_4$, each layer was heated at 400°C for 10 min and final annealing was performed at the same temperature for 2 hours [7, 8].

V. Characterization results

All samples were characterized for their morphology, surface area, structure, composition and electrochemical properties. Summary of our results is given below.

Scanning Electron Microscopy (SEM)

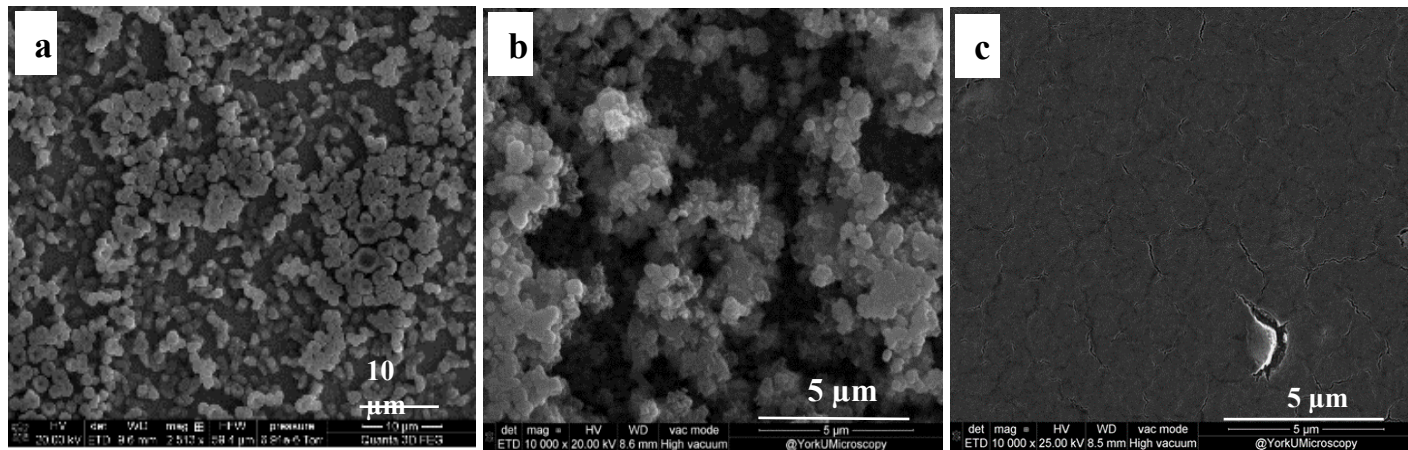


Figure 1. SEM image of (a) Co_3O_4 (b) $\text{Fe}_{0.1}\text{Cu}_{0.9}\text{Co}_2\text{O}_4$ (c) $\text{Ni}_{0.25}\text{Cu}_{0.25}\text{Co}_2\text{O}_4$. The SEM images of this work was obtained with SEM-FEI QUANTA 3D electron microscope.

- Co_3O_4 and $\text{Fe}_{0.1}\text{Cu}_{0.9}\text{Co}_2\text{O}_4$ displays a grainy and porous surface with some hexagonal platelets.
- Ni substituted samples appears to have a smooth surface.

Energy Dispersive X-ray Spectroscopy (EDX)

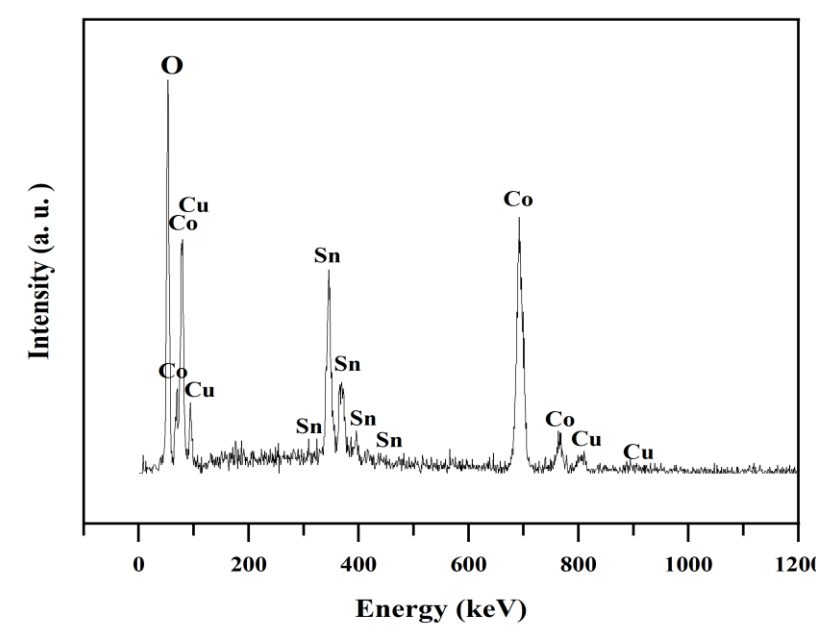


Figure 2. EDX spectrum of $\text{Cu}_{0.25}\text{Co}_{2.75}\text{O}_4$ prepared by thermal decomposition method. The EDAX Octane Elect EDS system was used in this work.

- EDX spectrum possess characteristic peaks of copper, cobalt, oxygen and tin
- Tin is originated from the substrate: Fluorine doped SnO_2 coated conductive glass is used as substrate
- Exhibit good correlation between stoichiometric and EDX composition.

V. Characterization results

X-ray Photoelectron Spectroscopy (XPS)

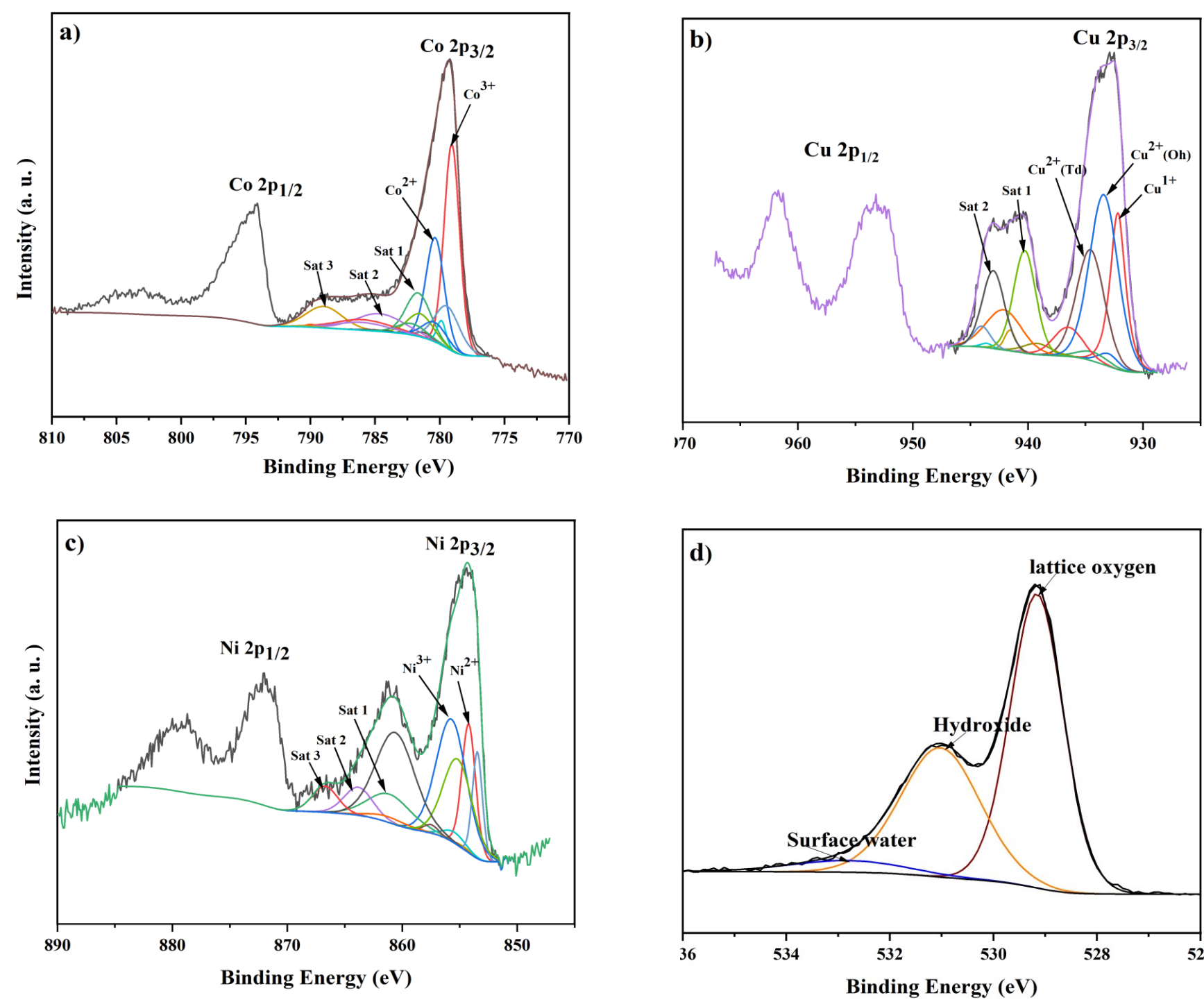


Figure 3. XPS core level spectra of (a) Co 2p_{3/2} (b) Cu 2p_{3/2} (c) Ni 2p_{3/2} (d) O 1s of $\text{Ni}_{0.5}\text{Cu}_{0.5}\text{Co}_2\text{O}_4$

- Surface of electrode contains different crystalline phases such as spinel, metal hydroxides and metal oxides
- Cations exist in different oxidation states.
- Oxygen peak is composed of lattice oxygen, hydroxide ion and surface water
- Co_3O_4 possess high $\text{Co}^{2+}/\text{Co}^{3+}$ ratio of 0.92 (stoichiometric ratio is 0.5)
- Significant amount of surface NiO is observed

X-ray Diffraction Analysis (XRD)

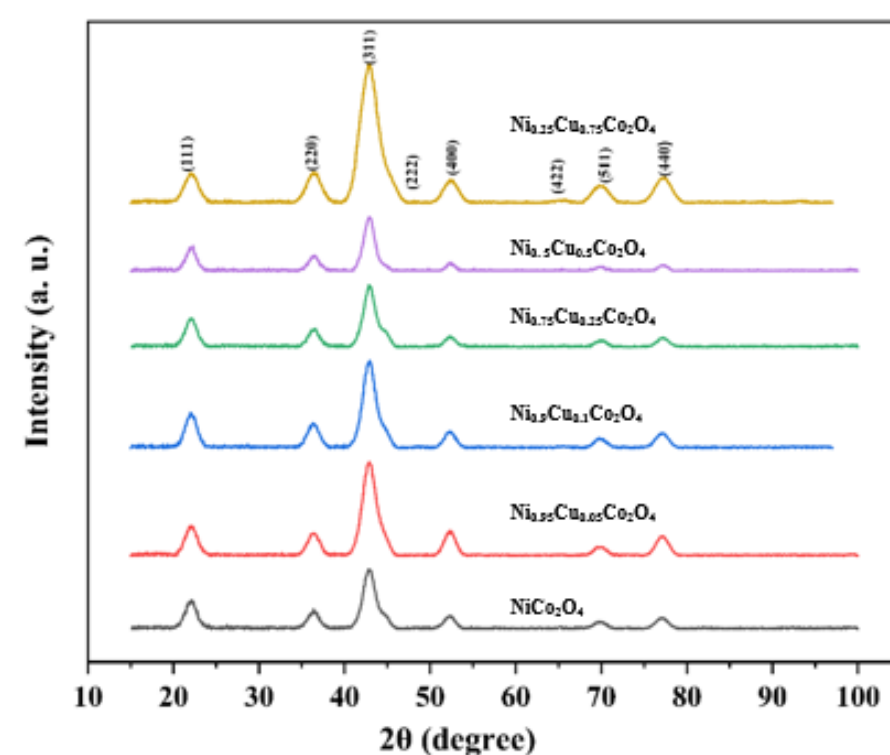


Figure 4. X-ray diffraction pattern of $\text{Ni}_{1-x}\text{Cu}_x\text{Co}_2\text{O}_4$. The specification of the XRD system used in this work include Bruker D8 DISCOVER, DAVINCI DESIGN diffractometer, and Vantec 500 (MikroGap TM technology) detector.

- Samples crystallized mainly in cubic spinel structure.
- Higher amount of Cu or Ni resulted in small amount of CuO or NiO phase respectively.
- CuCo_2O_4 (90.2 % spinel + 9.8% CuO)
- $\text{Fe}_{0.1}\text{Ni}_{0.9}\text{Co}_2\text{O}_4$ (94.2 % spinel + 5.8% NiO)
- Lattice parameter increased with Cu or Ni substitution

V. Characterization results

Cyclic Voltammetry (CV)

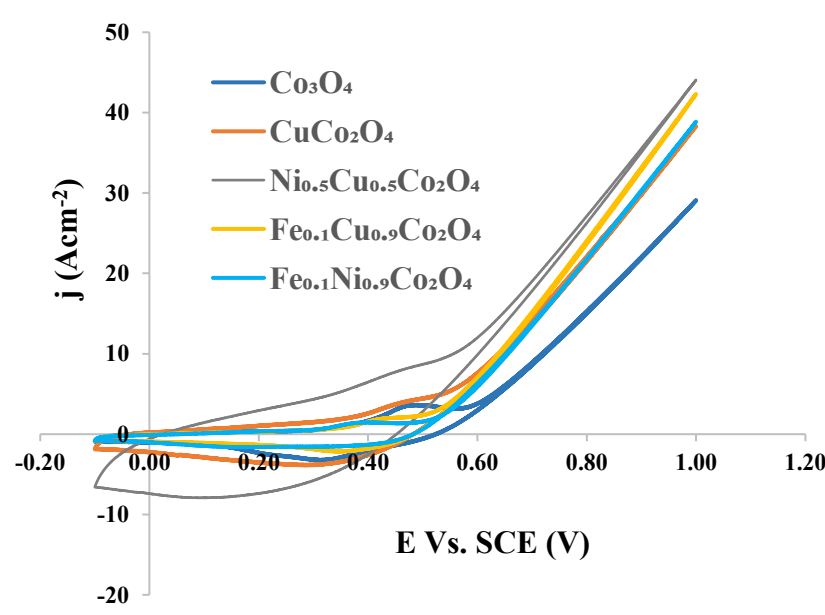


Figure 5a. Cyclic voltammograms of spinel oxides, in 1M KOH in a potential range of -800 mV to 1000 mV (SCE) at a scan rate of 50 mV /s

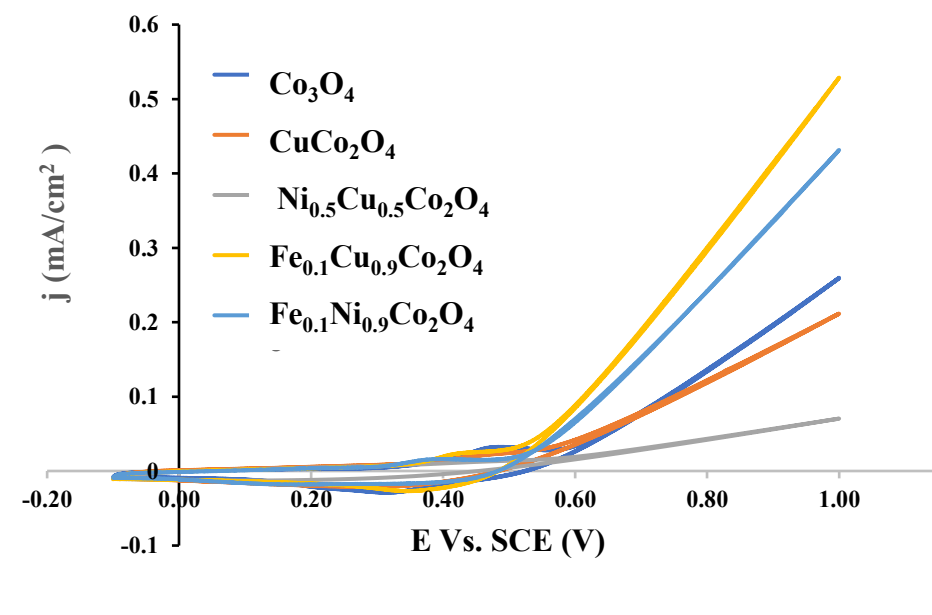


Figure 5b. Cyclic voltammograms of spinel oxides, in 1M KOH in a potential range of -800 mV to 1000 mV (SCE) at a scan rate of 50 mV /s, corrected for real surface area by roughness factor

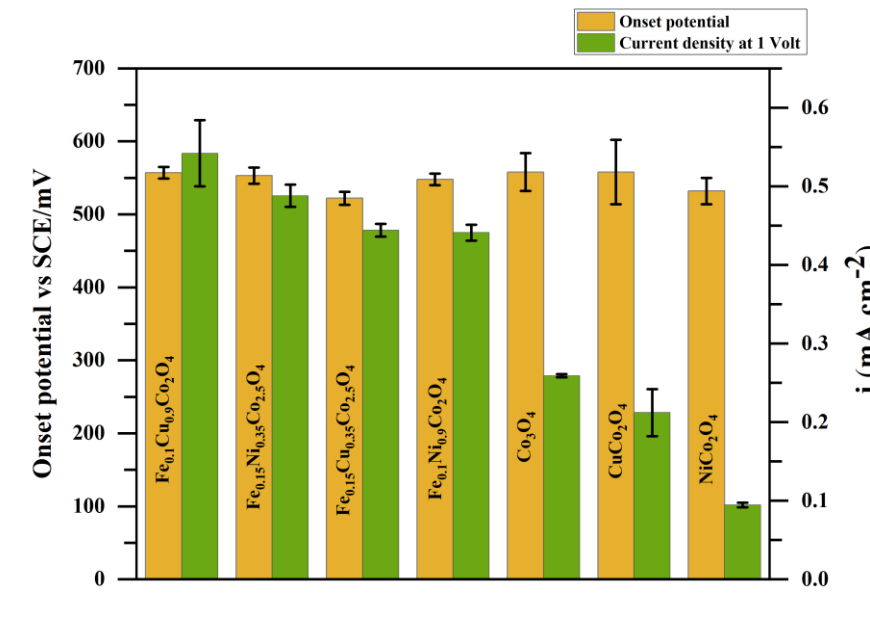


Figure 6. Onset potential and current density is plotted as function of composition

- Fe substituted cobalt spinel oxides showed high current density compared to pure and Ni or Cu substituted cobalt oxide.
- Ni substituted cobalt oxides showed lower catalytic activity is attributed to the presence of surface NiO
- Electrocatalytic activity greatly depends on the surface composition

VI. Discussion and Conclusions

Difference in surface and bulk composition is observed according to EDX and XPS analysis. The X-ray diffraction studies confirms that the sample is mainly crystallized in spinel structure, however, the XPS analysis indicates the presence of various phases on the surface. Pure Co_3O_4 possessed higher current density compared to Cu or Ni substituted cobalt oxide; Co_3O_4 possess highest Co^{2+} to Co^{3+} ratio and hence high inversion from normal cubic spinel structure is observed. This ratio decreases upon the substitution of other metals [7, 8]. As the Fe on the surface is negligible, the direct involvement of Fe in the OER can be ruled out. The current density obtained from unit geometric area (Figure 5a) was corrected using roughness factor to exclude the surface area effect is shown in Figure 5b. The high catalytic activity of Fe substituted cobalt oxides might be due to the electronic effect introduced by Fe doping of the spinel. As explained in various references, Fe has some synergic effect with Ni, Cu and Co, which promote catalytic activity [9]. The Fe-Cu-Co and Fe-Ni Co-spinel oxides are promising electrocatalysts for OER

Future work:

- Study the kinetics of the electrode reactions using rotating disk electrode (RDE)
- Analyze Tafel and Koutecky–Levich plots to study the electron transfer process and electrochemical reaction mechanisms
- Scaling the relation between the composition, active site occupation and electrocatalytic activity

VII. References

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VIII. Acknowledgement

Natural Science and Engineering Research Council (NSERC) of Canada and York University are acknowledged for support through the Discovery Grant program (RGPIN-2016-05321) and Minor Research Grant, respectively. Karen Rethoret and Dr. Magdalena Jaklewicz at York University, Imaging Facility for SEM and EDX analysis. Dr. S. Petrov, X-ray Analysis Lab at the University of Toronto and Victoria Jarvis at McMaster University, Analytical X-ray Diffraction Facility for XRD analysis. Dr. Zeynel Bayindir, Biointerfaces Institute, McMaster for XPS measurements.