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ADVANCED DOUBLE LAYER CAPACITOR

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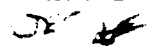
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1. TECHNICAL OBJECTIVES

The overall goal of this project is to develop electrochemical capacitors with no liquid electrolyte present. The liquid electrolyte is replaced by a solid ionomer electrolyte. An advantage of these devices over conventional electrochemical capacitors containing free acid would be greater safety and reliability.

In the fourth quarter, we concentrated our efforts in three areas: 1) preparation and characterization of RuO_x powders, 2) preparation of membrane and electrode (M and E) assemblies with high capacitance, and 3) scale-up of M and E structures to 2" x 2" size. *Keynote Electrochem Soc* 

2. EXPERIMENTAL METHODS

2.1 Preparation and Characterization of RuO_x Powders

2.1.1 Preparation

The thermal method was used to prepare RuO_x . The effect of temperature and method of dispersing the RuCl_3 precursor on powder physical properties were studied.

2.1.2 Surface Area

Surface area measurements on RuO_x samples were done using a Micromeretics FlowSorb II 2300 apparatus, as described in the 3rd Quarterly Technical Report.

2.1.3 Transmission Electron Microscopy

Transmission electron microscopy (TEM) was done to determine the fine structure of the RuO_x powders. The RuO_x samples were dispersed on Holey Film supports. Some samples were also examined by small area electron diffraction (SAED) to determine the degree of crystallinity in the sample. All TEM work was done at Eastern Analytical Laboratories (Billerica, MA).

2.1.4 Mercury Porosimetry

Mercury porosimetry was used to obtain information on inter- and intraparticle pore sizes. In this technique, mercury is forced into the sample pores by a constantly increasing pressure. The pore diameter can be calculated using:

$$d = \frac{-4 \gamma \cos \theta}{p}$$

where γ is the surface tension, θ is the contact angle, and p is the pressure. The volume of mercury in the pores is measured directly and the surface area is calculated by assuming cylindrical pores. The cumulative pore volume and pore surface area are plotted against pressure or pore diameter.

A sample of a Teflon bonded RuO_x electrode was sent to Micromeretics (Norcross, GA) for mercury porosimetry.

2.2 Preparation of Membrane and Electrode Assemblies

Electrodes were formed by suspending RuO_x particulates in a Nafion 117 solution (containing isopropyl alcohol and water). This suspension was used as a "paint" to make electrodes.

Initially, membrane and electrode assemblies were made by painting the RuO_x -Nafion mixture directly on a Nafion 117 membrane. After drying, a current collector screen was hot pressed into the assembly. M and E's were successfully prepared by this method, but the electrodes were somewhat uneven due to the difficulty of painting onto a wet membrane. Loading of the RuO_x -Nafion mixture was also difficult to determine. A modified method was developed that solved both these concerns and is described in the Appendix.

2.3 Electrode Testing

Electrode testing was done as reported in the 3rd Quarterly Report. A cell of 2" x 2" (25 cm²) size was built. The design was similar to the liquid electrolyte-free cell for 1 cm² M and E's described in the 3rd Quarterly Report.

3. RESULTS AND DISCUSSION

3.1 Preparation and Characterization of RuO_x Powders

3.1.1 Preparation

Several preparations of RuO_x were done during the 4th Quarter. Table I lists the preparation conditions and surface areas obtained. The baseline method (Powder 363-49) consisted of mixing RuCl₃ and NaNO₃ and crushing and grinding the mixture with a mortar and pestle. The mixture was then placed into a porcelain dish and heated to 500-550°C for 3 hours and allowed to cool inside the furnace. Powder 363-49 had a surface area of 18 m²/g which was considerably lower than the 50 m²/g powder made during the 3rd Quarter (using a similar method). This low surface area was attributed to poor temperature control by the furnace temperature controller. The controller was replaced. Powder 363-57 prepared in the furnace with the new controller gave a powder with a surface area of 58 m²/g.

Table I: RuO_x Preparations

Powder No.	Mixing Method	Temperature (°C)	Time (hr)	Surface Area (m ² /g)
363-49	Crush/Grind	550	3	18
363-57	Crush/Grind	500	3	58
363-74	Slush	500	3	95
363-82	Slush	500	3	73

The crushing/grinding method was not giving a very good dispersion of RuCl₃ in the NaNO₃. An improved method was developed that is described in the Appendix. Powders 363-74 and 363-82, made by this improved method, gave surface areas of 95 and 73 m²/g, respectively.

3.1.2 Characterization

Figure 1 shows a TEM photograph of a RuO_x particle from the 50 m²/g powder made during the 3rd Quarter. The particles have considerable internal porosity with crystallites on the order of 200 Å in size. The SAED pattern (Figure 2) shows weak diffraction rings indicating the material has some crystallinity.

00012



500 Å

Figure 1: TEM of 50 m²/g RuO_x Particulate.

The 50 m²/g powder was heat treated at 700°C. Its surface area was reduced to 3 m²/g. The TEM photograph of this heat-treated powder (Figure 3) shows that intraparticle sintering of the crystallites has occurred and the sintered particles are on the order of 0.1 μm in size. The SAED pattern in Figure 4 shows much more intense diffraction rings in the 3 m²/g material indicating a stronger degree of crystallinity.

The mercury porosimetry results are plotted in Figure 5. About half the pore volume is contained in pores greater than 0.5 μm. Almost all of the surface area is from pores less than 0.01 μm (100 Å) in diameter.

From the surface area, X-ray diffraction (see 3rd Quarterly Report), SEM (see 3rd Quarterly Report), TEM, and mercury porosimetry results, a consistent picture of the structure and morphology of the RuO_x powder begins to emerge. The powder is primarily RuO₂. It is made up of particles of less than 1 μm to over 100 μm in size. These particles are porous and consist of partially sintered crystallites. Assuming spherical crystallites, the surface area can be calculated from:

$$SA = \frac{6}{dR}$$

using $d = 7 \text{ g/cm}^3$ for RuO₂ and $R = 100 \text{ Å}$ (from Figure 1) gives $SA \approx 40 \text{ m}^2/\text{g}$ which is in good agreement with the 50 m²/g measured by nitrogen adsorption.

The mercury porosimetry results and TEM photographs show that most of the surface area is in the pores between the crystallites. These pores are less than 100 Å in diameter.

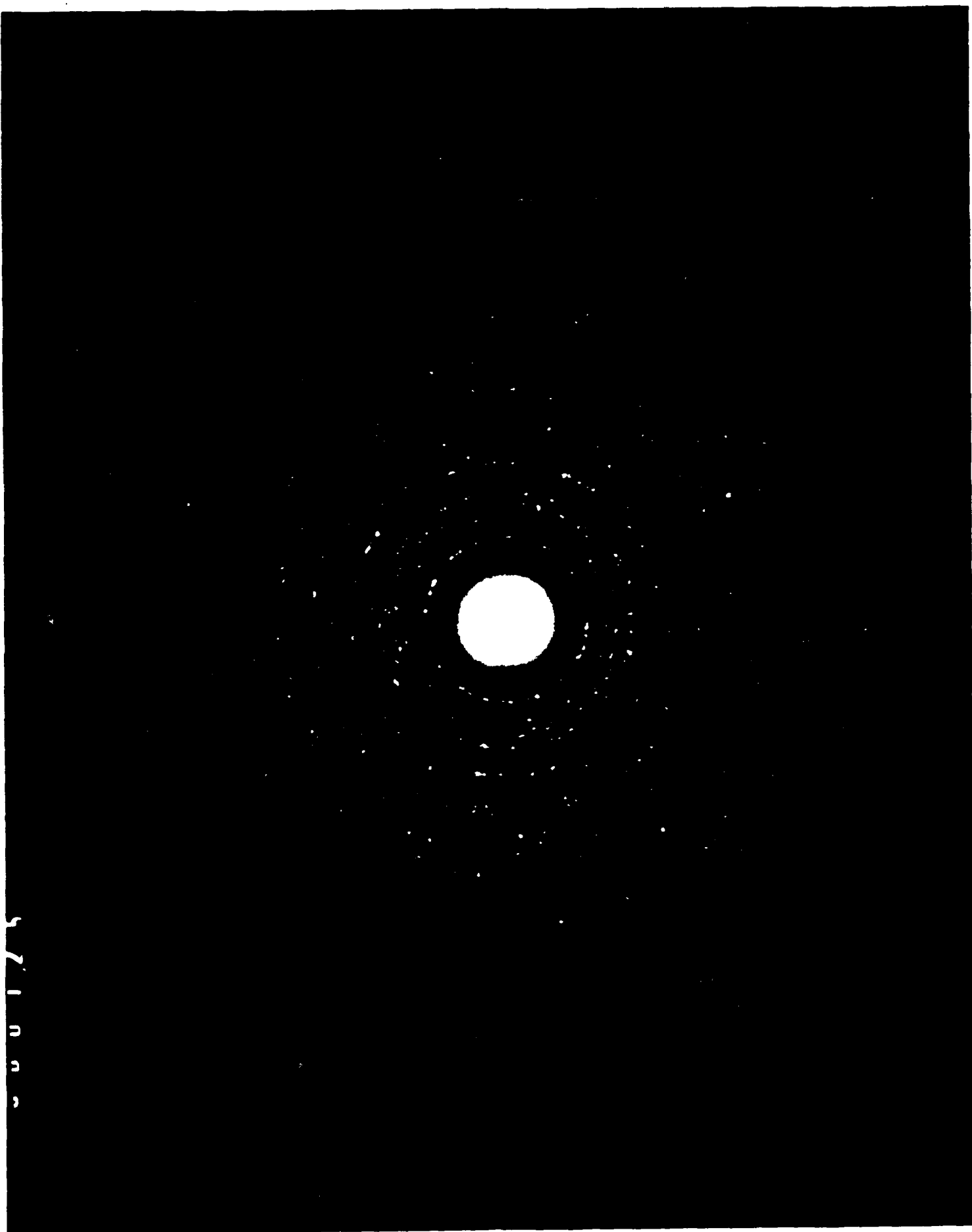
This type of morphology of the oxide is not unexpected. The density of RuCl₃ is 3.1 g/cm³, while RuO₂ has a density of 7 g/cm³. When the decomposition reaction is accompanied by a large decrease in specific volume (as is the case here) the final product has the external shape and dimensions of the precursor, but with many small voids (Volpe and Boudart, 1985). This appears to be the case here.

000126



500 Å

Figure 3: TEM of 3 m²/g RuO_x.



000175

Figure 4: SAED of 3 m²/g RuO_x.

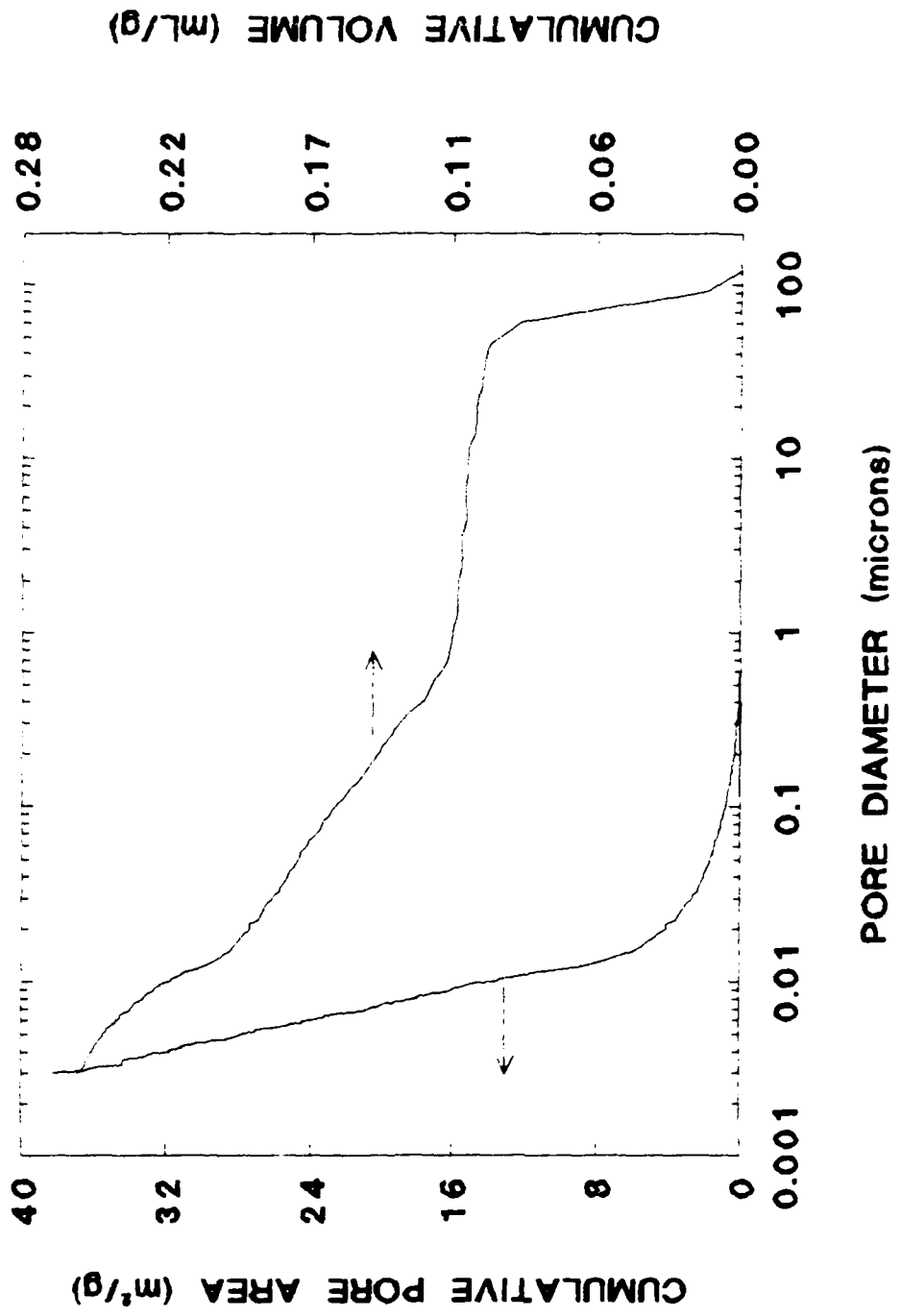


Figure 5: Mercury Porosimetry on a Teflon-Bonded RuO_x Electrode: Cumulative Pore Area and Cumulative Pore Volume vs. Pore Diameter.

3.2 Electrode Characterization

3.2.1 Cyclic Voltammetry

Capacitance of electrodes bonded to a Nafion membrane with no Nafion impregnation are near 0.1 to 0.2 F/cm². This capacitance arises because of the interfacial contact area between the RuO_x and membrane. By adding Nafion to the electrode structure, we hope to create the analog of a "flooded" electrode where the entire depth of the electrode is utilized. To determine whether the painting method was producing such electrode structures, M and E's were made with different loadings of RuO_x (and a constant 5 wt% Nafion). If a three dimensional structure is being formed, then the capacitance should be proportional to the RuO_x-Nafion loading.

Figure 6 shows capacitance vs. RuO_x loading for M and E's made from Powder 363-49. At loadings up to 20 mg/cm², capacitance is linearly proportional to loading. At higher loadings, it tends to level off.

Figure 7 shows a composite plot of capacitance vs. loading of M and E's made from several different RuO_x powders. Capacitances of up to 0.6 F/cm² were achieved at the highest loadings. Although a clear linear proportionality can be seen at loadings of 20 mg/cm² and below, considerable scatter in the data exists (even for M and E's made with the same RuO_x powder). There is only a small improvement from making electrodes from higher area powder.

Electrodes with higher loading of RuO_x, made by the painting method, sometimes had impurity peaks in their voltammograms. **Figure 8a** shows a voltammogram of one such electrode. A large cathodic peak was evident at 150 mV. We found that this peak could be removed by boiling the membrane in a dilute H₂O₂ solution. **Figure 8b** shows that this peak has been substantially removed by this treatment. The peak is probably due to an organic impurity which is then oxidized by the H₂O₂.

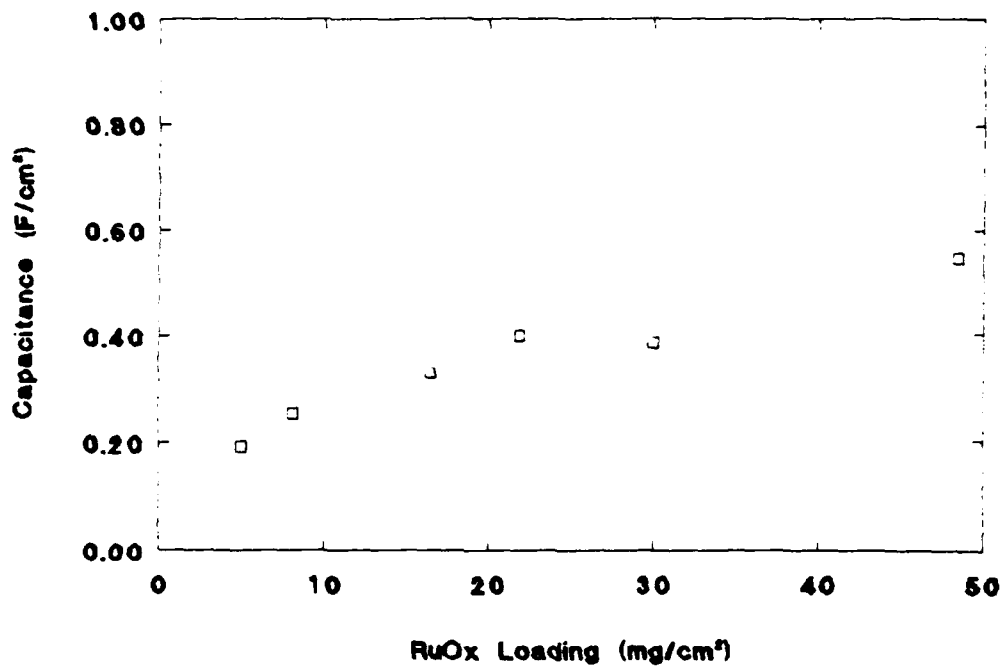


Figure 6: Capacitance vs. RuO_x Loading for M and Es Made from Powder 363-49.

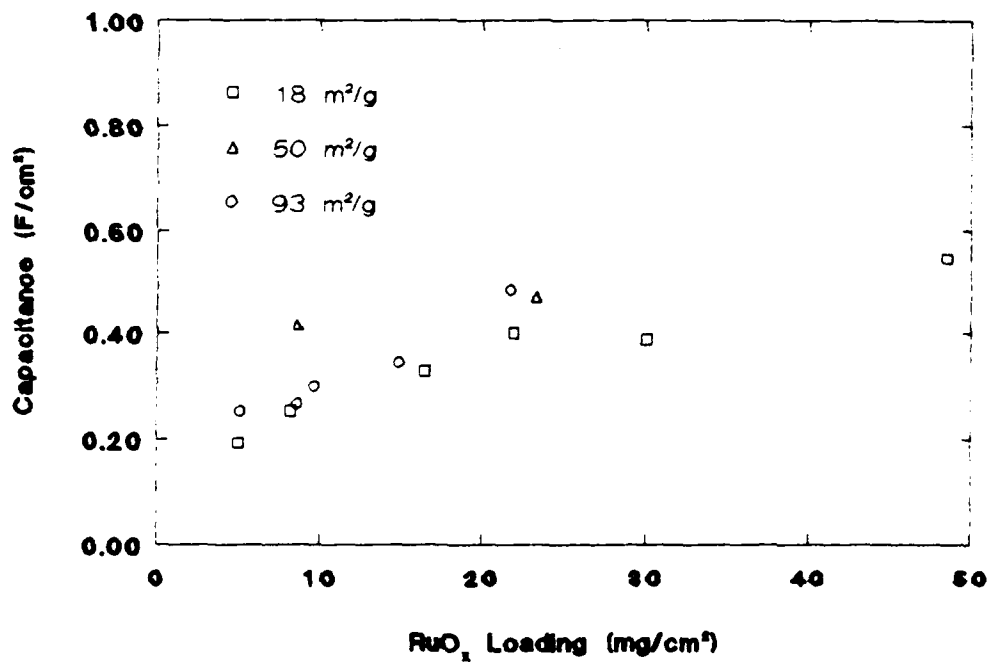


Figure 7: Capacitance vs. RuO_x Loading for M and Es Made from Different RuO_x Powders.

Figure 8a

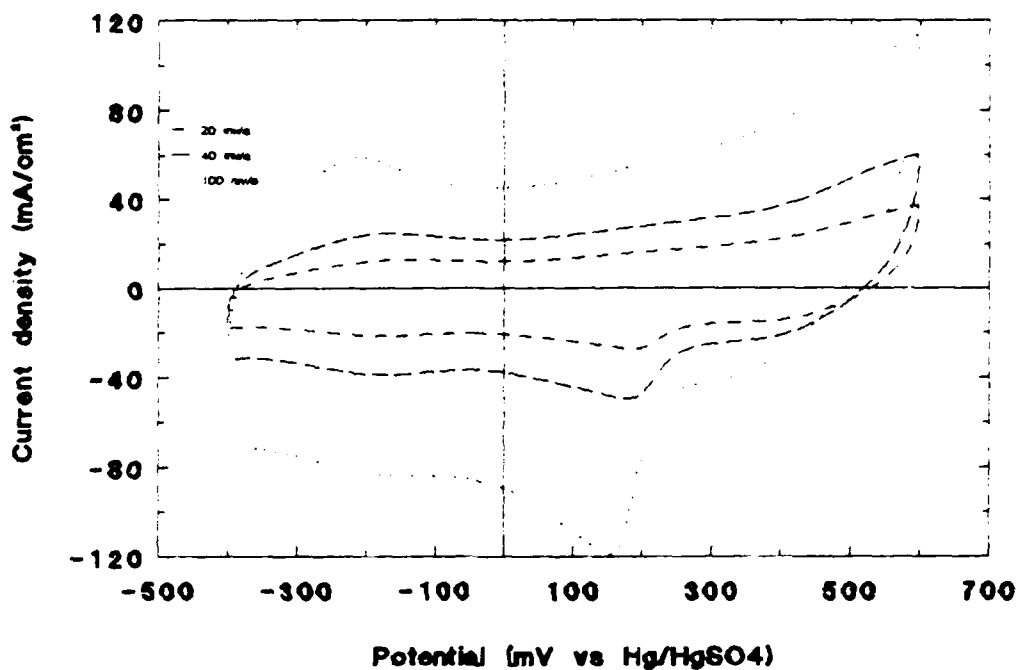


Figure 8b

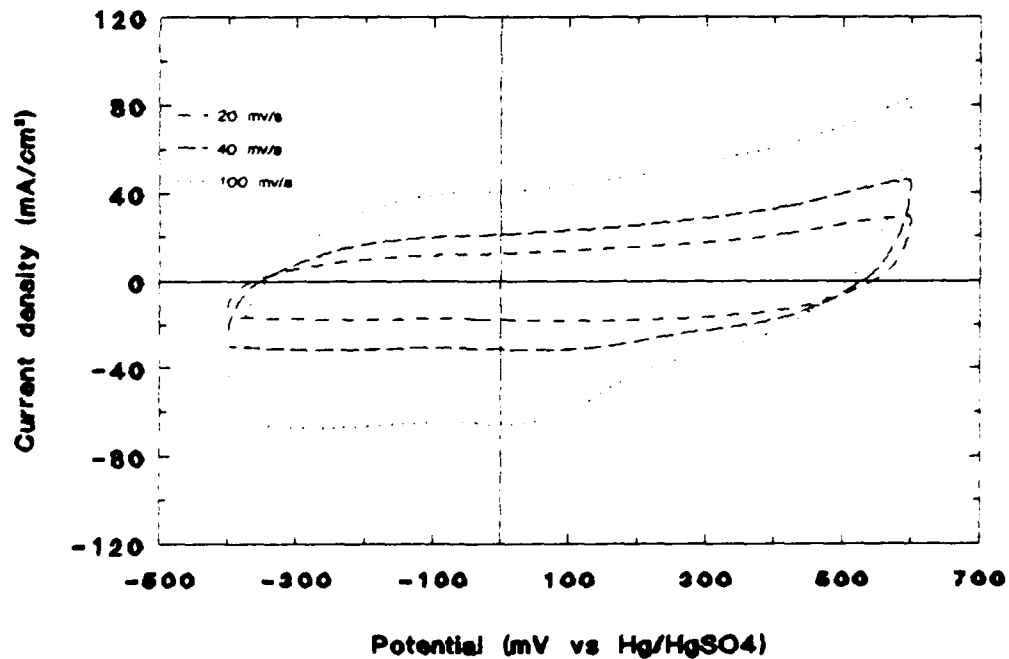


Figure 8: Voltammogram of High-Loading RuO_x Electrode Made by the Painting Method.
a) Before H₂O₂ Treatment; b) After H₂O₂ Treatment

It was found that electrodes made by painting RuO_x -Nafion mixture give capacitance higher than electrodes with no Nafion, but electrodes made by mixing RuO_x and Nafion, drying the powder and then fabricating electrodes do not. This fact can be explained by the requirements of the electrode-electrolyte interface necessary in a liquid electrolyte free cell. Figure 9 shows a representation of the RuO_x -Nafion interface. To effectively utilize the RuO_x in the interior of the electrode, a continuous ionic path must extend from the membrane to the RuO_x particulate. By painting, a continuous composite of RuO_x and Nafion can be formed. On the other hand, the previous method of mixing the RuO_x and Nafion, drying the powder and fabricating into an electrode likely lead to a non-continuous ionic path.

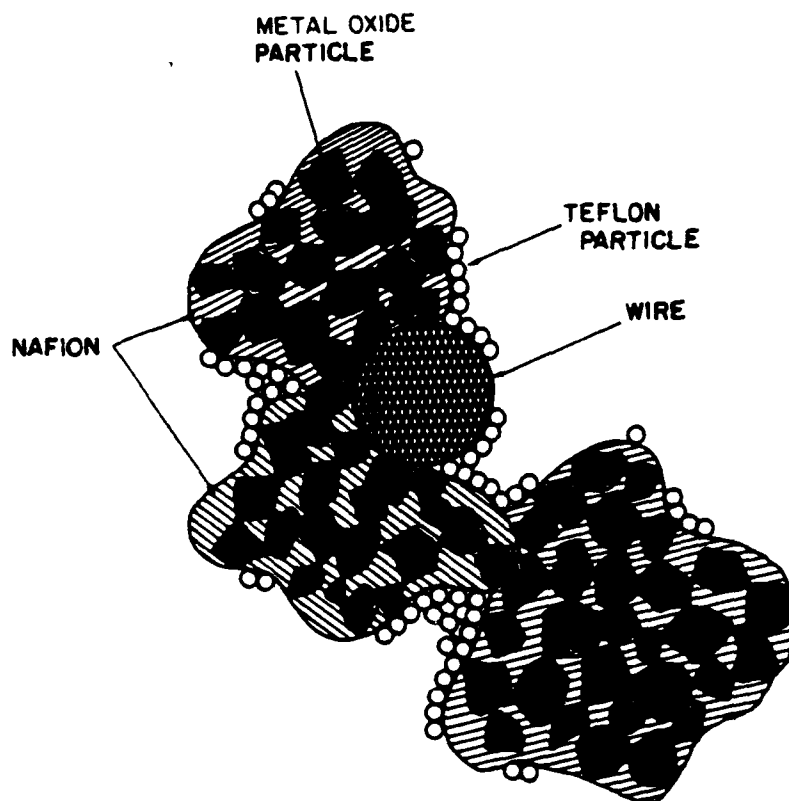


Figure 9: RuO_x -Nafion Interface.

The higher surface area powders do not seem to produce electrodes with much higher capacitance than a lower surface area powder (at similar total loadings). Most of the surface area of the RuO_x is developed in pores of less than 100 Å in size (see

Figure 5). Nafion is a polymeric electrolyte. Although the equivalent weight of Nafion 117 is 1100, the molecular weight is probably greater than 2×10^5 daltons. Figure 10 shows the structure of Nafion 117. In its solid (membrane) form, the units are intertwined. When solubilized, the weak bonds between units are broken apart, but the covalent bonds are not broken. Aldebert et al. (1986) have used small angle neutron scattering to show that Nafion units in solution are 20-40 Å in diameter and 200-400 Å long. Thus, the Nafion molecules probably cannot penetrate into the small pores between RuO_x crystallites.

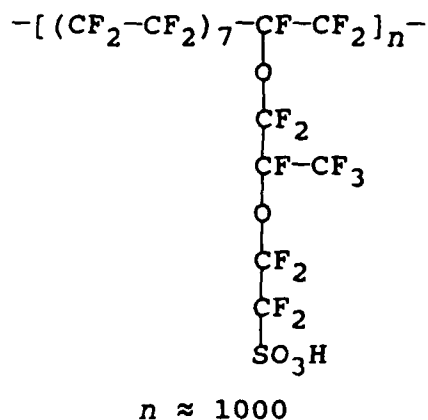


Figure 10: Structure of an 1100 EW Nafion Ionomer.

3.2.2 2" x 2" Hardware

2" x 2" M and Es were prepared and tested in the cell hardware built during this quarter. A 20 mg/cm² loading of RuO_x -5% Nafion electrode gave a capacitance of 14 Farads (0.56 F/cm²).

4. FUTURE WORK

The liquid electrolyte-free cell hardware allows us to test M and Es with no liquid electrolyte present. However, a water reservoir is still needed to keep the membrane hydrated. During the 5th Quarter, we will develop sealed cell hardware.

Characterization during the first year of this contract has been mostly done on single electrodes using cyclic voltammetry or AC impedance methods. We will be transitioning into evaluating capacitance by charging and discharging of the complete RuO_x electrochemical cell.

5. REFERENCES

Aldebert, P. B. Dreyfus and M. Pineri, "Small Angle Neutron Scattering of Perfluorosulfonated Ionomers in Solution," *Macromolecules*, 19, 2651 (1986).

Volpe, L., and M. Boudart, "Topotactic Preparation of Powders with High Specific Surface Area," *Catal. Rev. - Sci. Eng.*, 27, 515 (1985).