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

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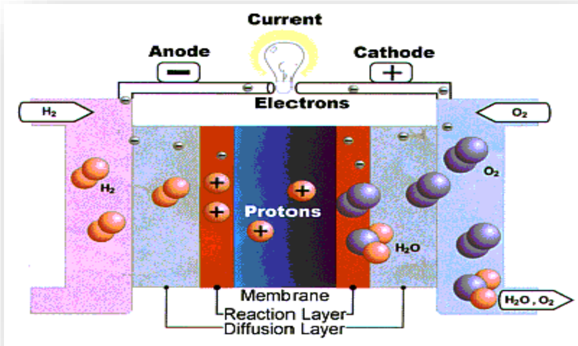
***Abstract:***
Nowadays, solar and fuel cells have become attractive devices to study, due to their high efficiency to convert and generate clean energy. Another attractive characteristic is the formation of bio-friendly products compared to those products that are formed by the combustion of fossil 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 synthesize 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 synthetized by a hydrothermal synthesis. We conducted different characterization techniques such as X-ray Diffraction (XRD), Photoelectrochemistry and Transmission Electron Microscopy (TEM) on different samples of ZnO doped with Cobalt (Co). 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 ($CIE^2M$).

***Introduction:***
A fuel cell operates like a battery. It generates electricity by combining hydrogen and oxygen electrochemically without any combustion, creating water vapor and electric power. There two main reactions:

- Anode- Hydrogen Oxidation Reaction (HOR)
  $H_2 + 2\,OH^- \rightarrow 2H_2O + 2e^-$

- Cathode- Oxygen Reduction Reaction (ORR)
  $O_2 + 4e^- + 2\,H_2O \rightarrow 4\,OH^-$

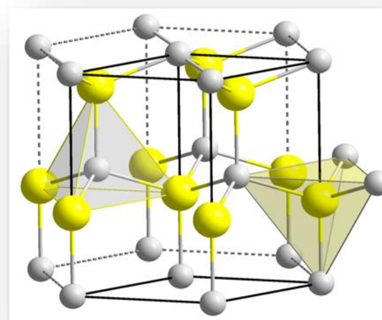



http://www.esru.strath.ac.uk/EandE/Web_sites/00-01/fuel_cells/fuel%20cell%20operation.html

Figure 1: Diagram of a Fuel Cell

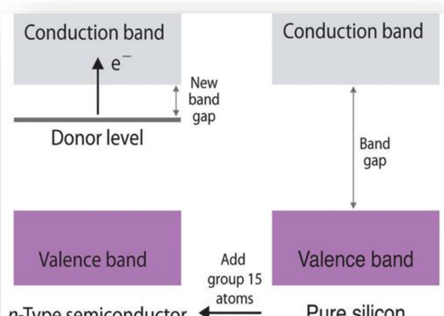
Some commonly used catalysts for ORR have a high cost. Often used catalysts for this reaction in alkaline media are Gold (Au), Palladium (Pd)/Vulcan, and Platinum (Pt). ZnO is a transition-metal oxide with a wurtzite crystal structure that will be studied.

- O atoms (white)- Arranged in a hexagonal closed-packed lattice.
- Zn atoms (yellow)- Occupy half of the tetrahedral sites.



https://whatiszincoxide.weebly.com/structure.html

Figure 2: Zinc Oxide Crystal




N-Type band gap behavior.
http://2012books.lardbucket.org/books/principles-of-general-chemistry-

Figure 3: Energy diagram of n-Type semiconductor

Zinc Oxide (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). That make ZnO suitable for a wide range of devices, for example in the application of fuel cells and solar cells.

Hydrothermal Method is one of the various techniques of crystallizing substances from high-temperature aqueous solutions at high vapor pressures. XRD works with a wave interacting against the crystal structure of the sample, complying with the Bragg equation: ($n\lambda = 2dSen\theta$).

- n= order of diffraction
- $\lambda$= Wavelength
- d= Distance
- q = angle of diffraction

It provides information on phase identification of a crystalline material. TEM will help us characterize furthermore the different catalysts to determine the position of the cobalt within the ZnO structure. For the Photoelectrochemestry studies we analyzed Cyclic Voltammetry and ORR Catalytic Activity of ZnO doped with Co ions at different loading concentrations. A Cyclic Voltammetry consist of a range of potential (E) is applied and current is measured. Once you go from E Initial (Ei) to E Final (E), then it returns from Ef to Ei.

**General conditions were:**

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

**Conditions for Cyclic Voltammetry:**

- Solution was saturated with $O_2$
- Potential window was from 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:***

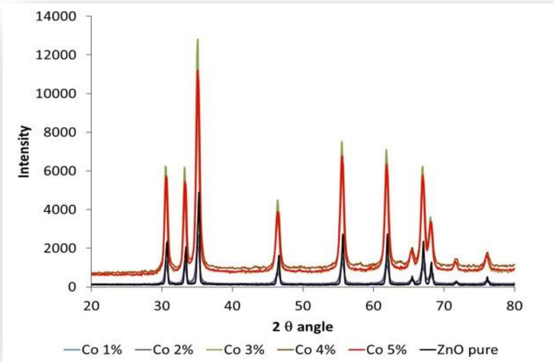



Figure 4: XRPD Diffractograms of ZnO doped with cobalt ions at different concentrations

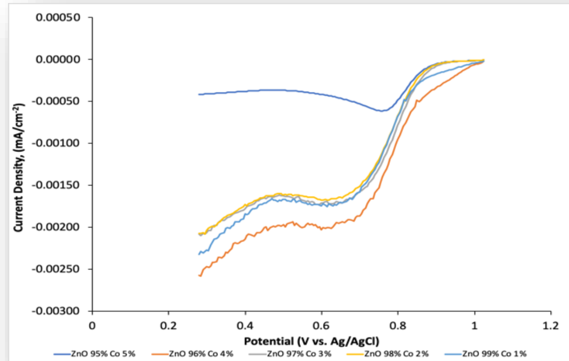
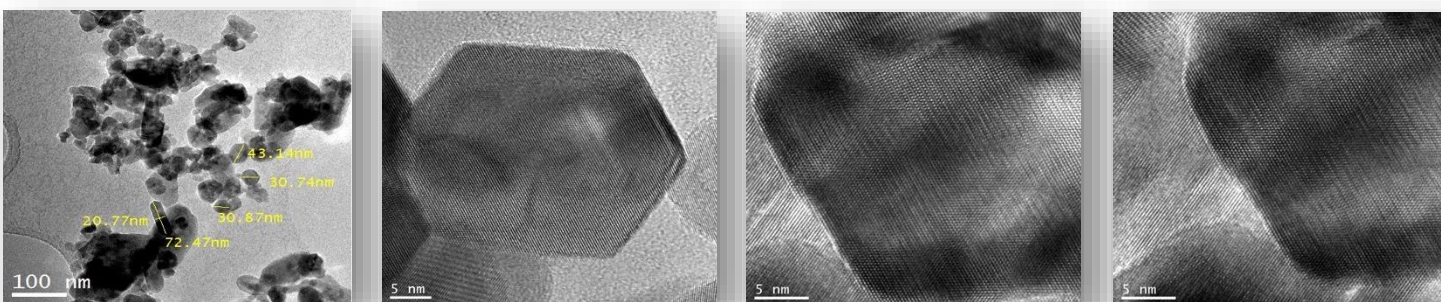
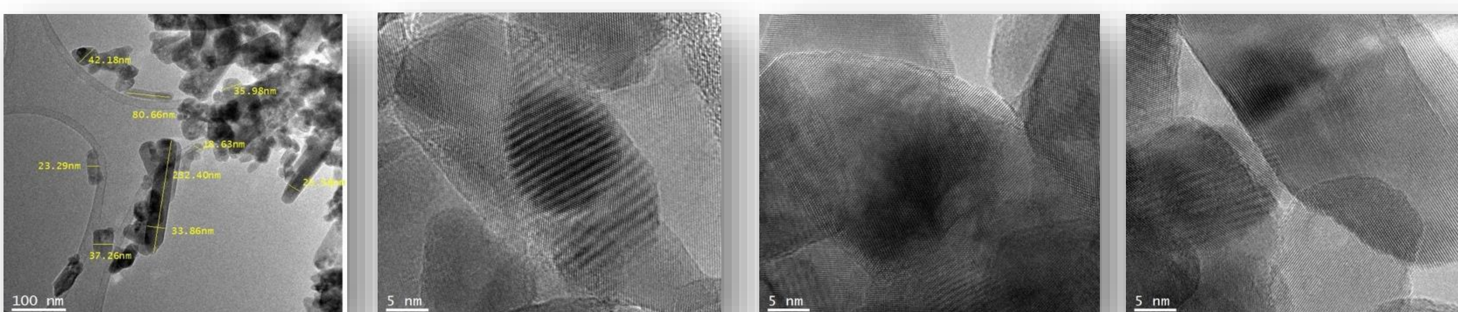



Figure 5: ORR Activity of a glassy carbon electrode modified with ZnO doped with cobalt ions at different concentrations in KOH, 1.0 M.




Figures 6,7,8 and 9: TEM images of ZnO 95% Co 5%




Figures 10, 11, 12 and 13: TEM images of ZnO 99% Co 1%

***Conclusion:***

In conclusion, the synthesis of ZnO doped with cobalt ions was performed successfully. The XRPD diffractor grams 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. We observe ORR catalytic activity. However, the mechanism of the reaction goes into a two-electron step, forming hydrogen peroxide at the electrode surface. We plan in the future to perform ring-disk electrode to confirm this hypothesis. 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. About the Co 4% seems that it has to be a loading effect. The maximum of loading that is actually available in the crystal structure of zinc oxide. 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.

***References:***

Department of Materials Science and Engineering, Tokyo Institute of Technology, 2-12-1 S8-26, Ookayama, Meguro-ku, Tokyo 152-8552, Japan. (September 19, 2016). *Estimation of the Inherent Kinetic Parameters for Oxygen Reduction over a Pt-Free Cathode Catalyst by Resolving the Quasi-Four-Electron Reduction.* Obtained from: https://pubs.acs.org/doi/pdf/10.1021/acs.jpcc.6b07905?rand=k5sjrugq

U.S. Department of Energy. (2015, November). *Fuel Cells.* Retrieved from Fuel Cell Technologies Office: https://www.energy.gov/eere/fuelcells/fuel-cells

Yin Xiong, Yao Yang, Xinran Feng, Francis J. DiSalvo, Héctor D. Abruña; “A Strategy for Increasing the Efficiency of the Oxygen Reduction Reaction in Mn-Doped Cobalt Ferrites”, *J. Am. Chem. Soc.* (2019)

Viyajaprasath , G., Ravi, G., Haja, H., & Mahalingam, T. (7 de April de 2014). *Effect of Cobalt Doping on Structural, Optical, and Magnetic Properties ZnO Nanoparticles Synthesized by Coprecipitation Method.* Obtained from: The Journal of Physical Chemistry: https://pubs.acs.org/doi/abs/10.1021/jp411848t

Xiaoming, G., Afriyanti , S., Delvin, W., Tao, A., Bing , L., Thomas Gob, F. W., . . . Zhaolin, L. (2015, June 29). *Oxygen Reduction Reaction in Alkaline Media: From Mechanisms to Recent Advances of Catalysts.* Retrieved from ASC Catalysis: https://pubs.acs.org/doi/abs/10.1021/acscatal.5b00524

Rong, F.; Zhao, J.; Su, P.; Yao, Y.; Li, M.; Yang, Q.; Li, C., Zinc-cobalt oxides as efficient water oxidation catalysts: the promotion effect of ZnO. *Journal of Materials Chemistry A* **2015,** *3* (7), 4010-4017.

Zhiani, M.; Gasteiger, H. A.; Piana, M.; Catanorchi, S., Comparative study between platinum supported on carbon and non-noble metal cathode catalyst in alkaline direct ethanol fuel cell (ADEFC). *International Journal of Hydrogen Energy* **2011,** *36* (8), 5110-5116.

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