

Title: Electrochemical studies for oxygen reduction reaction using $Zn_{1-x}Co_xO$ for fuel cell applications.

Authors:

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Abstract

Oxygen reduction reaction has several applications such as fuel cells and batteries. This reaction has two mainly pathways to occur: 4 electron reduction to form water or 2 electron reduction to form hydrogen peroxide (H_2O_2). The oxygen reduction reaction occurs in the cathode of fuel cells. Our study is based on zinc oxide doped material to catalyze the oxygen reduction reaction for fuel cell applications. Zinc oxide is a semiconductor with a wide band gap of around 3.45 eV. Areas from solar energy harvesting, biosensors among others, have been using Zinc Oxide due to its electronic properties. The purpose of this project is to study the effect and behavior of doping Zinc Oxide nanoparticles with cobalt ions at different concentrations $Zn_{1-x}Co_xO$ ($x=0.01,0.02,0.03,0.04,0.05$) with an eye on fuel cell applications. We performed electrochemical studies in alkaline media (KOH 0.2 M) for the detection of the oxygen reduction reaction. Two electrochemical characterization were performed. The first electrochemical characterization was Cyclic Voltammetry at a scan rate of 20 mV/s using Argon has our air source to determine catalytic activity on the surface of our glassy carbon electrode. In the second electrochemical characterization, the technique used was rotating disk electrode (RDE) to observe and evaluate the oxygen reduction reaction (ORR) at a scan rate of 5 mV/s. In the future, we will perform X-ray experiments at CHESS to observe and detect chemicals species in operando conditions. This study is in strong with Dr. Cabrera's research group with the purpose of constructing a fuel cell using $Zn_{1-x}Co_xO$ for the cathode.

Introduction

Fuel cell systems produces energy without pollution, the products released are heat and water [1]. These dispositive acts like batteries with the huge difference that they do not need to be charged after using. They are composed of three principal parts; the anode in which the electrons are oxidize, the cathode where the electrons are reduce and the electrolytic membrane which is the part where the ions pass from the anode to the cathode (acts as a diffusive membrane) [1]. In fuel cells the oxygen reduction reaction (ORR) occurs in the cathode [2]. Usually the kinetics of the ORR is slow, however, it can be speed up by achieving catalyst in the cathode [3]. This reaction is possible to occur through one of two pathways. This reaction is possible to occur through one of two pathways. The first and ideal is the four-electron transfer in which oxygen (O_2) forms water (H_2O) [3]. The second is the two-electron transfer [$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$] where oxygen forms hydrogen peroxide (H_2O_2). To study the ORR catalyst one of the technique used is rotating disk electrode (RDE). In this technique, the diffusion factor is being remove by convection, which means that during the experiment a constant flow of

the electrolyte will be in contact with the surface of the working electrode. Platinum (Pt) materials have been used commonly as catalyst [3]. Due to its high cost scientist have been developing other alternatives such as transition metals. These elements possess numerous properties such as structural, optical and magnetics as makes them useful for fuel cell applications. Some transition doped metals have are being studied due to potential UV detector and fuel cell application just to mention a few, one of them is Zinc Oxide. Zinc oxide (ZnO) is n-type semiconductor with wurtzite structure and a wide band gap semiconductor around 3.45 eV. The effect of doping ZnO nanoparticles with a transition metal such as cobalt (Co) generate a ferromagnetic behavior caused by intrinsic defects [4]. Doping ZnO nanoparticles with Co^{2+} increase the magnetization because Co^{2+} the 3d shell possess five spins which gives a high dipole moment. In our study, we will evaluate the oxygen reduction reaction through RDE electrochemical technique in alkaline media potassium hydroxide (KOH) 0.2 M.

Methods

The working electrode is a glassy carbon electrode in which 22.5 μL of a solution of nafion and $\text{Zn}_{1-x}\text{Co}_x\text{O}$ was deposited carefully on the surface. After the modification, the electrode was let dry for 20 minutes using a heat lamp to speed up the process. For the electrochemical analysis, the KOH 0.2 M solution was bubbled with Argon for 20 minutes to remove all the oxygen in the solution, then the experiment was carries out at 20 mV/s with a potential. After the first electrochemical analysis, we bubbled the same solution with oxygen to evaluate the catalytic activity and the oxygen reduction reaction.

Results

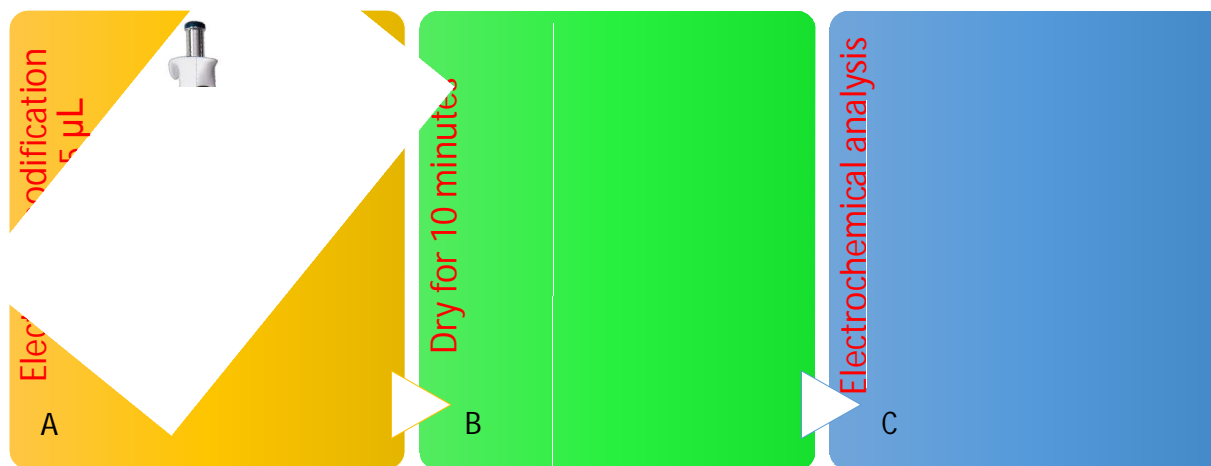


Figure 1: A) The glassy carbon electrode was modified with 22.5 μL of the catalyst. This procedure was repeated with each sample. B) Following the modification process the electrode was let dry for 10 minutes using a heat lamp to speed the process. C) For the electrochemical analysis, the KOH 0.2 M solution was bubbled with Argon for 20 minutes and then the experiment was carried out at 20 mV/s with a potential rate of -0.8844 V to 0.4 V. Then we bubbled the same solution with oxygen for 20 minutes to evaluate the ORR at 5 mV/s with a potential rate of -0.8844 V to -0.1 V.

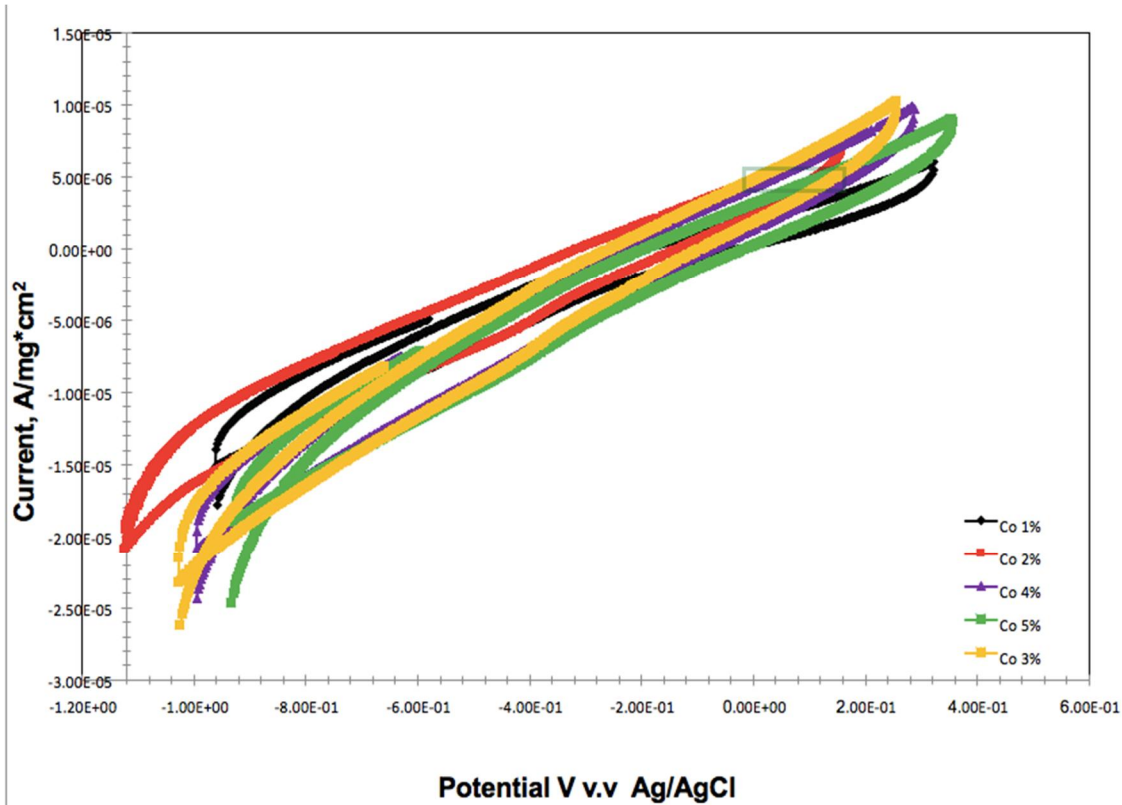


Figure 2: Cyclic voltammetry data of each $Zn_{1-x}Co_xO$ ($x=0.01,0.02,0.03,0.04,0.04,0.05$) under argon. Scan rate = 20 mV/s and 1600 rpm.

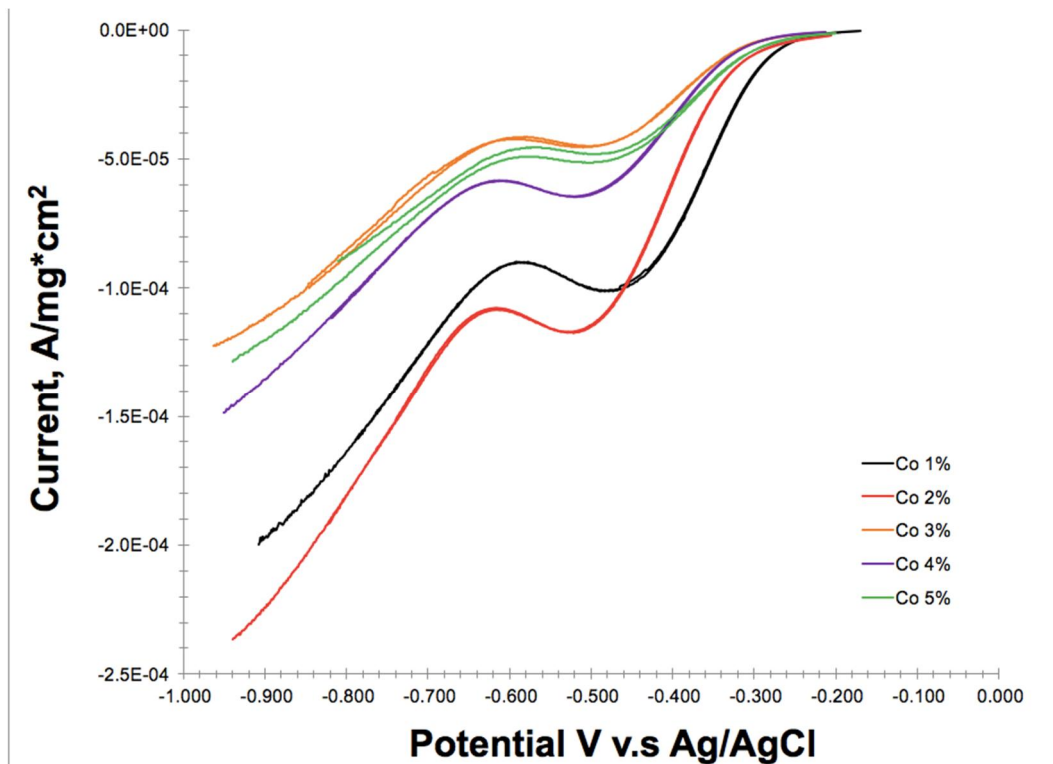


Figure 3: ORR data of each $Zn_{1-x}Co_xO$ ($x=0.01,0.02,0.03,0.04,0.05$) at a scan rate of 5 mV/s and 1600 rpm.

Discussion

Figure 2 and 3 shows the characteristics cyclic voltammograms of a gold electrode modified

with $Zn_{1-x}Co_xO$. In Figure 2 the cyclic voltammograms were performed under argon. As can be observed, only capacitive current is observed along with some electrode electrical resistance. This electrical resistance can be a result of a low concentration of electrolyte in the solution. However, no faradaic process is observed. Figure 3 shows the same cyclic voltammogram but under oxygen. Faradaic processes are observed showing the reduction of oxygen at the electrode surface. This result shows that our materials are capable to catalyze the oxygen reduction at the electrode surface. Among these materials, seems that when Cobalt ions are at a concentration of 1%, shows a better catalytic behavior since can perform the electrochemical reaction at a lower overpotential.

Conclusion

The main goal of this study was achieved because was possible determine which ZnO doped Co sample has better catalytic activity. However, the testing process is not over yet, the next step is to perform X-ray experiments using the Cornell High Energy Synchrotron (CHESS) in the near future. The purpose is to know which species are formed while the ORR is occurring. Knowing the species formed during the ORR will give us a clear view to determine if in fact is possible to create a fuel cell using $Zn_{1-x}Co_xO$ for the cathode.

References

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