

Title: Electrochemical Studies of Nanostructured Catalyst Materials for Oxygen Reduction Reactions

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Abstract

The purpose of this experiment was to test the effectiveness of different gold nanoparticles prepared by a chemical reductive process and by the Rotating Disk Slurry Electrodeposition (RoDSE) Technique for use in the oxygen reduction reaction (ORR). Cyclic voltammetry was done at a scan rate of 5 mV/s to observe the reduction and oxidation behavior of oxygen interacting with different samples of gold nanoparticle/Vulcan carbon, which may be employed at the cathode of the fuel cell. Tested in an alkaline media, the results showed that a negative potential of about 150 millivolts (versus the reference electrode) for the oxygen reduction, with similar results for each sample, with the exception of the Au/C catalyst prepared by RoDSE in KOH solution. This sample, required a more negative potential, at about -35 millivolts, which can be attributed to either synthesis contamination or improper modification of the electrode. It is a future objective to test these gold nanoparticles for possible use in ethanol oxidation alkaline fuel cells, as well as perform X-ray absorption spectroscopy at the CHESS facilities to better characterize the samples, under *operando* conditions. This experiment is part of a collaboration with Dr. Santiago's Research Group in order to achieve the construction a fuel cell using $Zn_{1-x}Co_xO$ as the anode and Au/C at the cathode electrode.

Introduction

Alkaline fuel cells have been an extraordinary breakthrough. These first appeared in the early 1960s, when NASA used hydrogen fuel cells for the Apollo mission. Amongst these fuel cells, oxygen reduction cells have shown particular promise. In proton exchange membranes or PEMs, the OR reactions occur at the cathode, converting either O_2 to H_2O in a 4-electron reduction process or O_2 to hydrogen peroxide (H_2O_2) in a 2-electron process.^[1] For this process, the noble metal Platinum (Pt) is used as a catalyst, due to its high activity and efficiency. Their high cost, however, requires the exploration of other more affordable metals to test their efficiency and develop more commercially attainable fuel cells.

In this research project, Cabrera's group focused preliminarily on the use of gold nanoparticles as a catalyst for ORR in alkaline fuel cells. The purpose of these catalysts is to employ them in the creation of these PEM electrodes at the cathode of the electrode, and later move on to ethanol-based alkaline fuel cells, producing energy via ethanol oxidation reactions at the anode of the electrode. A glassy carbon electrode was modified with several gold nanoparticles/Vulcan carbon (Au/C) catalysts prepared by the Rotating Disk Slurry Electrode (RoDSE) method. These Au particles are deposited on the carbon powder support, known as Vulcan Black, in order to reduce cost and provide a support that has a high conductivity, surface area, and porosity.^[2] Four different catalysts samples were used, three of which were prepared by Cabrera's Group, and one which is a commercial 20% Au/C powder sample; functioning as the control experiment. Of the three samples, two of them were prepared by using Rotating Disc Slurry Electrode (RoDSE) technique, using sodium hydroxide (NaOH) and potassium hydroxide

(KOH). The RoDSE technique is used as a method to electrochemically prepare bulk Au/carbon nanocatalyst material, using a slurry solution that is saturated with functionalized Vulcan, adding a gold precursor to the slurry solution and taking an electrochemical route to prepare the catalyst sample.^[3] The third sample was prepared by reducing Au^{3+} to Au^0 using sodium borohydride (NaBH_4). Cyclic voltammetry was performed on these catalyst samples in order to observe the oxidation and reaction processes that are occurring, allowing us to rapidly observe the redox behavior of the substance over a wide potential range, applying a controlled potential and measuring the current produced as a function of time.^[4]

Setup

The Au catalysts were tested by preparing an electrochemical cell, using a glassy carbon electrode (GCE), 3.0 mm in diameter, as a working electrode, a Silver/Silver Chloride (Ag/AgCl ; $[\text{Cl}^-] = 3.0\text{M}$) Electrode as reference, and a platinum rod as the counter electrode (see **Figure 1**). The cell was filled with an alkaline media, a 0.2M potassium hydroxide solution. For each test, the GCE was modified with a dropcast of 8 microliters (μL) of Au/Vulcan catalyst polymer solution, which was prepared by dissolving 1mg of Au/Vulcan powder in 450 mL of Nafion 0.05M in ethanol. The dissolution of the powder in this anionic fluoropolymer is useful to keep anionic interference away from the electrode surface during voltammetric measurements by making cations the only mobile species near the surface.^[5] Before each run, the cell was sealed and bubbled with nitrogen gas (N_2) to remove any leftover oxygen in the cell. Cyclic voltammetry was performed in a potential range of about -600 millivolts (mV) to 800 mV, at a scan rate of 5 mV per second. The GCE modified with commercial 20% Au/C catalyst was used as a control, as well as the unmodified GCE and a Au Disk electrode for comparison. The Au/C samples were prepared at UPR by chemical reduction with NaBH_4 and by the Rotating Disk Electrode Slurry Deposition (RoDSE) in NaOH , and KOH solution. Each cyclic voltammetry sweep was done with a new 0.2M KOH solution that had been sealed and bubbled with nitrogen for 15 minutes. Finally, a Glassy Carbon Rotating Disk Electrode was modified with an ink sample of the commercial Gold/Carbon powder, in order to do a linear potential sweep while eliminating the diffusion component of the current. The sample was tested at 100-intervals from 1600 to 2000 rotations-per-minute (rpm).

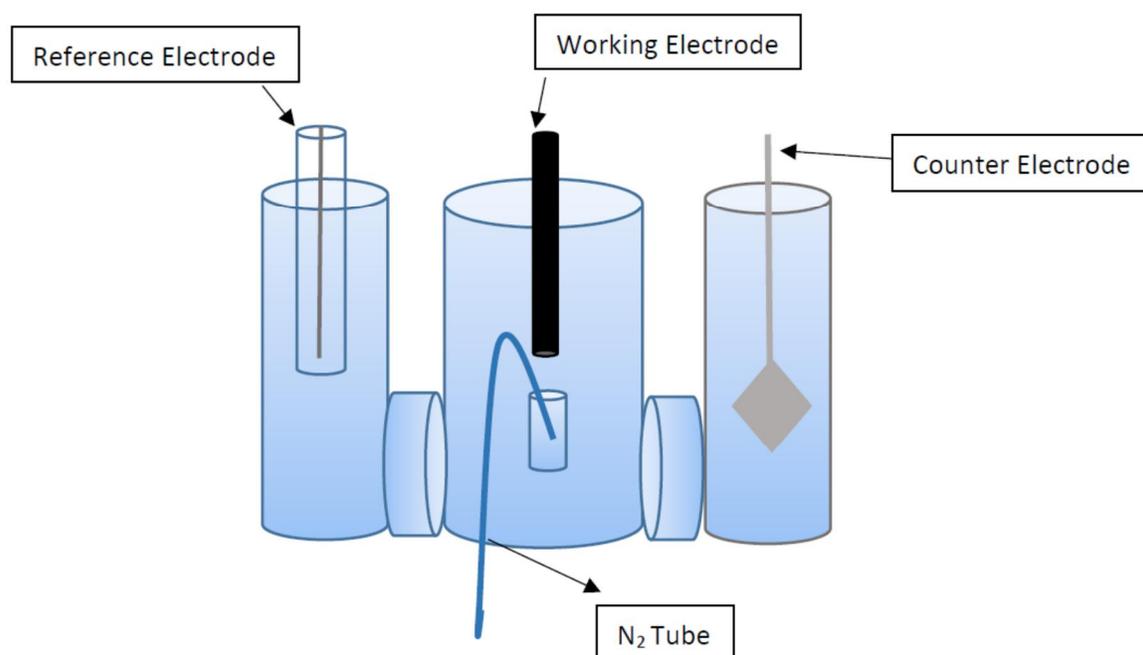


Figure 1. Electrochemical Cell used to perform Cyclic Voltammetry.

Results & Discussion

The cyclic voltammograms produced indicated that the reduction peak for oxygen consistently occurred at approximately -150 millivolts versus the reference electrode, at which point the current generated was about -2 microamperes for the commercial sample, and about -1 to -3 nanoamperes for the experimental samples. **Figures 2 and 3** show a clearly defined ORR peak using a commercial sample and Au nanoparticles reduced via NaBH₄, although they show a similar redox behavior at two different magnitudes of current. The Au oxidation peak at about 300 to 500 mV is better defined for the NaBH₄ experimental sample than for the commercial. **Figure 4** shows that the Au/C sample prepared by RoDSE in KOH requires a more negative potential of about -20 to -10 mV to reduce oxygen. Future experimentation should test these sample with a fresh ink preparation. **Figure 5** indicates that the Au/C sample prepared by RoDSE in NaOH resulted in less oxygen reduction reaction current, but also resulted in the oxidation of substance, presumably the decomposition of hydrogen peroxide into gas. The results obtained via RDE (**Figure 6**) indicated that Au nanoparticles are significantly less active than Platinum (Pt) or Palladium (Pd) nanoparticles for the oxygen reduction reaction; as a typical Carbon-dispersed Pt sample of good quality requires a much lower potential for ORR, as well as a limiting current twice that of Au. This indicates that while ORR on Pt and Pd is a 4-electron process at this potential range (0.1-0.9 V vs Ag/AgCl), ORR on Au stops at the peroxide stage, making it a 2-electron process.^[6] We intend to prepare by RoDSE a bimetallic Pd/Au for further in operando ORR studies at CHESS.

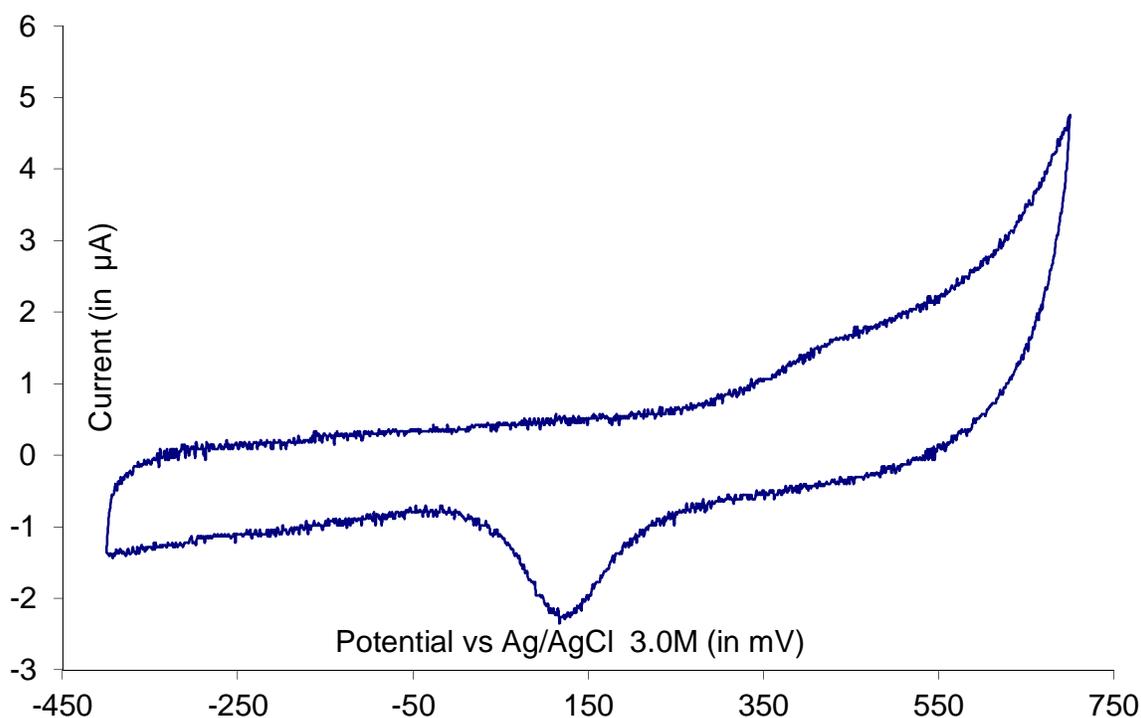


Figure 2. Cyclic Voltammogram for a Glassy Carbon Electrode modified with a Commercial 20% Gold/Vulcan Carbon + Nafion/Ethanol Solution in a 0.2M KOH Medium.

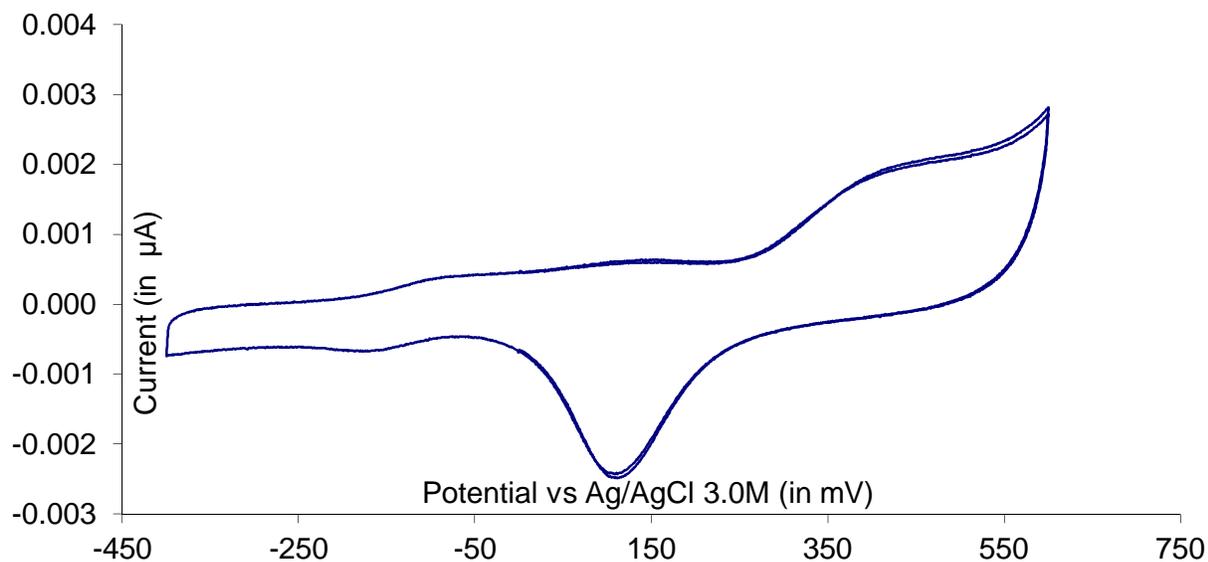


Figure 3. Cyclic Voltammogram for a Glassy Carbon Electrode modified with a Gold/Vulcan Carbon (prepared via reduction of Au^{3+} using NaBH_4) + Nafion/Ethanol Solution in a 0.2M KOH Medium.

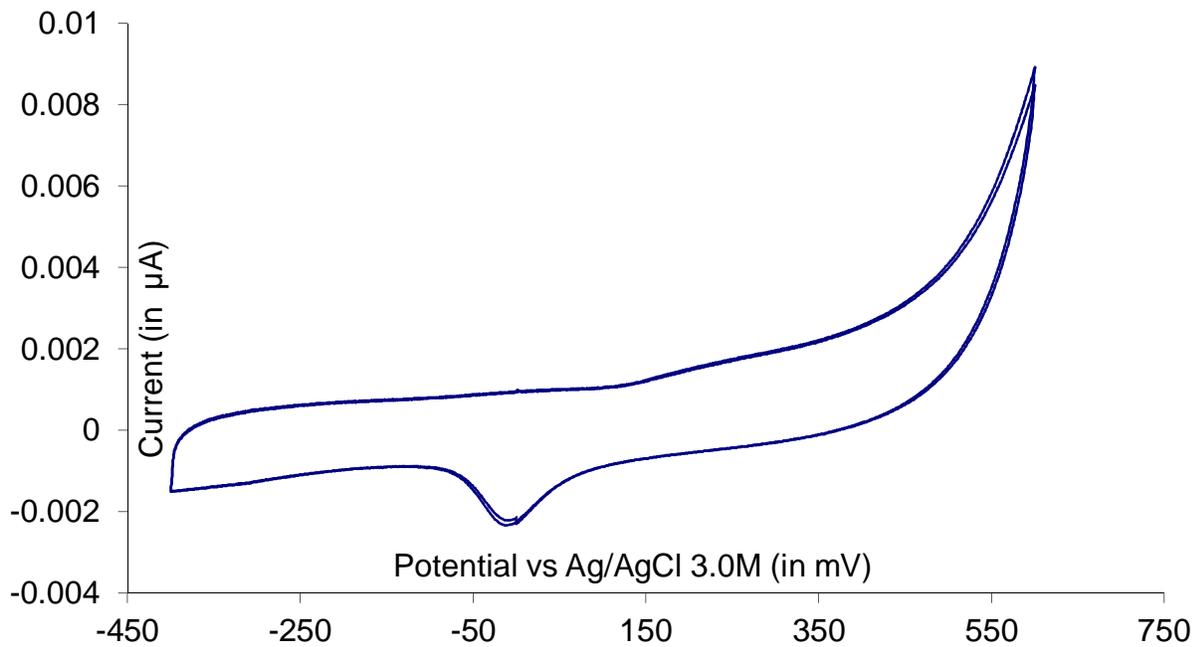


Figure 4. Cyclic Voltammogram for a Glassy Carbon Electrode modified with a Gold/Vulcan Carbon (prepared via a Rotating Flurry Disk Electrode using KOH) + Nafion/Ethanol Solution in a 0.2M KOH Medium.

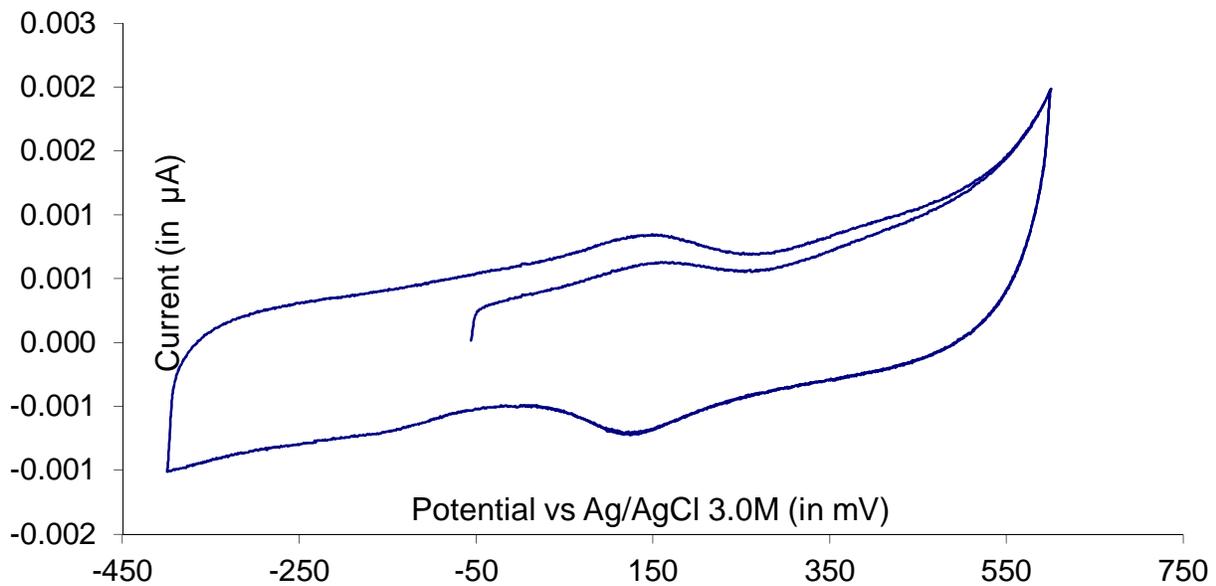


Figure 5. Cyclic Voltammogram for a Glassy Carbon Electrode modified with a Gold/Vulcan Carbon (prepared via a Rotating Flurry Disk Electrode using NaOH) + Nafion/Ethanol Solution in a 0.2M KOH Medium.

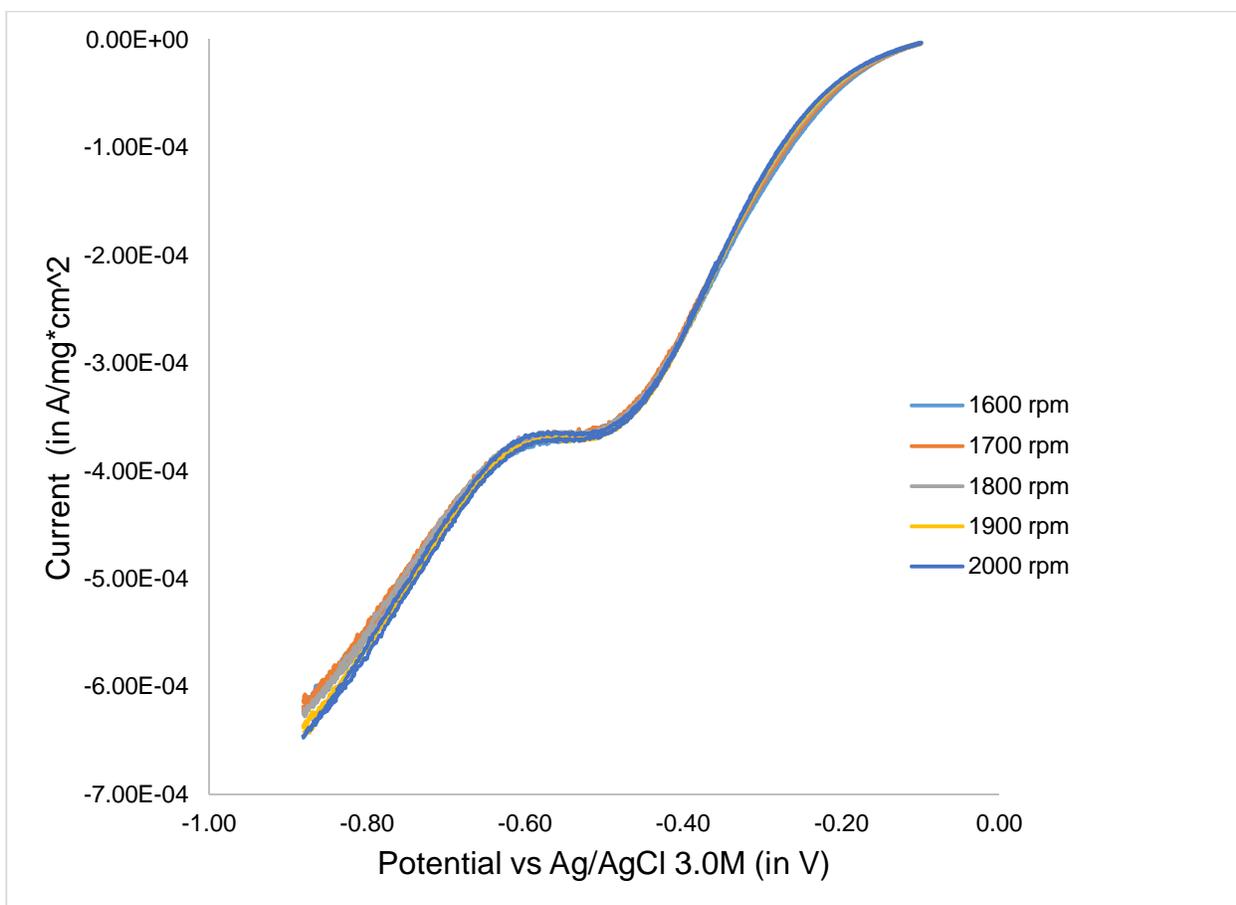


Figure 6. Polarization curve for a Rotating Disk Glassy Carbon Electrode modified with a Commercial 20% Gold/Vulcan Carbon + Nafion/Ethanol Solution in a 0.2M KOH Medium; Rotation rate: 1600-2000 rpm; Scan rate: 5 mV/s.

Conclusion & Future Goals

The preliminary results indicate that these electrochemical experiments showed that Au nanoparticles dispersed in carbon powder can be used as an effective catalyst for oxygen reduction reaction, and although they are less active than platinum nanoparticles, due to only undergoing a 2-electron transfer reaction, they can be used as a more economical alternative. Some possible errors include the fact that the voltammograms for the commercial catalyst resulted in a graph with a larger amount of "noise", very likely caused by the formation of bubbles during the potential sweep. Another possibility for the noise exhibited in several of the potential sweeps performed was improper cleaning of the electrode, specifically by leftover water droplets or debris from the wipes used when attempting to dry the electrode surface. In addition, the preparation and dilution of the catalyst powders in Nafion might have resulted in a more diluted solution if too much catalyst failed to dissolve and instead stuck to the container. In the continuation of this experiment, these gold catalysts will be tested in KOH/Ethanol solution. It is our objective to prepare samples of carbon paper doped with the gold catalysts in a cell and take these to CHESS for in operando studies. This would allow us to perform X-Ray Absorption Spectroscopy and obtain details on the Near Edge and Fine Structures (XANES & EXAFS) of our samples, in order to better characterize their structure under fuel cell operation. Additionally, we will be attempting to perform Transmission Electron Microscopy later on, on

these samples. This procedure would allow us to analyze and characterize the size distribution and dispersion of the gold nanoparticles in carbon Vulcan. Finally, we are looking forward to the use of Abruña's, Santiago's and Cabrera's Research Groups' results, in order to test the performance of the catalysts used in both research projects in an ethanol alkaline fuel cell, e.g. Zinc Oxide (ZnO), ZnO-doped Cobalt, and Au/C Vulcan.

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