

# ORR Activity of Zinc Oxide Doped with Cobalt Ions at Different Loading Concentrations

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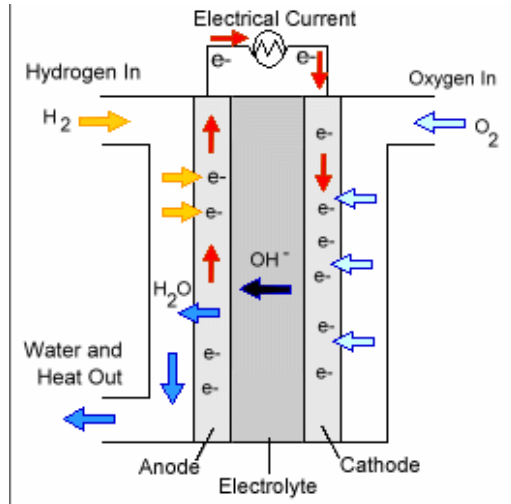
## **Abstract:**

Nowadays, solar and fuel cells have become attractive devices to study, due to their high efficiency to convert and generate clean energy. Another attractive characteristic is the formation of bio-friendly products compared to those products that are formed by the combustion of fossil fuels. Of the two main reactions involved in the fuel cell, the Oxygen Reduction Reaction (ORR) is the limiting component since the electrochemical reaction is irreversible. Therefore, to make this reaction accessible the need of novel yet bio-friendly electro catalysts which is one of the main interests of this research. However, commonly used catalysts for ORR have a high cost, making researchers focus on finding new low-cost catalysts such as non-precious metal oxides. Our research is interested in the ORR activity of Zinc Oxide (ZnO) doped with different materials. ZnO is a transition-metal oxide and n-type semiconductor with a wurtzite crystal structure. It has a high electron mobility, high thermal conductivity, wide and direct band gap, and a high exciting binding energy. This makes it a very good material to study for the application in solar and fuel cells. ZnO can be synthesized by various methods, becoming an interesting material for the construction of an extensive range of devices such as solar cells, biosensors, pH sensors, fuel cells, among others. In this project,  $Zn_xCo_{1-x}O$  nanoparticles were synthesized by a hydrothermal synthesis. We conducted different characterization techniques such as Diffuse Diffraction, X-ray Diffraction (XRD), Photoelectrochemistry, Transmission Electron Microscopy (TEM), Raman Spectroscopy, X-ray Absorption Near Edge Structure (XANES) and Extended X-ray Absorption Fine Structure (EXAFS) on different samples of ZnO doped with Cobalt (Co). In-situ and operando X-ray Absorption Spectroscopy (XAS) experiments were also conducted at the Cornell CHESS facilities. The electronic properties of the band gap and the flat band potential of dried and calcined samples were compared. The effect of the cobalt concentration was studied (concentrations varied from 0.05 thru 0.09 % per weight) during the synthesis. Our group is part of the PREM project: Center for Interfacial Electrochemistry of Energy Materials (CIE<sup>2</sup>M).

## **Introduction:**

A fuel cell is a useful device because it generates electricity by combining hydrogen and oxygen electrochemically without any combustion. There are different types of fuel cells but for our case we are going to be concentrating on the alkaline fuel cell (see Figure 1). This cell works by introducing Oxygen from the cathode which is reduced forming hydroxyl groups, which and

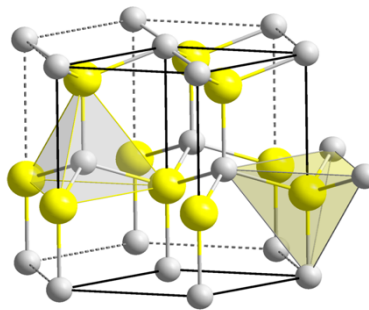
passes through a membrane by diffusion towards the anode. At the anode hydrogen is introduced and oxidized forming protons, which reacts with the hydroxyl groups forming water. There two main reactions in a fuel cell are in the Anode- Hydrogen Oxidation Reaction (HOR) [ $H_2 + 2 OH^- \rightarrow 2H_2O + 2e^-$ ] and in the Cathode- Oxygen Reduction Reaction (ORR) [ $O_2 + 4e^- + 2 H_2O \rightarrow 4 OH^-$ ].



[http://www.esru.strath.ac.uk/EandE/Web\\_sites/00-01/fuel\\_cells/fuel%20cell%20operation.html](http://www.esru.strath.ac.uk/EandE/Web_sites/00-01/fuel_cells/fuel%20cell%20operation.html)

**Figure 1:** Diagram of an Alkaline Fuel Cell

Some commonly used catalysts for the ORR have a high cost since they are mainly noble metals. Often used catalysts for this reaction in alkaline media are Gold (Au), Palladium (Pd, or in many cases (Pd)/Vulcan), and Platinum (Pt). There is an interest however, to find materials that cost less and more environmentally friendly<sup>i</sup>. Among the materials that have taken scientific interest are metal oxides. In this study we are very interested in zinc oxide doped with cobalt ions. Zinc Oxide (ZnO) is a transition-metal oxide with a wurtzite crystal structure that will be studied. ZnO has high electron mobility (around 2,000  $cm^2/Vs$  dependent on particle size and temperature), high thermal conductivity (50  $W/mK$ ), with a wide and direct band gap (3.37 eV) and large exciton binding energy (60 meV)<sup>ii</sup>. That make ZnO suitable for a wide range of devices, for example in the application of fuel cells and solar cells<sup>iii</sup>. In Figure 2, we observe the wurtzite crystal structure of ZnO. The oxygen atoms are represented by the white balls arranged in a hexagonal close-packed lattice and the Zinc atoms are represented by the yellow balls occupying half of the tetrahedral sites.



<https://whatizincioxide.weebly.com/structure.html>

**Figure 2:** Zinc Oxide Crystal Structure. O atoms (white)- Arranged in a hexagonal closed-packed lattice. Zn atoms (yellow)- Occupy half of the tetrahedral sites.

We observe how the Co doping affects the electrocatalytic properties of CoZnO materials doped at different loading concentrations. Observing that the catalysis points towards a two-electron pathway for the production of hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) in the ORR activity. By using X-ray absorption at operando conditions, we can comprehend the changes on valence state of the catalysis. In addition of wanting to produce good working material for the ORR catalytic activity, we seek to make the production of this materials as simple as possible. For this, we chose the hydrothermal synthetic method. This method consists of various techniques of crystallizing substances from high-temperature aqueous solutions at high vapor pressures.

### ***Methodology:***

Zinc oxide materials were prepared by the hydrothermal method. In a common synthesis, we prepared three solutions, one of 0.45 M of  $\text{Zn}(\text{NO}_3)_2$ , another of 0.45 M of  $\text{Zn}(\text{NO}_3)_2$  and  $\text{Co}(\text{NO}_3)_2$  and finally the solution for the precipitating agent 0.75 M of NaOH. The of 0.75 M NaOH solution was maintained at a constant temperature of  $65^\circ\text{C}$ . Then, either of the 0.45 M solutions was titrated to form a precipitate. If we wanted to prepare pure ZnO, we used the first solution. However, for ZnO doped with Co, we used the second solution. At room temperature, the materials were vacuum filtered and washed with 95% Ethanol/Nano-pure Water and transferred to a watch glass. Finally, the samples were calcinated at  $300^\circ\text{C}$  for 3 hours.

For the electrochemistry, a 1.0 M KOH Solution (pH  $\sim 13.0$ ) was used. For the working electrodes we used a glassy carbon electrode, Graphite for the counter electrode and Ag/AgCl for the reference electrode. For the ORR activity, the solution was saturated with  $\text{O}_2$ , the potential window was from 0 V to  $-0.75$  V (vs. RHE), the scan rate was at 50 mV/s and did 10 Cycles. For the Lineal Sweep Voltammetry, the conditions were the same at 1600 RPM. To prepare the working electrode, ZnO doped with Co at 4% per weight was used since it demonstrated the best catalytic current and lowest overpotential among all the samples.

**In situ experiments.** A piece of carbon paper with 200 mm of thickness was cut to a dimension of 1cm x 8cm. The ink was prepared by sonicating 10 mg of the sample in 1 mL of solution, for 15 minutes until homogeneous. To achieve an even layer of the sample, 200 mL of the ink was drop casted in an area of 1cm x 1cm at one end of the carbon paper. This ensure that the sample correctly occupied the window of the electrochemical cell. The carbon paper was placed under a heating lamp for a few minutes until the ink completely dried. The electrochemical cell was then fully assembled with the prepared electrode and filled with a 0.1 M KOH solution. All the air trapped inside the cell must first be removed before proceeding to experiment. Ag/AgCl reference electrode and carbon counter electrode were then inserted to the cell after all air was removed. We utilize the X-ray radiation from the synchrotron that is produced by electronic transitions of electrons in the inner atom's orbitals or by deceleration of high-energy electrons. This will describe the radiation from charged particles travelling at relativistic speeds in curved paths (storage rings) by the application of applied magnetic fields. The In-situ and operando Co K-edge XAS experiments were performed at the PIPOXS beamline at the Cornell High Energy Synchrotron Source (CHESS).

## **Characterization**

Zinc oxide was characterized by different techniques:

Powder X-ray diffraction (XRD) works with a wave interacting against the crystal structure of the sample, complying with the Bragg equation:  $n\lambda=2dsen\theta$ . Where  $n$  is the order of diffraction,  $\lambda$  is the wavelength of the incident beam,  $d$  is the distance between atomic planes and  $\theta$  is the angle of diffraction. It provides information on phase identification of a crystalline material as well an understanding on the type of crystal structure.

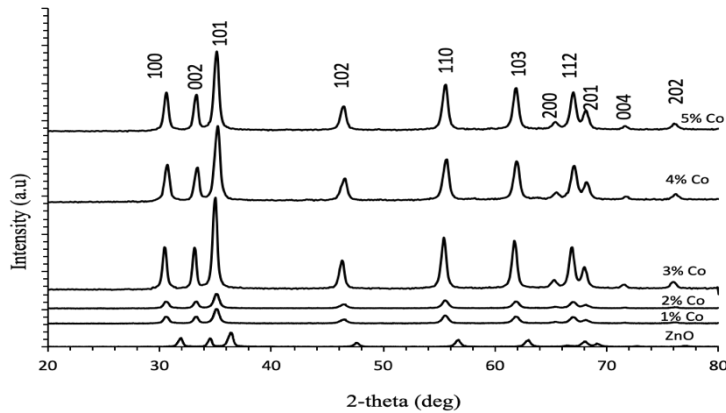
The materials were also characterized by Transmission Electron Microscopy (TEM). TEM imaging helped us characterize furthermore to determine the distribution of the cobalt within the ZnO structure. Raman Spectroscopy will provide us with the changes in vibrational modes of the unit cell so we can analyze where the Co ions are located in the crystal structure.

ORR activity was analyzed using different electrochemical techniques. We used cyclic voltammetry to determine which catalyst is better. Once we determined which catalyst was better, we performed linear sweep voltammetry at 1600 rpm to have an insight on the catalytic mechanism.

For the in-situ experiment, we used the facilities of CHESS to determine the mechanism of the reaction for the ORR. X-ray absorption spectroscopy (XAS) were used for qualitative and quantitative analysis of the catalysts. XAS is a helpful tool to study the electronic and geometric structure of materials through X-ray absorption near-edge structure (XANES) and Extended X-ray absorption fine structure (EXAFS). Analysis of the XANES spectra can provide the oxidation states of the metal centers. Analysis of the EXAFS is useful for studying the local short-range structure around the central absorbing atom and provides the interatomic distances and the coordination numbers for the neighboring atoms. In-situ and operando Co k-edge XAS measurements were performed at the PIPOXS beamline, at the Cornell High Energy Synchrotron Source (CHESS).

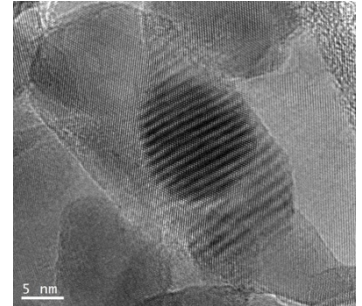
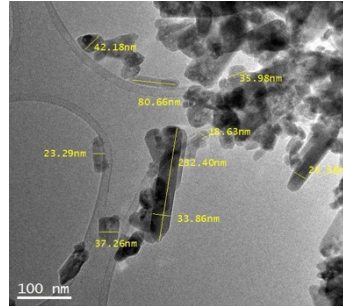
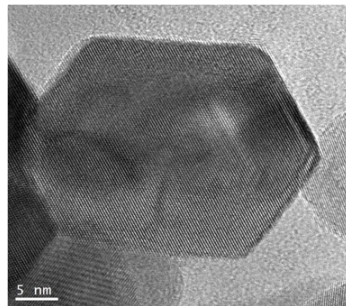
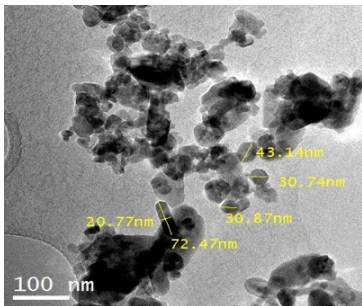
## ***Results and Discussion:***

X-ray powder diffraction (XRPD) confirmed the wurtzite crystal structure of ZnO. However, we observed that the diffraction peaks are shifted to lower angles. This is caused by the presence of the cobalt ions in the samples.



**Figure 3:** XRPD Diffractograms of ZnO doped with cobalt ions at different concentrations.

The TEM imaging confirms the crystal structure showed in the XRD data. TEM demonstrated that the sample of ZnO 95% doped with Co 5% showed particles with a tendency to agglomerate. However, in this sample, sizes smaller than 100 nm are presented, different morphologies are also presented, although in this sample there is a lower tendency to form rods. The EDS analysis confirms the Presence of Zn, O and Co. The sample of ZnO 99% doped with Co 1% showed agglomerated particles with sizes smaller than 250 nm are observed, they are presented different morphologies, with a tendency to form rods. The EDS analysis confirms the presence of Zn, O and Co.

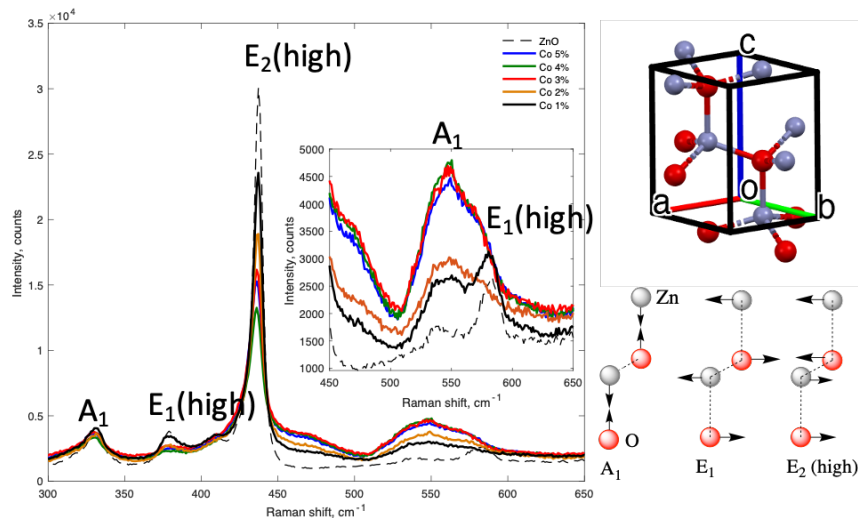


**Figures 4 and 5:** TEM images of ZnO 95% Co 4%

**Figures 6 and 7:** TEM images of ZnO 99% Co 1%

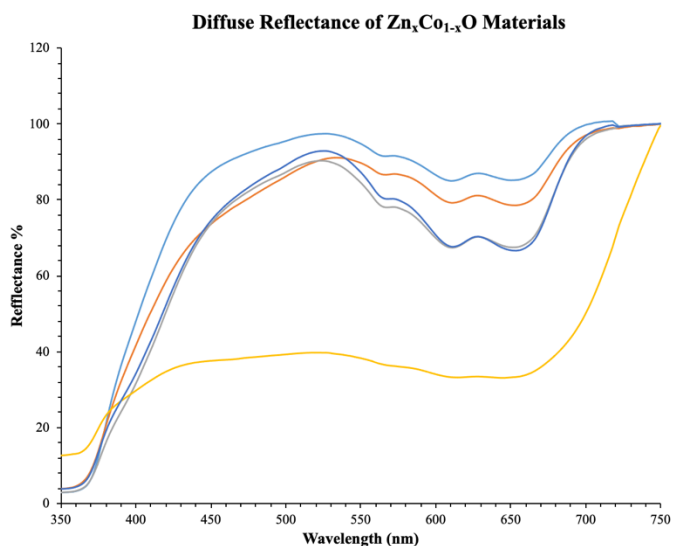
Knowing that Zinc Oxide has a  $C_{6v}$  point group theory ( $\Gamma = 2A_1 + 2B_1 + 2E_1 + 2E_2$ ), its vibrational bands can be detected using Raman spectroscopy. We obtained the irreducible from the vibration that are observed in the Raman spectroscopy. The 3 vibrations of interest are the  $E_1$ ,  $E_2$  and  $A_1$ . By increasing the concentration of Cobalt, we see a decrease in the vibrations of  $E_1$  and  $E_2$ . In the region of  $580\text{cm}^{-1}$ , the peaks change were the  $A_1$  vibrations are. Seeing that almost all of the vibrations are being affected, we can say that the Cobalt ion is located in tetrahedral holes

inside the unit cell. These results were also obtained by Russo, V.; Ghidelli, M.; Gondoni, P.; Casari, C. S.; Li Bassi in their publication<sup>iv</sup>.

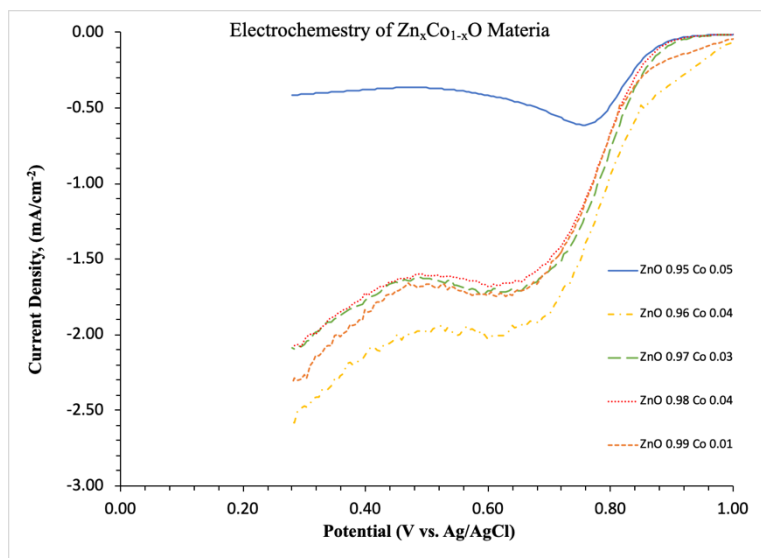


**Figure 8:** Raman spectra of ZnO and  $\text{Co}_x\text{Zn}_{(1-x)}\text{O}$  at different Co doping levels

The materials demonstrated new energy levels as demonstrated in the diffuse reflectance spectra as shown in Figure 9. The experiments will be done for the sample of 4% to determine the ORR activity. We believe that this sample has the maximum cobalt content without the risk of forming cobalt oxide with crystal structures other than wurtzite. In Figure 10, we see that the ORR activity was optimized with the material with a concentration of cobalt at 4% per weight during the synthesis. This is the material that was used in the rest of the study.

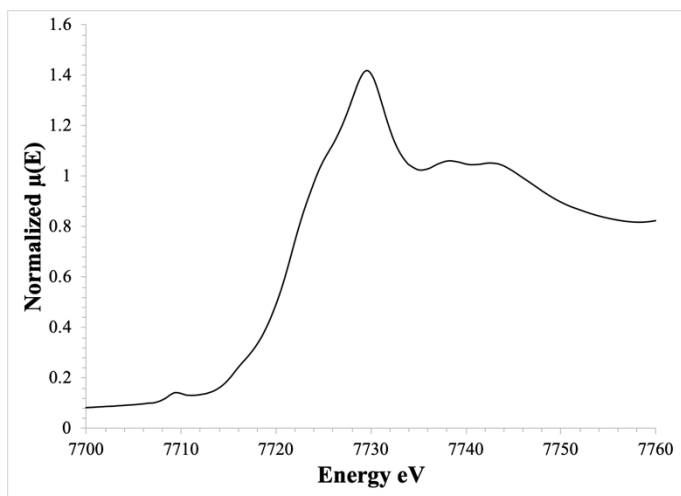


**Figure 9:** Diffuse Reflectance of ZnO doped with cobalt ions at different concentrations.

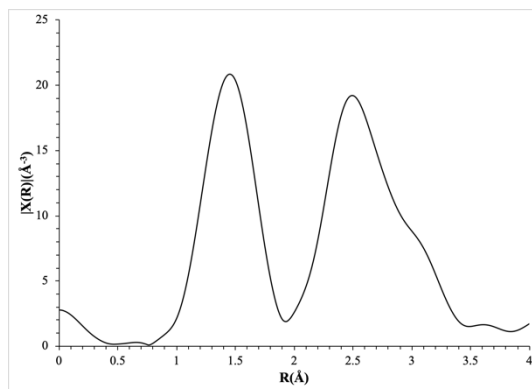
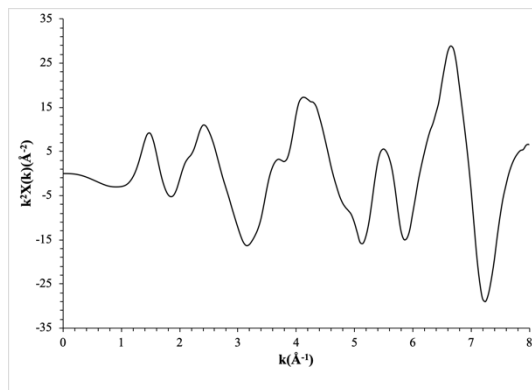


**Figure 10:** ORR Activity of a glassy carbon electrode modified with ZnO doped with cobalt ions at different concentrations in KOH, 1.0 M.

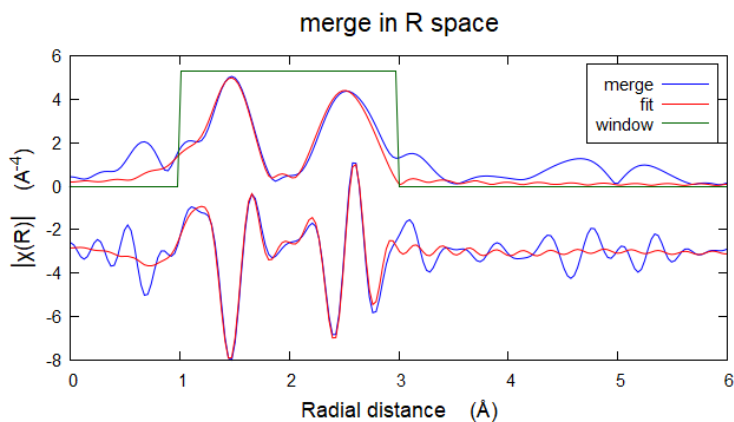
We analyzed the catalysts ex-situ to understand the structure before performing in situ electrochemical reactions. In the Co K-edge XANES spectrum, there is a pre-peak at  $7709.5 \pm 0.1$  eV which gives indication about the Co-O tetrahedral coordination<sup>v</sup>. Observing the Chi and R spectra's we see the peaks that represent the Cobalt-Oxygen and Cobalt-Oxygen-Zinc bonds. In the R spectra, the first peak is the Cobalt-Oxygen bond and the second peak is the Cobalt-Oxygen-Zinc bond.



**Figure 11:** XANES spectrum of CoZnO at the Co K-edge



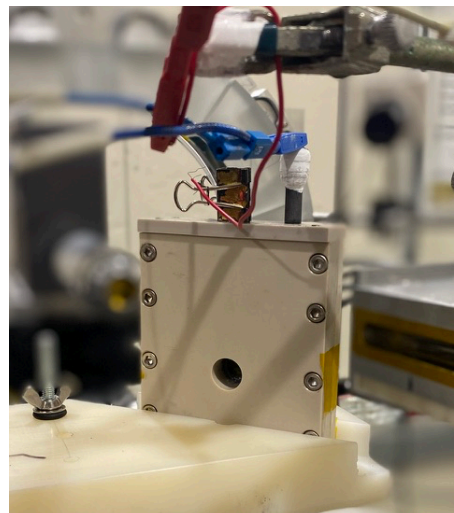
**Figure 12 and 13:** Co-EXAFS chi-spectrum weighted by  $k^2$  and corresponding Fourier Transform for CoZnO at the Co K-Edge



**Figure 14:** EXAFS Fitting Using CoO in a Cubic Structure as Reference for the CoZnO at the Co K-Edge

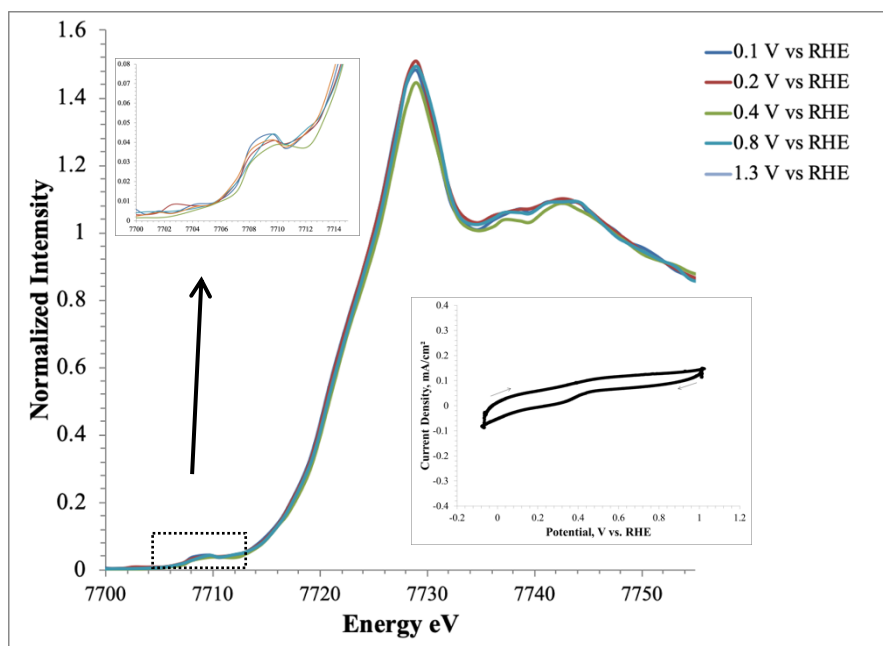
After choosing the best fit in the Artemis software that Demeter package provides, we used to fit the signal using CoO cubic structure, as a reference for the CoZnO materials. As we analyzed the data some of the parameters have negative values. We have the idea that it might be due to the difference of the crystal structure of CoO in comparison with the wurtzite structure of ZnO. This will be analyzed further during the semester.

We monitored the ORR using the CHESS facilities. We modified a carbon paper for an electrode with 4 milligram per centimeter square with our catalyst. The device was a new cell that was created in Dr. Abruña's laboratory. It was mounted and we added a solution of potassium hydroxide 1 molar and we deaerated using nitrogen for 30 minutes, this is to make sure that no Oxygen is present because we want to see that the catalyst is unharmed before the catalysis is occurring. We used as reference Ag/AgCl, with saturated potassium chloride and a graphite rod as a counter electrode. We performed electrochemistry using cyclic voltammogram and we obtained XAS spectra focusing on the XANES data in fluorescence mode. This is because since we formed a thin layer on a carbon paper, the amount of cobalt is very low so to increase the signal and to avoid any interference from the device, we performed the experiments in the fluorescence mode.



**Figure 15:** Prototype fuel cell made in Dr. Abruña's laboratory in Cornell

As a control experiment, we obtained XANES spectra at different potentials is that the in-situ experiments of the ORR in the presence of  $N_2$ . Since no oxygen is present, no catalysis and no redox activity (practically we observe the double layer). It was expected that this would happen so that we could use this as a reference. We do see some differences in the samples, but this could be caused by different causes. One of them, if the cell was aesthetically not sealed correctly a percent of oxygen bubbles could be trapped inside the cell interfering with the incoming signal. To determine any geometrical structural change during this experiment, we analyzed the average in energy of the pre-edge peak of each of the samples with changes in potentials. The average in energy of all the pre-edge peaks is about 7691eV. This demonstrates that there are no real big changes in the pre-peak in the ORR. This result backed up that there was no catalytic reaction under nitrogen environment.



**Figure 16:** In-situ ORR Activity of CoZnO in a  $N_2$  Environment Monitored at the Co K-edge



### **Conclusion:**

In conclusion, the synthesis of ZnO doped with cobalt ions was performed successfully. The XRPD diffractograms showed that the material remains with a wurtzite structure, although the diffraction peaks are shifted towards lower angles due to the presence of the cobalt ions. TEM imaging confirmed the crystallinity of the samples. Raman spectroscopy showed the changes that the Cobalt ions had in the structure of Zinc Oxide confirming that it's located in the tetrahedral hole of the unit cell. The materials demonstrated new energy levels as demonstrated in the diffuse reflectance spectra. XANES spectrum at the Co K-edge indicates the presence for a  $\text{Co}^{2+}$  with tetrahedral geometry and the transition of the 1s electron arising to an empty valence 3d orbital. EXAFS spectrum confirmed the formation of CoZnO materials which is comparable with the ZnO wurtzite crystal structure materials. The formation of mixed phases of CoO were not detectable in the spectrum. These results are important for the determination in the mechanism of the ORR at the electrode surface. The fact that Co is in a tetrahedral hole in the unit cell makes the catalytic properties of the ORR a bit difficult. The in-situ electrochemistry in a  $\text{N}_2$  environment showed no catalysis and no redox activity as expected. We observe ORR catalytic activity in the  $\text{O}_2$  environment. However, the mechanism of the reaction goes into a two-electron step, forming hydrogen peroxide at the electrode surface. Nevertheless, cobalt is also known to be a catalyst for the OER reaction instead of the ORR. Back in Puerto Rico, we are analyzing other candidates such as manganese, iron, etc.

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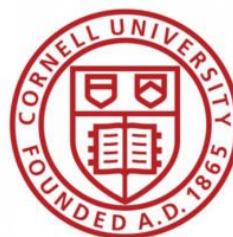


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