Characterizing Cobalt-Doped Zinc Oxide Catalysts for Fuel Cells Applications

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Abstract

In present day, fuel cells are becoming attractive devices to study for energy harvesting applications due to their high efficiency to convert energy and generate clean by products compared to the combustion of fossil fuels. Of the two main reactions involve in the electrochemistry of a fuel cell, the Oxygen Reduction Reaction (ORR) is the limiting component for being highly irreversible, making necessary the use of electrocatalysts to undergo the reaction. However, commonly used catalysts for ORR have a high cost, making researchers focus on finding new low-cost catalysts such as metal oxides and N-doped carbon. Zinc Oxide (ZnO) transition-metal oxide with wurtzite lattice and a n-type semiconductor with a wide band gap that can be easily synthesized by a broad variety of methods, becoming an interesting material for the construction of an extensive range of devices such as solar cells, biosensors, pH sensors, among others. In this project, ZnO and Co-doped nanoparticles were created by hydrothermal synthesis and characterized using Raman Spectroscopy along with STEM to observe the position of cobalt in ZnO crystal structure. Also, an electrochemical analysis on Pure and Co-doped nanoparticles was performed to observe the catalytic activity of the nanoparticles to undergo ORR.

Introduction

A fuel cell is an electrochemical cell in which several compounds, such as H_2 and O_2, is used as source material to directly convert chemical energy into electricity. They consist essentially of an electrolyte sandwiched between two electrodes called the anode and the cathode, respectively.

There are different types of fuel cells, mainly classified depending conditions used to carry out the electrochemical reaction, whose common half reactions are:

Anode – Hydrogen Oxidation Reaction

$$H_2 + 2\,OH^- \rightarrow 2H_2O + 2e^-$$

Cathode – Oxygen Reduction Reaction

$$O_2 + 4e^- + 2\,H_2O \rightarrow 4\,OH^-$$

Where the Oxygen Reduction Reaction (ORR) is the kinetically limiting component due to its high irreversibility, making the use of electrocatalysts imperative to undergo as close the reversible reaction as possible.

Recent studies show great interests in alkaline fuel cells to undergo ORR for: (1) showing being favorable for the absorption of anions, (2) exposing the catalysts to less a corrosive environment and (3) involving faster kinetics.

Common catalysts used for ORR in alkaline media (Pd, Pt/Vulcan, and Au) on the are expensive, making latest researchers focus on finding low cost catalysts such as: (1) Non-Precious Metal Oxides and (2) Nitrogen Doped Carbon.

Zinc Oxide (ZnO) transition-metal oxide with wurtzite structure and a n-type semiconductor with a wide band gap of ~3.37 eV that can be easily synthesized by a broad variety of low cost methods, which makes it an attractive material for the construction of a extensive range of devices.

Recent research shows that cobalt doping of ZnO can have an effect in the electrical, optical and magnetic properties as well as its catalytic activities on oxygen electrochemistry.

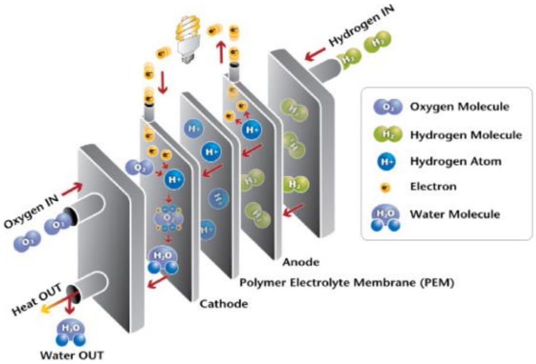


Figure a. Diagram of a Fuel Cell

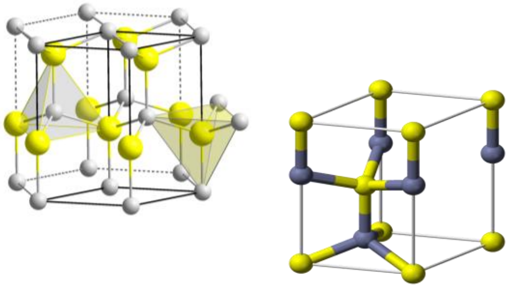


Figure b. ZnO wurtzite structure, where the yellow spheres correspond Zn atoms and the others to O atoms.

Synthesis

Solutions

For Pure ZnO:

0.45M $Zn(NO_3)_2$ Soln.

For $Zn_xCo_{1-x}O$:

X = 0.999, 0.995, 0.99, 0.98, 0.97, 0.96, 0.95

0.45M of $Zn(NO_3)_2$ and $Co(NO_3)_2$ Soln.

0.90 M NaOH Soln.

Hydrothermal Synthesis

0.9 M NaOH solution was heated at a constant temperature of 55°C.

Then, either of the 0.45 M solutions was titrated to form a precipitate:

Pure ZnO – White

Co-Doped ZnO – Green

Filtration

At room temperature, the material was vacuum filtered and washed with 95% Ethanol/Nano-pure Water.

Then, the material was transferred to a watch glass.

Desiccator

For 3 days

Annealing

At 1000°C for 3 hours

Nanoparticles Characterization

Raman Spectroscopy

Observe the effect Cobalt has on ZnO Lattice

TEM

Locate Cobalt Atoms in ZnO Crystal Structure

Electrochemical Studies

Analyze Cyclic Voltammetry and ORR Catalytic Activity of Co-Doped Samples Compared to ZnO.

General Conditions:

- 0.20 M KOH Solution (pH ~ 13.3)
- Glassy Carbon (WE)
- Graphite (CE)
- Ag/AgCl (RE)

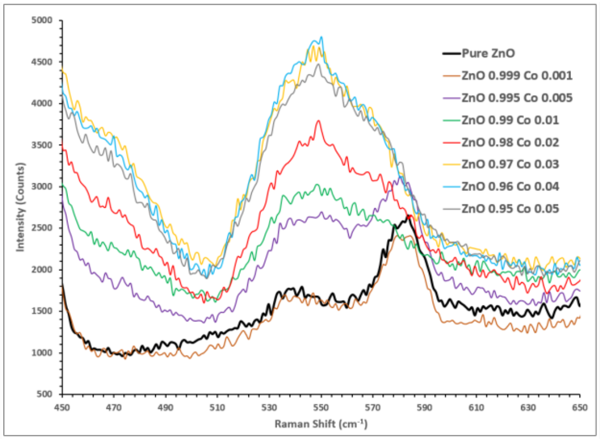
For CV

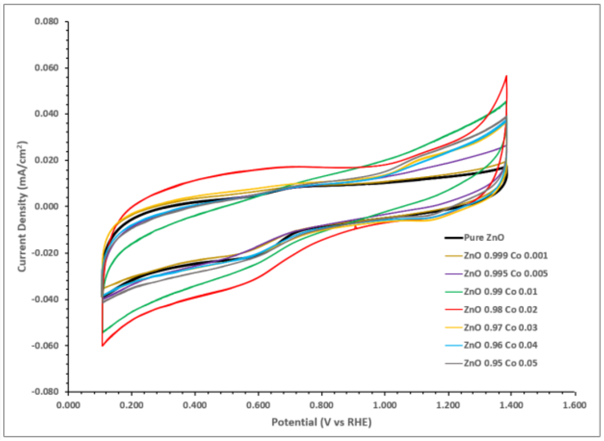
- Solution was saturated with Ar
- Potential window was from 0.10 V to 1.39 V (vs. RHE)
- Scan Rate: 20 mV/s
- 25 Cycles

For ORR

- Solution was saturated with Ar
- Potential window was from 0.10 V to 0.88 (vs RHE)
- Scan Rate: 5 mV/s
- 10 Cycles

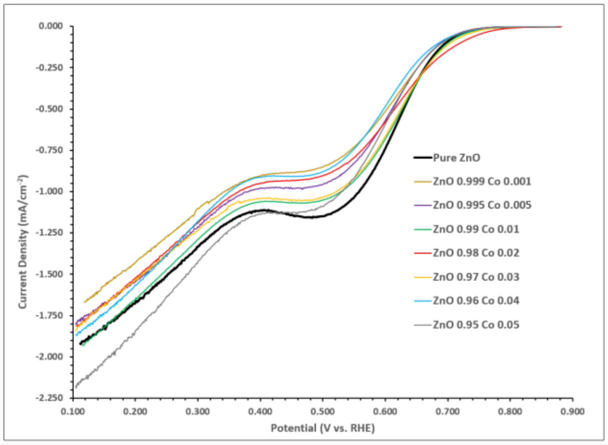
Results

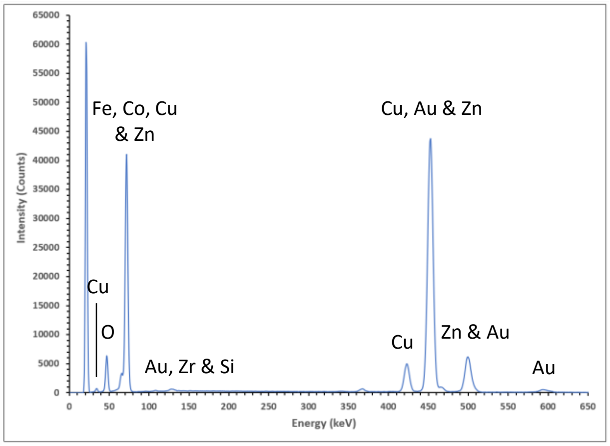




Figures 1. Raman Spectra of Pure and Co-doped ZnO where a shift to lower wavenumbers and band broadening of the 580 cm^{-1} peak is observed.

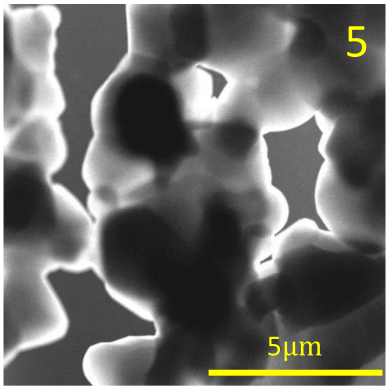
Figures 2. Cyclic Voltammogram of Pure and Co-doped ZnO done at 20 mV/s in 0.2M KOH under Ar atmosphere.

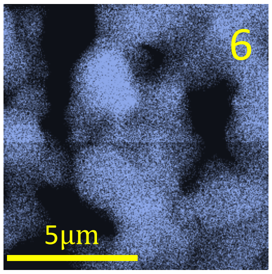


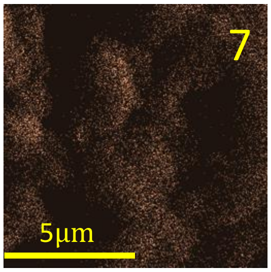


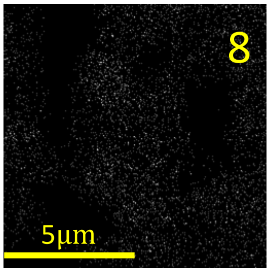
Figures 3. Polarization Curves of Pure and Co-doped ZnO done at 5 mV/s and 1600 RPM in 0.2M KOH under O_2 atmosphere.

Figure 4. Energy Dispersive Spectroscopy (EDS) analysis, confirming the presence of Zn, O, and Co in conjunction with some impurities of known source.









Figures 4-7. High-Angle Annular Dark Field Image Co-doped ZnO nanoparticles clustered along with the X-Ray Mapping of Zn, O, and Co atoms, respectively.

Conclusions

A. **Raman Spectra**

The Raman shift in 580 cm-1 to lower wavenumbers suggests the vibrational modes of cobalt become more prominent when its concentration is increased, meaning the atoms may be bound to the donor defects of the ZnO lattice.

B. **TEM**

We were unable observe zinc oxide's wurtzite nanocrystals for them being too clustered, which prevented us from locating through X-Rays the cobalt atoms on ZnO lattice as suggested by the Raman Spectra.

C. **Cyclic Voltammetry**

The cobalt doped samples, compared to pure ZnO, show a high double layer current.

D. **ORR**

The cobalt doped samples do not show a significant catalytic activity compared to ZnO nor other common catalysts commonly used for ORR.

Future Work

A. Attempt to observe $Zn_xCo_{1-x}O$ nanoparticles again after successfully braking the clusters.

B. Latest research studies show that Co_3O_4 is a good catalyst for Oxygen Evolution Reaction, which suggest testing both pure ZnO and Co-doped samples for OER activity.

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