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Area and Capacitance Characterization of Nickel, Cobalt, and Nickel-Cobalt Electrodeposited Thin Films

Matthew Gira

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Matthew J. Gira, Dr. Jennifer R. Hampton

Department of Physics and Department of Chemistry, Hope College, Holland, MI 49423

Electrochemical Processes

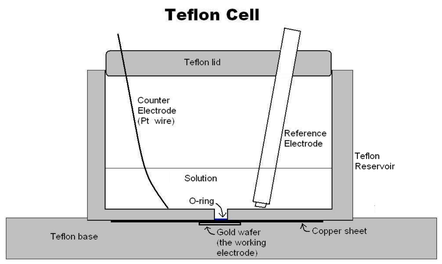


Figure 1. Rendering of the custom Teflon cell for electrochemical measurements and fabrication of samples.

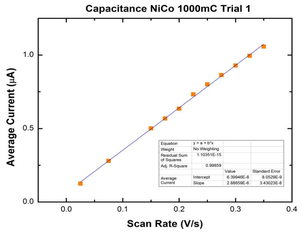
For the fabrication of each sample, controlled potential electrolysis is completed. This method in electrochemistry applies a constant potential,-1000mV in this case, and causes the metal ions in solution to be oxidized, turning the metal ions into metal solids. As a result, the metal(s) are deposited onto a Gold/Silicon wafer for further analysis.

Cyclic voltammetry is completed for electrochemical measurements on each sample. This method increases the potential from the initial value at a constant rate, and inverses the potential at the turning point. Capacitance potentials were from 0mV to 400mV for sodium sulfate, and from -50mV to -350mV for potassium hydroxide measurements. Area potentials were from 100mV to -600mV for a solution containing 5mM hexaaimineruthenium (III) chloride and 1M potassium chloride.

Capacitance Measurements

Instead of using two solid materials as in regular capacitors, the solution of sodium sulfate or potassium hydroxide form an electrochemical double layer with a sample. This electrochemical double layer is then able to store charge acting as a capacitor. Cyclic voltammetry stores the charge as the potential increases to the turning potential, and the charge is released after the reaching the turning potential.

Using the averages of the forward current and the reverse current for varying scan rates, the capacitance can be calculated. The capacitance is the slope of the average current vs. scan rate as seen in the equation below.



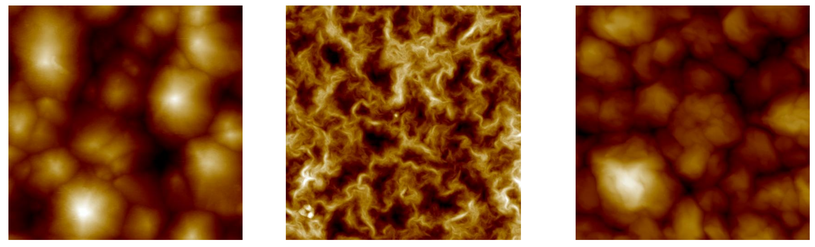
$$i = C\frac{dE}{dt} = Cv$$

Figure 2. Plot of the average current and scan rate. The slope of this linear trend is the capacitance value for one trial on a given sample, the NiCo 1000mC sample in this example.

Abstract

Many catalysts in energy production, specifically hydrogen and methanol fuel cells, use platinum as an effective catalyst. Platinum used in these fuel cells is uneconomical causing any energy production mechanisms that use platinum to be cost ineffective. There have been many studies with different combinations of platinum with different metals such as nickel, copper, iron, and cobalt to lessen the amount of platinum needed. However, these studies have relied on platinum being in the thin film electrodes. Through the use of electrodeposition, nickel, cobalt, and nickel-cobalt thin films were created with controlled potential electrolysis without the need of platinum. Characterization of these thin film electrodes were done with cyclic voltammetry and atomic force microscopy. With these methods, the electrochemical area, capacitance, and roughness factor of each thin film electrode were able to be determined. Correlation of these data and the significance of these measurements help to determine the effectiveness that these thin film electrodes could have as catalysts or in other energy applications.

Atomic Force Microscopy (AFM) Images



Cobalt **Nickel-Cobalt** **Nickel**

10 μm scan size and 1000mC thickness for all images

Comparisons

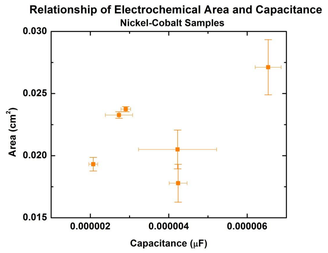


Figure 3. The nickel-cobalt samples seem to have a linear trend for area and capacitance. This capacitance was done with 0.5 M potassium hydroxide.

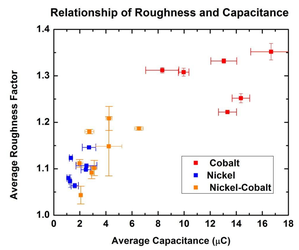


Figure 4. The cobalt samples have the highest roughness factors. The nickel-cobalt samples seem to be more related with the nickel samples from a roughness standpoint.

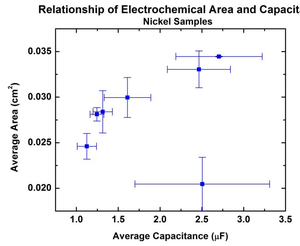


Figure 5. The nickel samples seem to have a linear trend for area and capacitance. This capacitance was done with 1M sodium hydroxide.

Acknowledgements

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Conclusions and Future Plans

These characterization measurements give a baseline for use in future catalysts in helping to determine which compositions and structures are most effective. In addition, the roughness, capacitance, and area measurements correlate with each other in some ways.

Further work still needs to be done with different elemental compositions such as tin, nickel-tin, nickel-copper, and other transition metal compositions. These different compositions would allow for better comparison and many more cost effective options for use as catalysts.

AFM Characterization

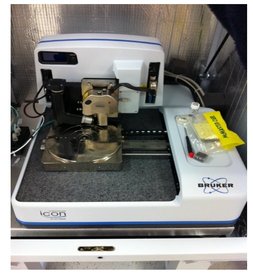

Figure 6. AFM used for roughness characterization. The model is the Bruker, Dimension Icon .

The AFM is a versatile instrument that can be used for material mapping, electrical characterization, lithography, or thermal analysis. Using the ScanAsyst in Air mode, a mode unique to Bruker AFMs, the topography of a sample is measured and produces an image. The more white a region is, the higher the region is in relation to what is around the region in the image, and vice versa.

These images can be analyzed for how rough the samples are. The roughness is the ratio between the actual surface area of the image and the projected surface area of the image if the image was completely flat. An example calculation is below:

$$Roughness\ Factor = \frac{Actual\ Area}{Projected\ Area} = \frac{106\mu m^2}{100\mu m^2} = 1.06$$

These roughness factors are important in determining the potential for catalytic activity. The greater the roughness, the greater the potential of a thin film electrode being successful as a catalyst.

Area Measurements

A surface area measurement, like the roughness factor, is useful for analysis, but how much of that surface area is productive can be a much more effective way of analysis. The electrochemical area refers to how much of that surface area is active as a catalyst or for any electrochemical reaction. This measurement is done by measuring the height of the peak in the "duck curve" as shown in figure 7. When relating the peak height and scan rate, this allows for calculation of the prefactor in the Cottrell equation shown below. This relation can only be done because of the electroactive species for cyclic voltammetry has been highly characterized and is well defined.

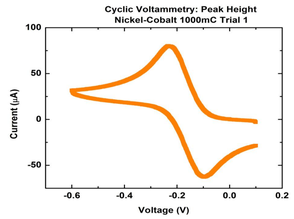

Figure 7. Cyclic voltammogram using 5mM hexaaimineruthenium (III) chloride and 1M potassium chloride as the electrolyte. Example of a "duck curve" for peak height to be measured.

$$i_p = 0.4463nFAC\left(\frac{nF}{RT}\right)^{1/2} v^{1/2}D^{1/2}$$