

A Comparative Study Between Amorphous and Crystalline Transition Metal Oxides as Catalysts for the Oxygen Evolution Reaction

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I. Abstract

Designing an efficient water electrolyser catalyst for the OER using transition metal oxides would decrease the cost associated with hydrogen gas production. Previous work in the Morin's group shows good electrocatalytic activities of various binary and ternary spinel oxides containing Fe, Ni, Cu and Co, where the highest current density is observed when iron is added to the Cu-Co and Ni-Co oxides. Recently amorphous transition metal oxides have gained popularity due to their improved electrocatalytic performance over those of crystalline materials of identical compositions. To investigate the effect of increasing iron concentration the catalyst structure (amorphous versus crystalline) and their electrochemical properties, we have synthesized different materials in two morphologies spinel and amorphous, (Co_3O_4 , $\text{Fe}_y\text{Cu}_{x-y}\text{Co}_{3-x}\text{O}_4$, and $\text{Fe}_y\text{Ni}_{x-y}\text{Co}_{3-x}\text{O}_4$, $0 < x < 1$, $0 < y < 1$) using the thermal decomposition method. These materials have been characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). Moreover, their electrocatalytic activity was investigated using cyclic voltammetry (CV). The goal of this study is to understand the relationship between amorphous material composition, structure and catalytic activity as a function of iron concentration and comparing these results with those obtained for crystalline materials of identical composition.

II. Introduction

Today, fossil fuels are the main source of energy production and power generation, which also account for the main pollution source. Renewable energy sources, such as wind power and solar energy cells have faced the challenge of being expensive and unavailable to be used everywhere. Therefore, they have failed to produce mass energy required to support the world's needs. This has led to focused attention towards electrochemical technology which is a cleaner approach and can offer environmental protection through nonpolluting energy sources. The oxygen evolution reaction (OER) plays an important role in electrochemistry. OER is the oxidation part of the water electrolysis, an environmentally approach to produce hydrogen. However, this electrochemical process involves a high OER overpotential and hence consumes a large amount of electrical energy. Therefore, it is necessary to minimize the anodic overpotential of OER through designing appropriate electrode material for achieving the lowest possible overpotential.

III. Rational and Hypothesis

Rational

- Dr. Morin's group has studied previously a wide range of spinel oxides.
- Using EDX and XPS some differences were observed in the bulk and surface compositions of the oxides, respectively.
- The surface compositions and phases observed using XRD do not correspond to that of spinel alone. In all our crystalline samples about 59±5% corresponds to the spinel phase.
- Small amount of Fe, resulted in improved catalytic activity.

Hypothesis

- There maybe an amorphous component present together with some crystalline phases at the surface for our samples, comparing performances of crystalline and amorphous samples would help understand our materials' behaviour.

Objectives

- To rule out any dominant effects of an amorphous phase and to investigate the effect of Fe, we will prepare various amorphous and spinel materials of different compositions.
- Study their electrocatalytic properties.
- Compare electrocatalytic, structural and morphological properties for different compositions.

IV. Sample Preparation

Amorphous oxides:

- Metal precursors (metal 2-ethyl hexanoate) were dissolved in hexane and deposited as layers on FTO glass, then these thin films were positioned under NIR lamp for a total of 1.5 h.

Spinel oxides:

- Metal precursors (metal nitrates) were dissolved in a mixture of water isopropanol and deposited as layers on FTO glass, then these glasses were heated for 10 minutes at 400 °C followed by final annealing for two hours at the same temperature.

V. Characterization results

Scanning Electron Microscopy

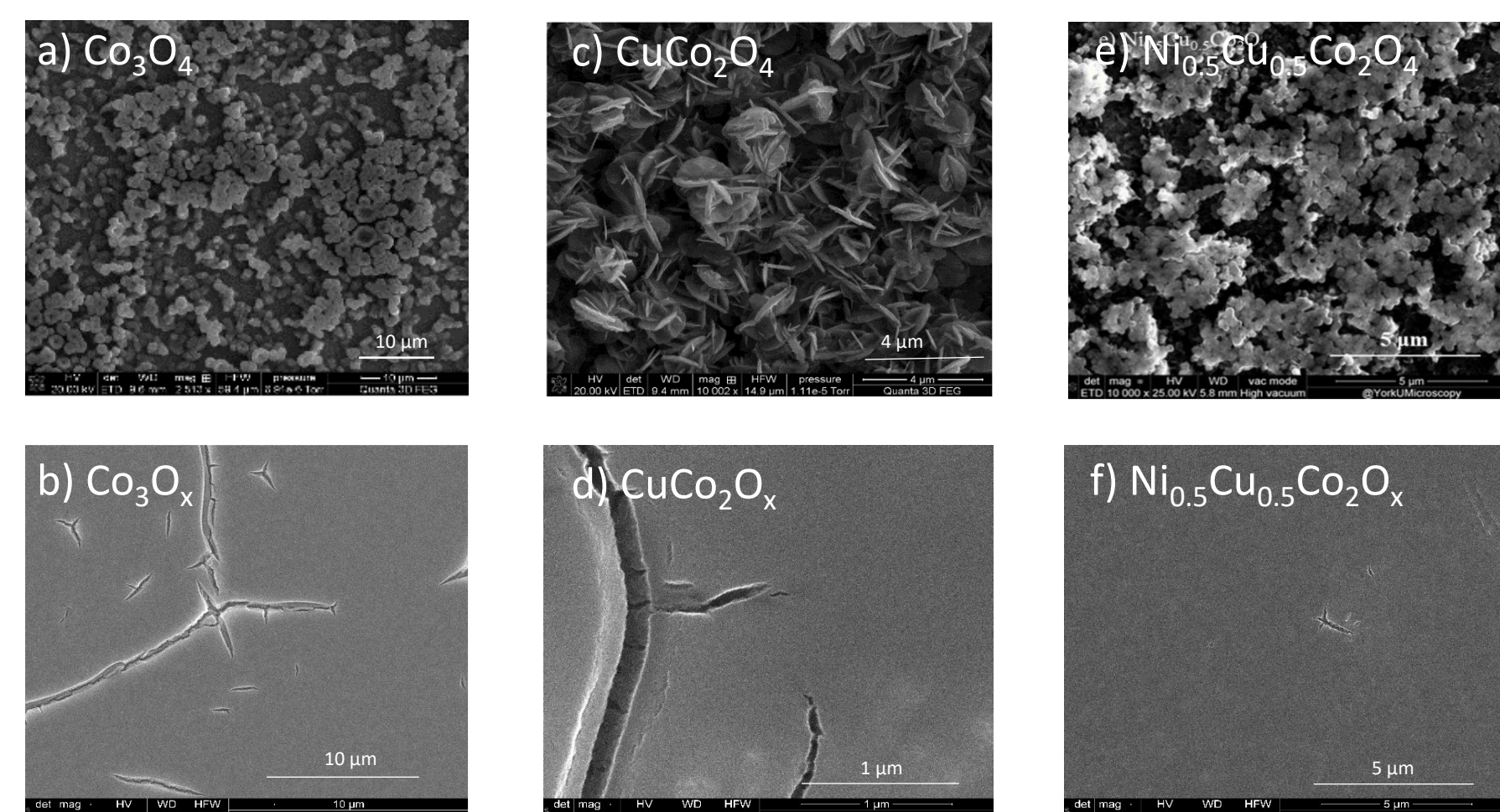
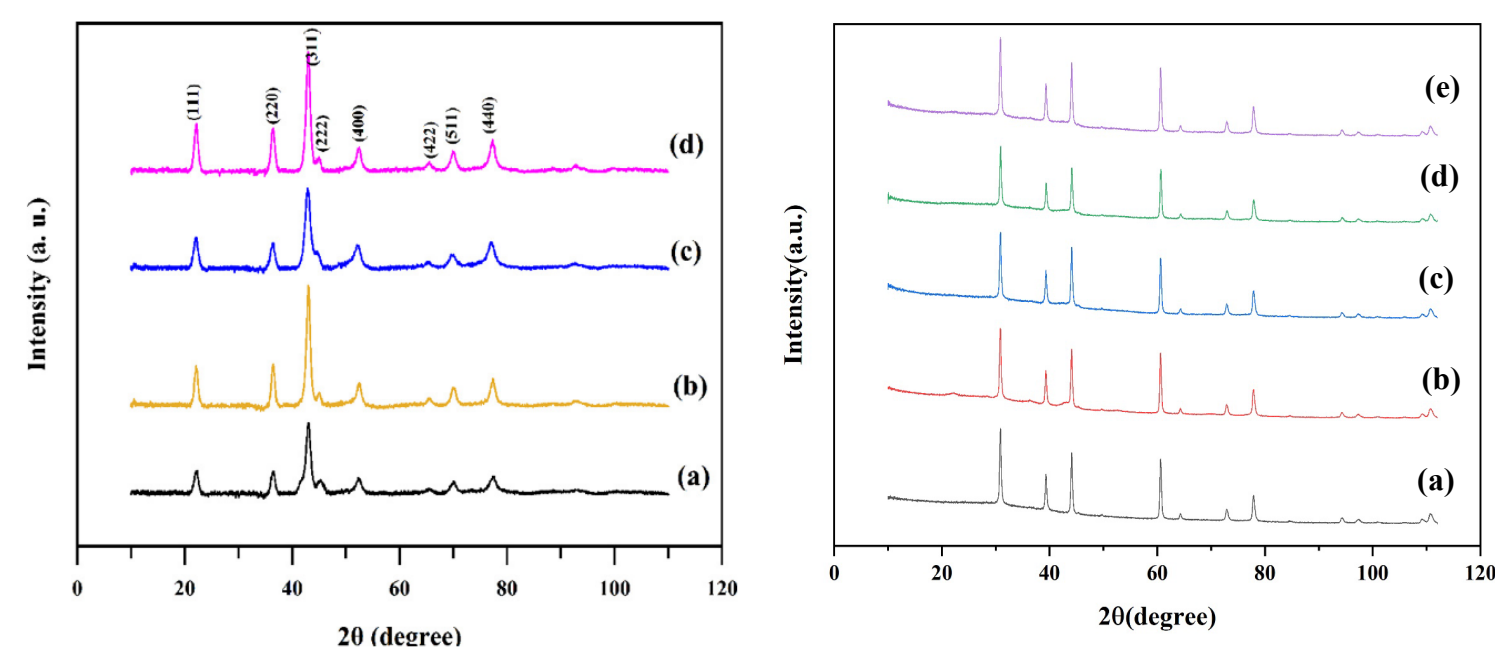


Figure 1. (a), (c), and (e) SEM image of spinel Co_3O_4 , CuCo_2O_4 , and $\text{Ni}_{0.5}\text{Cu}_{0.5}\text{Co}_2\text{O}_x$ respectively. (b), (d), and (f) SEM image of amorphous CoO_x , CuCo_2O_x , and $\text{Ni}_{0.5}\text{Cu}_{0.5}\text{Co}_2\text{O}_x$ respectively. Note that the magnification varies.

- There is a marked difference between the morphology of crystalline (spinel) oxides and amorphous ones. Fig. 1 a), c) and e) display grainy and porous surfaces with some hexagonal platelets, which are typical of spinel oxides.
- Amorphous samples (Fig. 1 b), d) and f) have a smooth surface. Some cracks are also visible.

X-ray Diffraction Spectroscopy



- Thin film XRD patterns show similar features to that of FTO covered glass which proves there are amorphous.

Figure 2. XRD patterns of on the left are for a) $\text{Fe}_{0.1}\text{Cu}_{0.9}\text{Co}_2\text{O}_4$, b) $\text{Fe}_{0.15}\text{Cu}_{0.35}\text{Co}_{2.5}\text{O}_4$, c) $\text{Fe}_{0.1}\text{Ni}_{0.9}\text{Co}_2\text{O}_4$, and d) $\text{Fe}_{0.15}\text{Ni}_{0.35}\text{Co}_{2.5}\text{O}_4$; and on the right for a) FTO glass, b) CoO_x , c) $\text{Cu}_{0.5}\text{Ni}_{0.5}\text{Co}_2\text{O}_x$, d) $\text{Fe}_{0.1}\text{Cu}_{0.9}\text{Co}_2\text{O}_x$, and e) $\text{Fe}_{0.1}\text{Ni}_{0.9}\text{Co}_2\text{O}_x$.

X-ray Photoelectron Spectroscopy

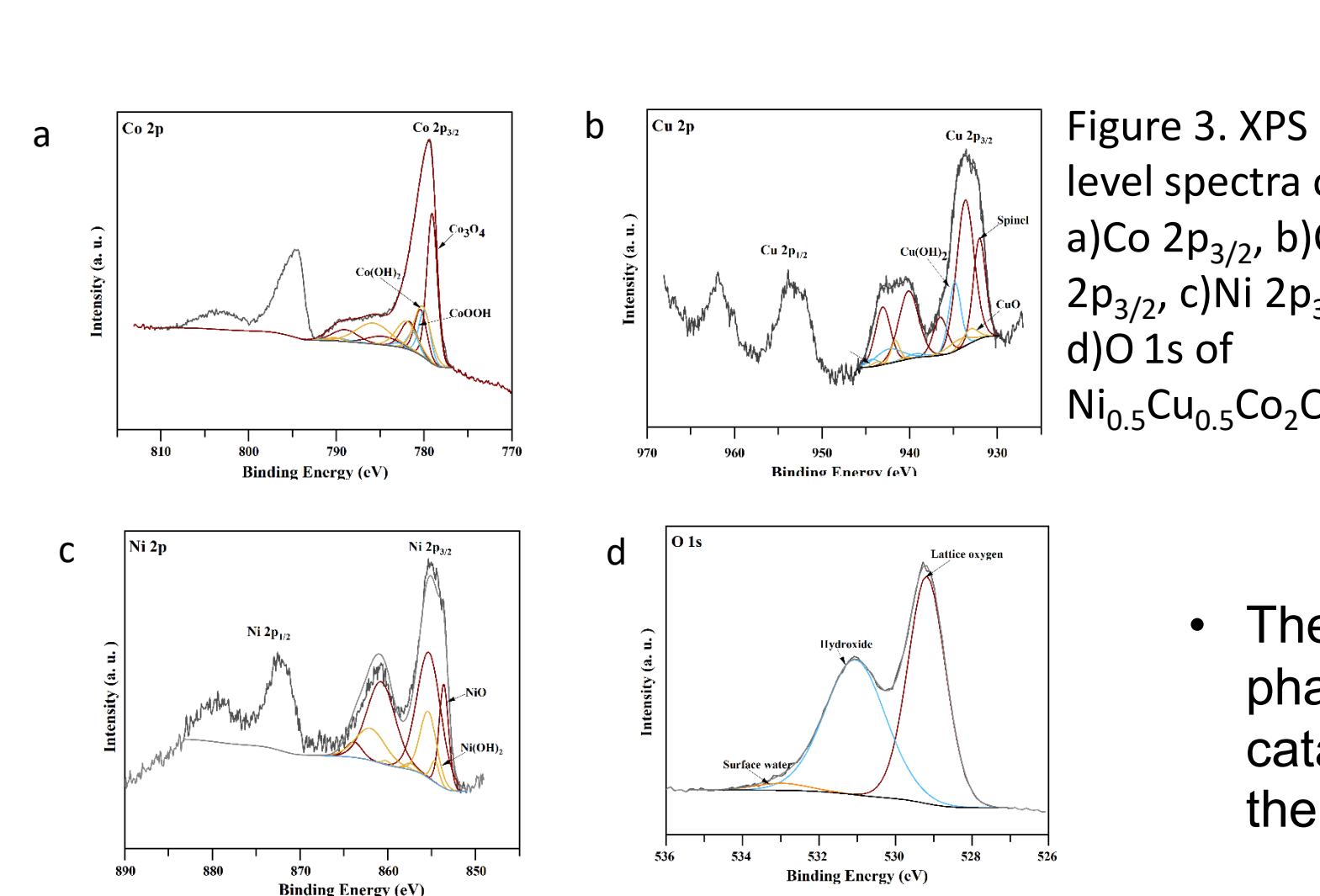


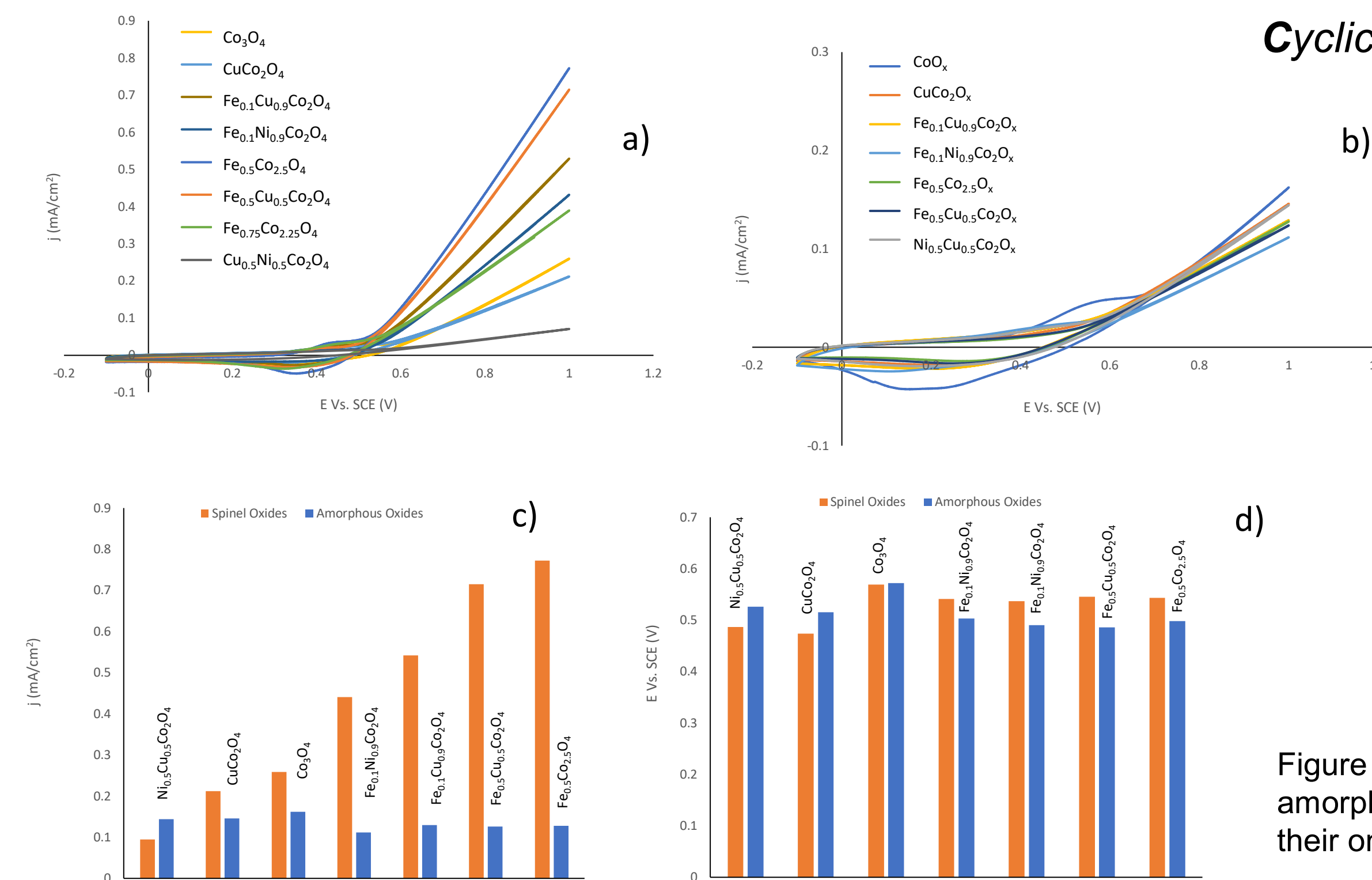
Figure 3. XPS core level spectra of a) Co $2p_{3/2}$, b) Cu $2p_{3/2}$, c) Ni $2p_{3/2}$, d) O 1s of $\text{Ni}_{0.5}\text{Cu}_{0.5}\text{Co}_2\text{O}_x$.

Different phases observed in XPS

Peak	Phase	Percentage	Peak	Phase	Percentage
Co 2p	Co-Spinel	39.9-70.8	Ni 2p	NiO	71.1-73.7
	Co(OH) ₂	12.3-31.2		Ni(OH) ₂	26.3-28.9
	Co(OH) ₂	16.9-34.9			
Cu 2p	Cu-Spinel	57.1-75.8	O 1s	lattice oxide	44.0-62.8
	Cu(OH) ₂	16.2-38.6		hydroxide	32.4-53.1
	CuO	4.3-8.0		surface water	1.0-6.3

- The high-resolution spectra show different phases that are present at the surface of the catalyst and are listed in the above table with their corresponding percentages

V. Characterization results



Cyclic Voltammetry

- Amorphous oxides have lower performance than their spinel counterparts in terms of producing current density at 1.00 V.
- Amorphous and spinel oxides have almost same onset potentials.

Figure 4. Cyclic voltammograms (corrected for real surface area) of (a) spinel and (b) amorphous metal oxides, (c) comparison of their current density and (d) comparison of their onset potential.

VI. Discussion and Conclusions

- Different compositions of amorphous and spinel oxides were prepared using thermal decomposition and XRD measurements confirmed their structure.
- According to XPS different chemical environment exist at the surface of the amorphous materials. This data is similar to what is observed at the surface of the crystalline samples.
- SEM images of their surface showed a different surface texture for amorphous to that of the crystalline samples.
- Our preliminary electrochemical results show that a-MOx display lower activity than their crystalline counterparts.
- Further increase in Fe content does improve the catalytic activities of our crystalline materials.

Future work:

- Perform kinetic measurements using rotating disk electrode.
- Establish the relationship between the surface composition of the catalysts and their electrocatalytic activity.

VII. References

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