

Structure Analysis of Zinc Oxide Doped with Cobalt as Catalyst for the Oxygen Reduction Reaction.

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Abstract

Scientists has gain interested in the production of alternative catalyst to produce clean energy which can be produced by solar cells or fuel cells. Fuel cells are energy conversion systems that involved the oxygen reduction reaction to produce electricity. This reaction is very important for the energy production of these fuel cells and requires a catalyst. Unfortunately, the actual catalyst such as platinum palladium and gold are expensive making the scientist focus in the production of a low-cost alternative catalyst such as non-precious nonmetal oxides. As a result, the main goal of this research is produce a Zinc oxide electrocatalyst doped with Cobalt ions for the Oxygen Reduction Reaction. Zinc Oxide is a semiconductor metal oxide with a wurtzite structure which has gain interest due to his high catalytic capacity, chemical stability and its excellent oxidative capacity. Also the doping or surface modification with transition metals cations and/or their oxides have been considered as a possible way to modify the electronic energy band structure of ZnO resulting in a electrical potential catalyst Our samples were made by a hydrothermal method and were analyzed by X-Ray Photoelectron Diffraction (XRPD), Transmission Electron Microscopy (TEM), Raman Spectroscopy, X- Ray Absorption Near the Structure (XANES) and Extended X-Ray Absorption Fine Structure (EXAFS). To analyze the ORR activity, we use the X-Ray Cornell Synchrotron Facilities where we analyze the Oxygen reduction reaction process in operando with Dr. Abruña's electrochemical cell prototype by Cyclic Voltammetry and XANES analysis to analyze the local atomic structure of our sample.

Introduction

Currently most of the world's energy is produced by burning different types of fossil fuels such as coal, oil, and natural gas. When fossil fuels are burned to produce energy, they emit noscive gasses which get trapped on our atmosphere producing a raise of the planet's overall temperature resulting in the actual global warming that affects human's health. In consequence scientist had been interested in produce energy conversion systems that generates clean energy and also generates eco-friendly by products such as fuel cells. Fuel cells are energy conversion systems that requires the oxygen reduction reaction to produce energy. This reaction can occur in two different ways: by a four-electron reduction pathway resulting in water or by a two-electron reduction pathway resulting in hydrogen peroxide. The alkaline fuel cell which is the one that we use, generates electricity by fueling hydrogen thru the anode and oxygen thru the cathode. Then, oxygen is reduced at the cathode into hydroxyl ions and these hydroxyl ions travels through the electrolyte to the anode where hydrogen is oxidized to form water. To carry out this reaction is important to have a catalyst. As we know and we had saw in the literature there exist different type of good

catalyst with different metals such as platinum, palladium and gold but unfortunately, they are very expensive. Due to the high cost and scarcity of these catalyst the main interest of this research is to produce an eco-friendly and affordable alternative catalyst such non-precious metals oxides due to its high catalytic capacity. As a result, this research is focused in the synthesis of a Zinc Oxide electrocatalyst doped with transition metals for the Oxygen Reaction Reduction.

Zinc Oxide

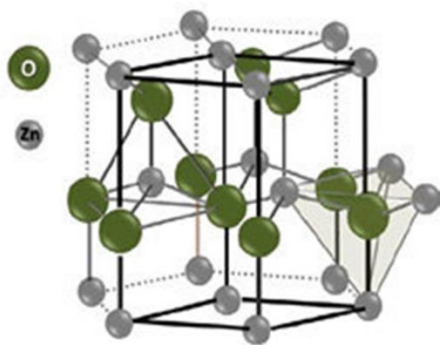


Figure 1. Zinc Oxide Crystal Structure

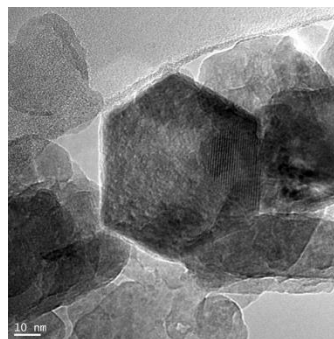


Figure 2. ZnO doped with different amounts of Co ions via XRPD

The Zinc oxide is a transition metal and a semiconductor with a 3.37eV bandgap which has been recognize as a promising catalyst due to its high catalytic capacity. ZnO is a metal oxide with potential technological industrial applications such as solar cells, pH sensors, and biosensing. Zinc oxide provides a wurtzite hexagonal structure that belongs to the space group C_{6v}^4 , which is essentially anisotropic, and these characteristics are reflected in its piezoelectric and pyroelectric properties. Zinc oxide contains four cations at the corners of a tetrahedron which means that the Zn and O atoms are tetrahedrally coordinated by four atoms of the other type. This tetrahedral coordination is characteristic of sp^3 covalent bonding nature. Also, as a fact these materials have a good ionic character which tends to increase the bandgap beyond the one expected from the covalent bonding. The ionicity of ZnO is found at the borderline between the covalent and ionic semiconductor. These characteristics makes ZnO a very good material to study on solar or fuel cells. The doping of Zinc Oxide with transition metals and or their oxides produce a surface modification on the sample modifying the electronic band structure of ZnO resulting in a electrical potential catalyst.

X-Ray Absorption Spectroscopy

For the analysis of our samples we used different techniques including X-ray Absorption Spectroscopy (XAS). XAS is a useful tool to study and deduce the electronic and geometric structures of materials. In this technique the X-ray strikes an atom and excites a core electron that can be promoted to an unoccupied level, or ejected from the atom, creating a core hole producing a photoelectron. The excited electrons are typically from inner shell what means that XAS requires high-energy X-ray excitation, which can be obtained by the synchrotron facilities at CHESS. X-ray absorption spectra of any material it can be atomic or molecular are characterized by sharp

increases in absorption at specific X-ray photon energy. This energy is characteristic of the absorbing element making XAS an element-selective technique. The increases in absorption are called absorption edges and are defined by the energy required to eject a core electron. Edges are named based on the origin of the electron being excited.

- Electrons excited from the $n = 1$ shell are K-edges
- Electrons excited from the $n = 2$ shell are L-edges
- Electrons excited from the $n = 3$ are M-edges

This technique is a non-destructive method which is convenient for the analysis of the samples. X-Ray Absorption Spectroscopy provides a spectrum that is divided in two analysis regions: the X-Ray Absorption Near Edge Structure better known as XANES or Extended X Ray Absorption of Fine Structure better known as EXAFS.

The analysis of the XANES spectra provide us the oxidation states and coordination number of the metal center and is the Spectra region from 0 eV to 50 eV. The XANES in spectra consists in three parts: pre-edge, edge and XANES. The pre- edge is affected by the length of the bond molecules due to the exponentially decay of wavefunctions and covers the transitions from the 1s to 3d states. The edge indicates the ionization energy of core electrons, and **XANES**, which is the main absorption edge study the transitions between 1s-4p states. The higher the oxidation state of the metal, the more positive the overall charge of the atom, and therefore more energy is required to excite an electron from an orbital. On the other hand, EXAFS is the part of the spectra that is characterized by the oscillating part of the spectrum next of the absorption edge starting at 50 eV and extending to 1000 eV above the edge. This technique provides local structural information of the atom in analysis through a mathematical analysis with a function called the EXAFS equation.

$$\chi(k) = \sum_i \frac{(N_i S_0^2) F_i(k)}{k R_i^2} \sin[2kR_i + \delta_i(k)] e^{-2\sigma_i^2 k^2} e^{-\frac{2R_i}{\lambda(k)}}$$

This equation provides a quantitative analysis of the local structural information. The amplitude is represented by $f(k)$ and the phase shift by $\delta(k)$. These two parameters can be calculated for a specific k value (wave vector) and obtain the information of the radius (R), coordination number (N) (number of scattering atoms), and the measure of disorder in neighboring atoms (σ).

In-situ Electrochemistry for ORR of CoZnO

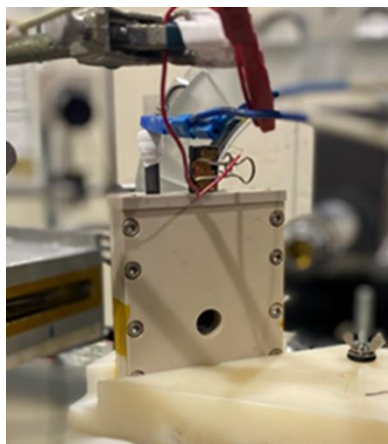


Figure 3. Abruña's Electrochemical Cell Prototype

The in-situ analysis of the Oxygen reduction reaction was made at CHESS facilities. A carbon paper was modified for an electrode with 4 milligram per centimeter square with our catalyst (Cobalt). The electrochemical cell used for carry out the analysis was a new cell prototype that was created in Dr. Abruña's laboratory. A solution of potassium hydroxide 1 M was added and fluxed with nitrogen for 30 minutes and then with Oxygen. This step was made to make see the difference between the intensities at different applied potentials. The reference electrode was Ag|AgCl saturated with KCl and a graphite rod as the counter electrode. The electrochemistry analysis was made using cyclic voltammogram and the obtained XAS spectra was on the XANES fluorescence mode. This is because since we formed a thin layer on a carbon paper, the amount of cobalt is very low to increase the signal and to avoid any interference from the device.

Methodology

In this project, $Zn_xCo_{1-x}O$ nanoparticles were synthesized by Hydrothermal Method. First, three solutions were created: first solution was labeled as pure Zn made with $Zn(NO_3)_2$ 0.45M as Zn precursor, the second solution was made with 0.45 M of $Zn(NO_3)_2$ and $Co(NO_3)_2$ labeled as Co-doped ZnO and the last solution for the precipitating agent made with 0.75 M NaOH. This last solution was heated at a constant temperature of 65 °C. Then, the 0.45 M solutions was titrated to form a precipitate. At room temperature, the material was vacuum filtered and washed with 95% Ethanol/Nano-pure Water and were transferred to a watch glass. and calcinated at 300°C for 3 hours.

General conditions
1.0 M KOH Solution (pH ~13.0)
Glassy Carbon (WE)
Graphite (CE)
Ag/AgCl (RE)

Conditions for Cyclic Voltammetry
Solution was saturated with O_2 or N_2
Potential window: 0 V to -0.75 (V vs. RHE)
Scan Rate: 50 mV/s
10 Cycles

Conditions for Lineal Sweep Voltammetry
Solution was saturated with O_2
Potential window was from 0 V to -0.75 V (vs RHE)
Scan Rate: 50 mV/s
1600 RPM

Results

Characterization process via XRPD Diffractograms, TEM Imaging of ZnO Doped With Co Ions at Different Loading Concentrations

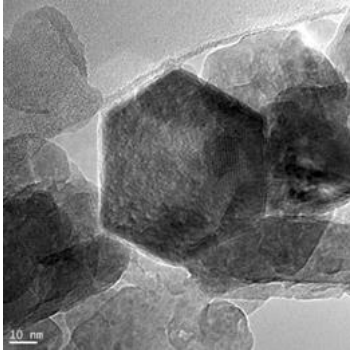


Figure 4. TEM CoZnO 5%

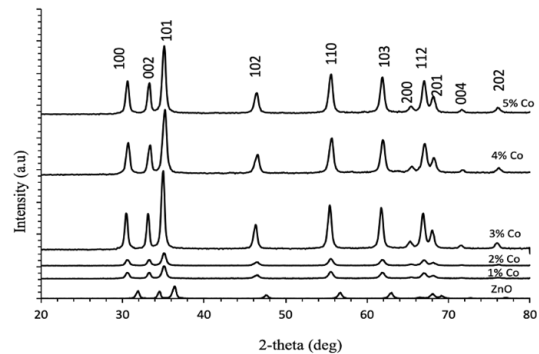


Figure 5. XRPD CoZnO

The TEM analysis showed that the sample provides a high crystalline hexagonal structure confirming the wurtzite structure of the sample. In the XRPD we saw that the Cobalt ions diffraction peaks are shifted lower than the pure ZnO peaks confirming that the Cobalt ions directly affect the cell parameters of the unit cell.

Raman Measurements

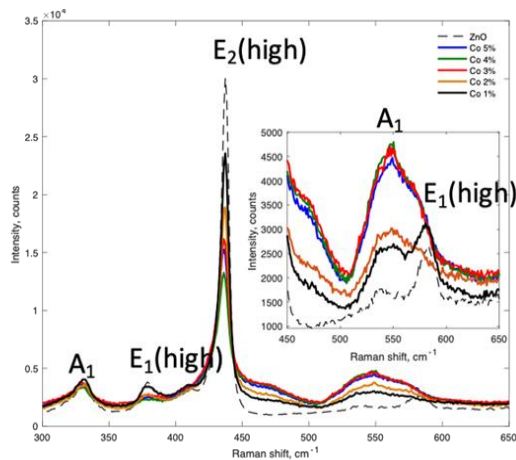


Figure 6. Raman Spectra

In this analysis we saw that the A₁ vibrations increase as the concentration of Co increases, this indicates that Cobalt is occupying the tetrahedral holes and/or the defects of the unit cell. Also, we obtain the irreducible vibrations in the Raman spectra. Considering that zinc oxide contains a C_{6v} group space we focus on E₁, E₂ and A₁ vibrations and by the increasing of Cobalt concentration, we observed a decrease in the vibrations of E₁ and E₂ and a change in the A₁ peaks in the 580 region. As a result, we saw most of the vibrations are being affected, confirming that the Cobalt ion is in tetrahedral holes inside the unit cell.

XANES Spectrum of CoZnO at the Zn K- Edge and Co K- Edge

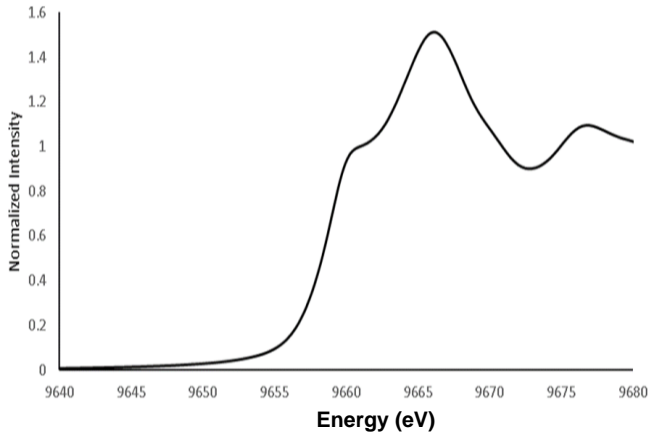


Figure 7. XANES of Zn K-Edge

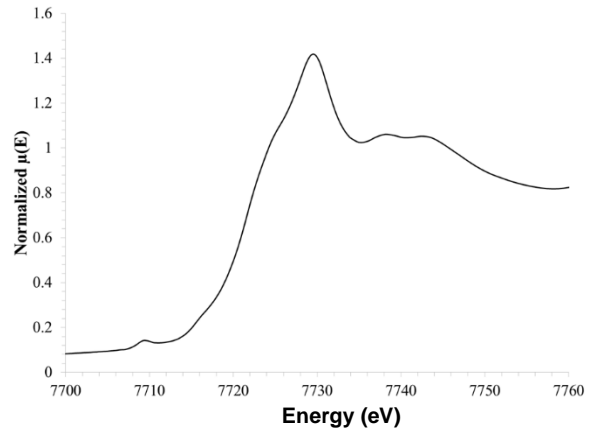
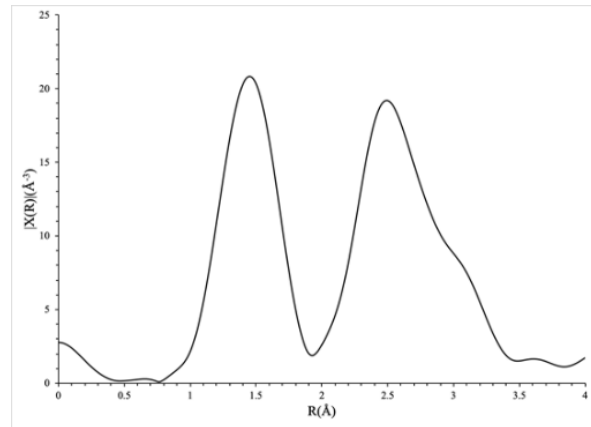
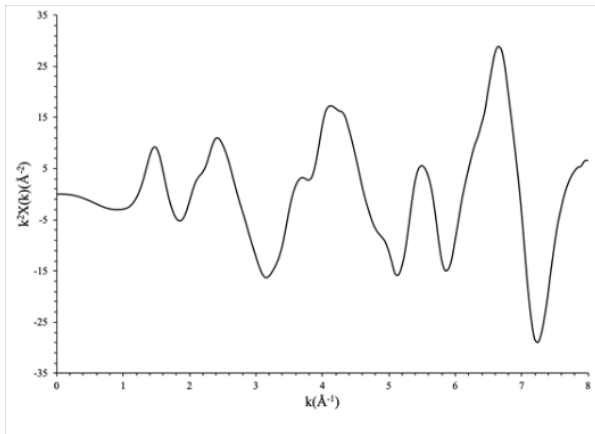


Figure 8. XANES of Co K-Edge

In the Zn K-edge XANES, there is no pre-edge peak, and this is due to the whole filling of the 3d orbital. We can also see a shoulder on 9600.5 ± 0.1 eV which is characteristic of a oxygen vacancy confirming the presence of oxygen in our sample and the rise signal observed on 9666.2 ± 0.1 eV is characteristic of the Zn-O tetrahedral coordination and confirmed the presence of Zn^{2+} . In the Co K-edge XANES spectrum, there is a pre-peak at approximated 7709.5 ± 0.1 eV which is characteristic of the Co-O tetrahedral coordination. By the rise in the signal, the presence of Co^{2+} is confirmed and the pre peak represents the transition of the 1s electron arising to an empty valance 3d orbital.

EXAFS Fitting and Co-EXAFS chi-spectrum weighted by k2 and corresponding Fourier Transform for CoZnO at the Co K-Edge



Name	N	S02	sigma^2	e0	delr	Reff	R
[Co2O2-Cubic] O3.1	14.3	-0.14	0.00539	-3.031	-0.23258	2.1394	1.90682
[Co2O2-Cubic] Co0.1	12	-0.165	0.0071	-0.866	-0.14608	3.0256	2.87952

Figure 9. Co-EXAFS chi-spectrum and corresponding Fourier Transform at the Co K-Edge of the CoZnO sample. Table 1. EXAFS Co K-edge fitting results

For the EXAFS fitting on Artemis we used this as a reference for the CoZnO the CoO cubic structure. On the Table 1 we can see the parameters used for this fit, we can observe some negative values indicating that these parameters still need some improvement. Regarding this, the values obtained on the R factor are very good because they are at values lower than 5. The Chi and R-space spectra show us the peaks that are characteristic of the Cobalt-Oxygen bond and Cobalt-Oxygen-Zinc bonds. The first peak of the R spectra is due to the Cobalt-Oxygen bond and the second peak is produced by the Cobalt-Oxygen-Zinc bond.

In-situ ORR Activity of CoZnO in N₂ and O₂ Environment Monitored at the Co K-edge

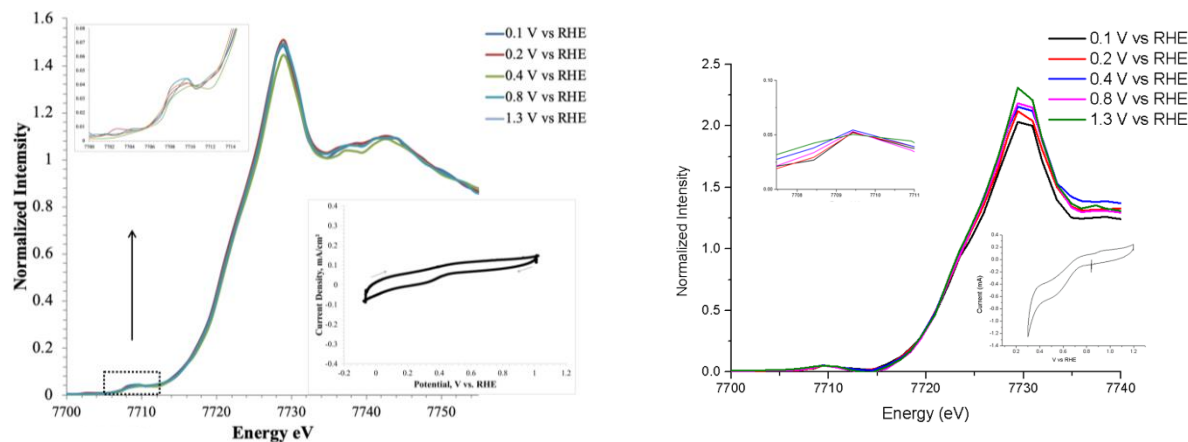


Figure 10. a) XANES Co K-edge of CoZnO saturated with N₂. b) XANES Co K-edge of CoZnO saturated with O₂

For the electrochemical analysis of the Oxygen Reduction Reaction of our catalyst we made a cyclic voltammetry to analyze our samples at different potentials and also, we made XANES to analyze the changes in the intensity these potentials. First, we analyzed the ORR activity in presence of N₂ and from the XANES analysis we can say that there is not catalyst activity but in the cyclic voltammetry we can see a redox activity at 50mV/s. We also can see some differences in the samples and these differences could be attributed to the sealing of the cell which is possible that it was not sealed correctly producing some percent of oxygen bubbles trapped inside the cell causing changes in the signals. From the analysis of the ORR activity in presence of O₂ we can see a reduction in the intensity while the potential is reducing and if we compare it with the cyclic voltammetry we can see a small reduction peak around 0.6 V which means that the Cobalt is feeling a reduction environment but is not enough to get reduced.

Discussion

With the results obtained we were able to conclude the structure of our sample. The XRPD confirmed the ZnO wurtzite structure and showed low Cobalt ions shifts caused by the its presence. With the SEM image we confirmed the results of the structure that were presented by the XRPD. Through Raman spectroscopy we can were able to see the changes that Cobalt ions produce in the structure of Zinc Oxide. With this analysis we confirmed that Cobalt its located in the tetrahedral hole of the unit cell. The XANES analysis at the Co K-edge tells us the oxidation state of our

Cobalt with its t_{2g} and in the pre-edge we saw the transition produced by the 1s electron arising to an empty valence 3d orbital. With the XANES spectra of Zn K-edge we were able to confirm the oxidation state of Zn^{2+} and the rising peak is characteristic of its tetrahedral coordination. The EXAFS let us confirm the presence of the Cobalt-Oxygen bond and the Cobalt-Oxygen-Zinc bond. In the in-situ electrochemistry to analyze the ORR in a N_2 environment we did not see any catalysis but we see a redox activity in the cyclic voltammetry and in the sample saturated with O_2 we saw a decrease in the XANES intensity at the K-edge which could be attributed to the presence of hydroxyl groups at the metal centers.

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