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ADVANCED DOUBLE LAYER CAPACITOR

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1. TECHNICAL OBJECTIVES

The overall goal of this project is to develop electrochemical capacitors utilizing an electrode-solid ionomer electrolyte composite. An advantage of these devices over conventional double layer capacitors would be the absence of free liquid electrolyte and thus greater safety and reliability.

In the first quarter, we have concentrated our efforts on Task IA of the Work Plan. Specifically we have 1) fabricated noble metal oxides of the RuO_x type, into electrodes and 2) constructed a laboratory test cell to determine which electrode structures are the most promising. In addition, in conjunction with a NIH funded project, we have investigated several methods of forming catalyst-ionomer composites.

2. EXPERIMENTAL METHODS

2.1 Preparation of Electrodes

2.1.1 Noble Metal Oxides: Two methods have been used to prepare electrodes of noble metal oxides: 1) thermal oxidation of a noble metal salt on a Ti substrate and 2) preparation of a noble metal oxide powder followed by fabrication of the powder into a TFE bonded electrode.

Preparation of a noble metal oxide electrode by decomposition of a precursor salt is well known; it is used extensively in preparing DSA anodes for chlorine production. We adapted the procedure reported by Raistrick and Sherman (1). A Ti sheet was roughened with emery paper and then etched in HF-HNO_3 . This sheet was then attached to a hot plate whose temperature was controlled at 140°C . A 1% RuCl_3 solution in isopropanol was sprayed on the sheet. Between each spray coat the solution was allowed to dry. About 10-15 coats were applied. The RuCl_3 -Ti was then fired at 250°C for 30 min and at 325°C for 15 min. Electrodes were punched from the sheet using a die punch.

To prepare RuO_x in particulate or powder form a "Thermal Method" based on the oxidative decomposition of Ru salt at elevated temperature was used.

2.1.2 Catalyst-Ionomer Composites: In conjunction with an NIH glucose sensor program, we have been investigating ways of preparing electrodes from electrocatalysts and solid ionomer electrolytes. Because of the requirements of the NIH program, Pt was chosen as the electrode material. Results of this investigation should be directly applicable to formation of the electrode-ionomer composites that will be fabricated and tested under the ONR program.

2.2 Electrochemical Testing

Electrodes were tested in 1M H_2SO_4 . A $\text{Hg}/\text{Hg}_2\text{SO}_4$ electrode was used as a reference. An electrode holder was fabricated so that approximately 1.7 cm^2 was exposed to solution. The counter electrode was a spectroscopically pure carbon rod. The solution is deaerated with nitrogen before measurement.

3. RESULTS AND DISCUSSION

The purpose of the initial experiments is to determine which electrode structures give the best capacitive behavior. It is desirable that the processes occurring at the electrode be double layer or reversible surface processes over a wide range of potentials and that the total value of capacitance be as high as possible. The first requirement is related to the intrinsic chemistry of the electrode while the second requirement depends both on chemistry and electrode fabrication techniques.

We are initially screening electrode structures in sulfuric acid. The surface and capacitive processes in sulfuric acid are expected to be similar to those of the electrode-Nafion composites. In addition, the electrode is completely wet with sulfuric acid. This gives us some idea of the "ultimate" capacitances obtainable with a given electrode structure.

The response of RuO_x electrodes prepared by thermal oxidation of RuCl_3 on a Ti substrate is shown in **Figures 1a** and **1b**. The response was measured in 1M H_2SO_4 versus a $\text{Hg}/\text{Hg}_2\text{SO}_4$ reference electrode. All potentials are reported with respect to this electrode. The potential was scanned from -0.4 to $+0.7 \text{ V}$ at sweep rates from 20 to 300 mV/s. There is a relatively flat region between -0.1 and $+0.3 \text{ V}$. A plot of anodic current density (at 0.1 V) versus sweep rate is shown in **Figure 2**. The points fall on a straight line. If the response is assumed to be purely capacitive in this region then:

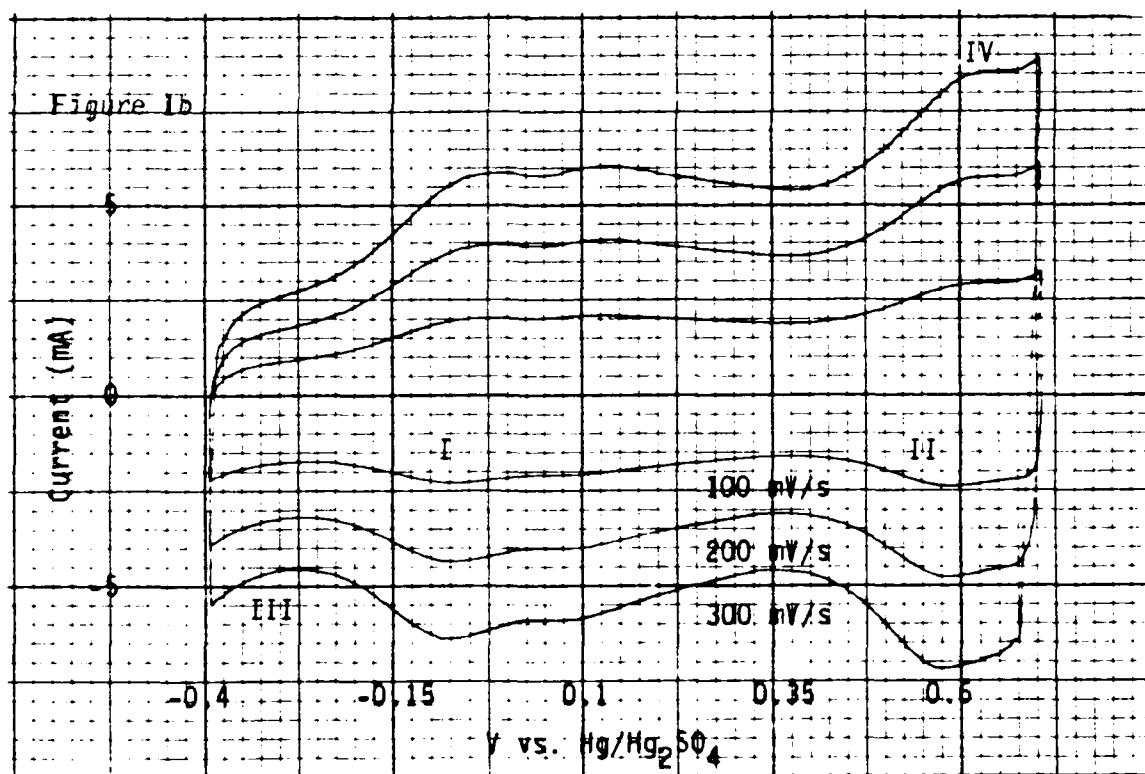
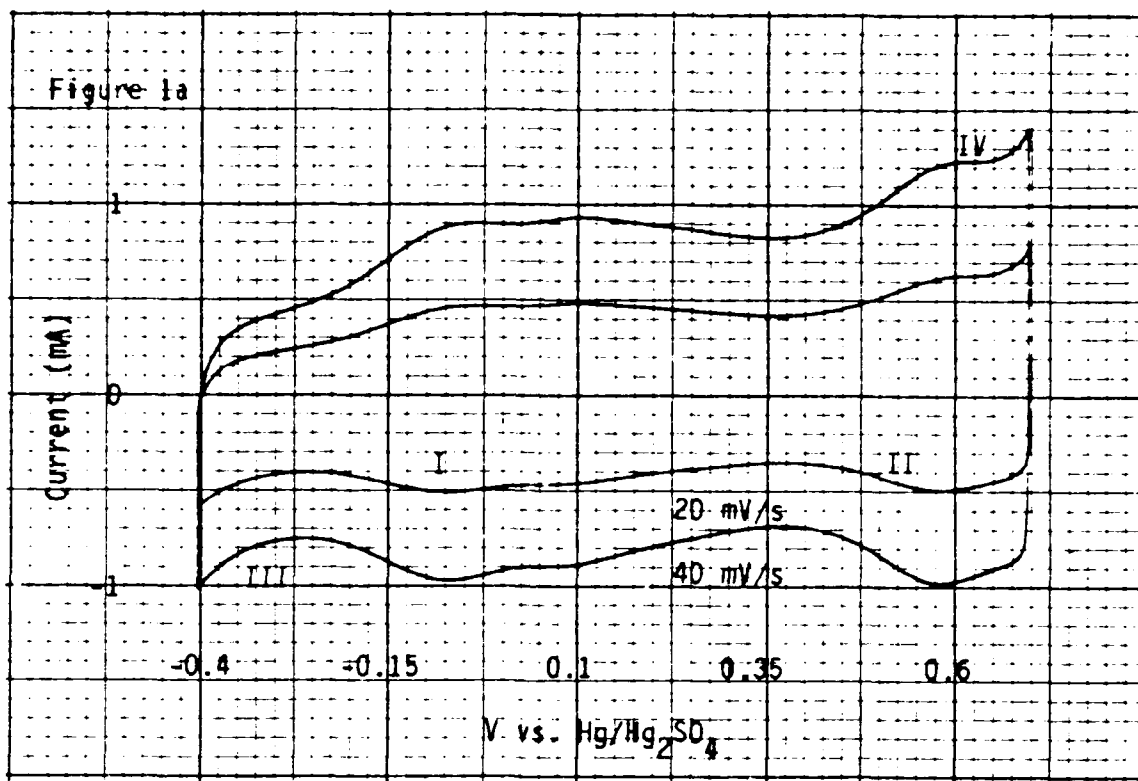


Figure 1: Response of Thermally Prepared RuO_x on Ti in $1\text{M H}_2\text{SO}_4$

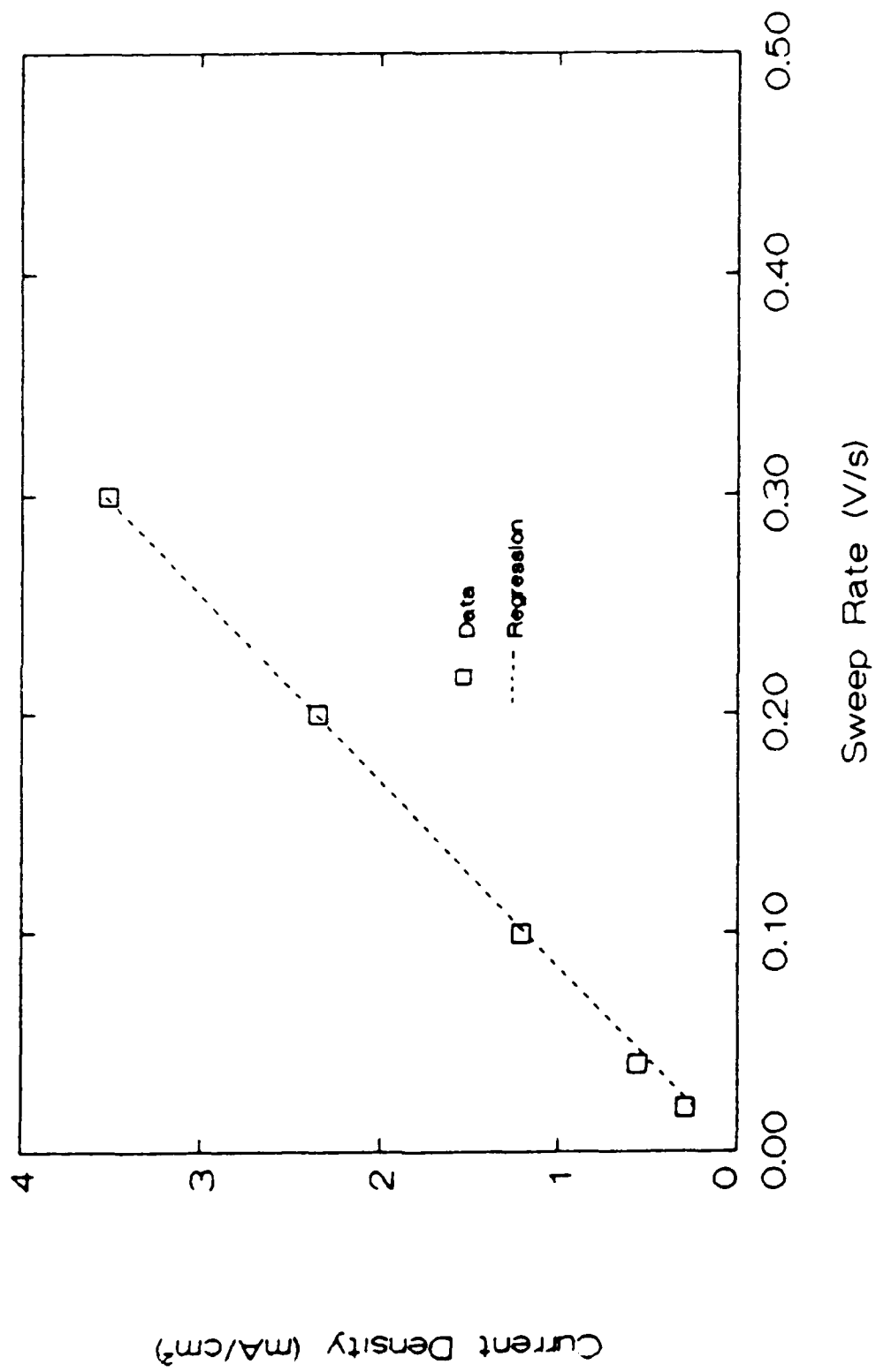
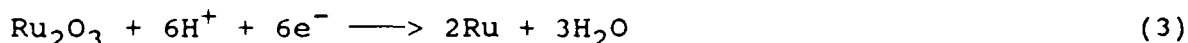
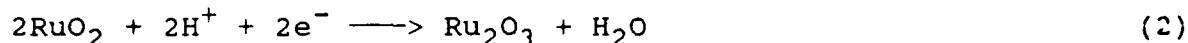


Figure 2: Current Density at 0.1 V vs. Hg/Hg₂SO₄ vs. Sweep Rate for RuO_x on Ti in 1M H₂SO₄

$$i = C \frac{dV}{dt} \quad (1)$$

The slope of the regression line in Figure 2 is 11.8 mF/cm².

There are voltammetric peaks at -0.075 V and +0.575 V (Peaks I and II). These peaks have been assigned to the Ru/Ru₂O₃ and Ru₂O₃/RuO₂ couples respectively (2). These redox couples involve the reactions of surface species with protons in solution:



If the supply of H⁺ is sufficient, charge storage should be possible using these reactions.

There are beginnings of voltammetric waves at -0.275 V and +0.65 V (labeled as III and IV). The cathodic wave is due to the reduction of RuO₂ while the anodic wave is due to the beginning of oxygen evolution. The 0.925 V window between these reactions represents the usable voltage range in sulfuric acid.

4. FUTURE WORK

Several electrodes, such as those made from powder prepared by the Thermal Method, were fabricated but not tested during the first quarter. They will be tested during the second quarter. We will also begin testing electrode-ionomer composites. The electrode-ionomer composite will be separated from the sulfuric acid by a piece of ionomer membrane. The voltammetric response of the electrode-Nafion composite will be compared to the electrode-sulfuric acid response to determine if the electrochemistry differs in any respect. The values of current and derived capacitance will be compared to determine the effective coverage of the Nafion on the electrode material. This work will ultimately be extended to fabrication of ionomer-catalyst composites that are in intimate contact to a Nafion membrane with no liquid electrolyte present.

5. REFERENCES

- 1) Raistrick, I. and R. Sherman, Electrode Materials and Processes for Energy Conversion and Storage, S. Srinivasan, S. Wagner and H. Wroblewski, eds., The Electrochemical Society Proceedings, Vol. 87-12, 1987.
- 2) Arikado T., C. Iwakura and H. Tamura, "Electrochemical Behavior of the Ruthenium Oxide Electrode Prepared by the Thermal Decomposition Method," *Electrochim. Acta*, **22**, 513 (1977).