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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 a solid ionomer electrolyte. 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 sixth quarter, we concentrated our efforts in three areas: 1) preparation and characterization of electrode materials, 2) preparation of membrane and electrode (M and E) assemblies that have high capacitance and minimum internal resistance, and 3) development of cell hardware that can contain the M and E for extended periods of time without loss of water and contributes negligibly to the total internal resistance. - RRH

2. EXPERIMENTAL METHODS

2.1 Preparation and Characterization of Electrode Materials

2.1.1 Preparation

RuO_x was prepared by thermal treatment of $\text{RuCl}_3 \cdot \text{NaNO}_3$ for three hours at 500°C followed by rapid quenching in water. The powder was washed until free of chloride (by the AgNO_3 test) and then centrifuged to collect the RuO_x particulates.

2.1.2 Particle Size Analysis

A sample of RuO_x powder was sent to Micromeritics (Norcross, GA) for particle size analysis by gravity sedimentation. For this type of analyses, particles are allowed to settle slowly in a viscous medium. X-Ray absorption is used to determine the concentration of particles at each depth in the liquid. Stoke's law is used to calculate the equivalent spherical diameter of the particles at each depth in the liquid.

2.1.3 Nitrogen Porosimetry

A sample of RuO_x was sent to Micromeritics for determination of surface area (by the multipoint BET method), pore volume, and pore size distribution (by the BJH method).

2.2 Preparation of M and Es

Prior to this quarter, the M and E preparation procedure had evolved from painting the RuO_x mixture directly on the membrane to a modified Giner, Inc. proprietary method. During this reporting period, further optimization of M and E fabrication methods were made to improve quality and enhance the electrochemical capacitance of the RuO_2 electrode structures.

The modified Giner, Inc. method involves bonding the RuO_x -Nafion composite directly to a carbon-Ti screen current collector. The carbons used and typical fabrication parameters are listed in Table I. Black Pearls (Cabot Corporation) was chosen because it is a high surface area ($1000 \text{ m}^2/\text{g}$) and highly conductive carbon black. Heat treatments lower the surface area (to about $250 \text{ m}^2/\text{g}$) and the heat treated material requires less Teflon to make a mechanically stable electrode. PANEX is a carbon paper; it is lightly Teflonized for mechanical stability. Vulcan XC-72 (Cabot Corporation) is a conductive carbon black of surface area $250 \text{ m}^2/\text{g}$.

Table I: Current Collector - Backing Layers

Type	Loading (mg/cm^2)	Teflon (%)
Black Pearls	5	25
Heat-Treated Black Pearls	10	5
PANEX		
Vulcan XC-72/PANEX	10	40

2.3 Cell Hardware

During the 5th Quarter, sealed cell hardware with polymeric endplates and an O-ring was developed. This hardware continued to be used during the 6th Quarter. We have also developed hardware based on metallic endplates and fluoropolymer gasketing. An exploded view of this hardware is shown in Figure 1. The endplates are machined from titanium metal ($0.125''$ thick). Each plate is lightly platinum plated (0.5 to $1 \text{ mg}/\text{cm}^2$) in the area that contacts the M and E current collector. A fluoropolymer gasket (TFE or FEP) of appropriate thickness is placed around the M and E. The plates are compressed against the M and E and gasket using insulated metal bolts. Contact to the external circuit is via gold-plated tabs.

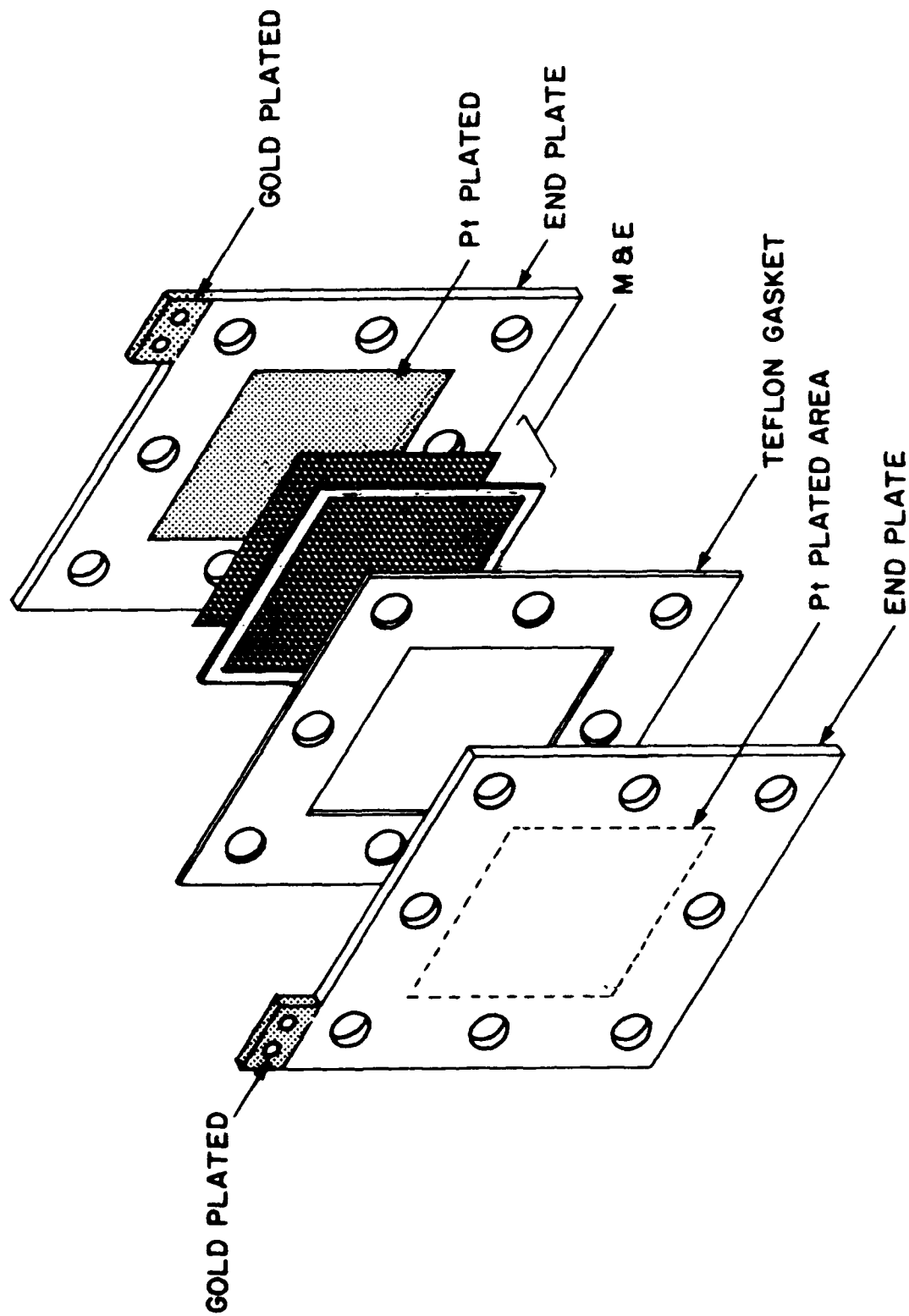


Figure 1: Exploded View of Capacitor Cell Hardware with Titanium End Plates

2.4 Cell Testing

Cells were tested for capacitance by discharge through a resistive load. Current interruption was used to measure internal resistance. The equipment and procedures for these tests have been described in the 5th Quarterly Report.

3. RESULTS AND DISCUSSION

3.1 Electrode Materials

Figure 2 shows the particle size distribution expressed as mass % in an interval vs. particle diameter. Most of the particle mass is in the 5 to 10 μm diameter interval. The median diameter based on the mass distribution is 5.52 μm . The median diameter based on the number distribution is 0.42 μm . These results of particle size analysis by gravity sedimentation are in agreement with those measured by computerized particle counting on the SEM.

TEM observation showed that the size of the individual crystallites was on the order of 0.02 μm . These crystallites are aggregated into porous particles with sizes ranging from the submicron to several tens of microns (particles of diameter greater than about 40 μm were removed by sieving). The size range of the porous aggregates is due to either the precursor (RuCl_3) morphology or sintering of crystallites during transformation.

A multipoint BET analyses was done on this sample to check the validity of the BET isotherm for RuO_x and to check the assumptions of the single point method. Figure 3 is a plot of $1/[V(P_0/P-1)]$ vs. P/P_0 . If the BET equation:

$$\frac{1}{C[P_0/P-1]} = \frac{1}{V_m C} + [(C-1)/V_m C] \frac{P}{P_0}$$

is obeyed, then this plot should be a straight line with an intercept of $V_m C$ and a slope of $[(C-1)/V_m C]$. Figure 3 shows that a straight line is obtained; and, therefore, the BET equation is obeyed. From the plot a surface area of 103.26 m^2/g is obtained. Solving for V_m and C gives $V_m = 23.72 \text{ cm}^3/\text{g}$ (STP) and $C = 91.23$. If $C \gg 1$, then the single point BET surface area should be a good approximation. The single point surface area is 100.59 m^2/g which is within 2.6% of the multipoint surface area.

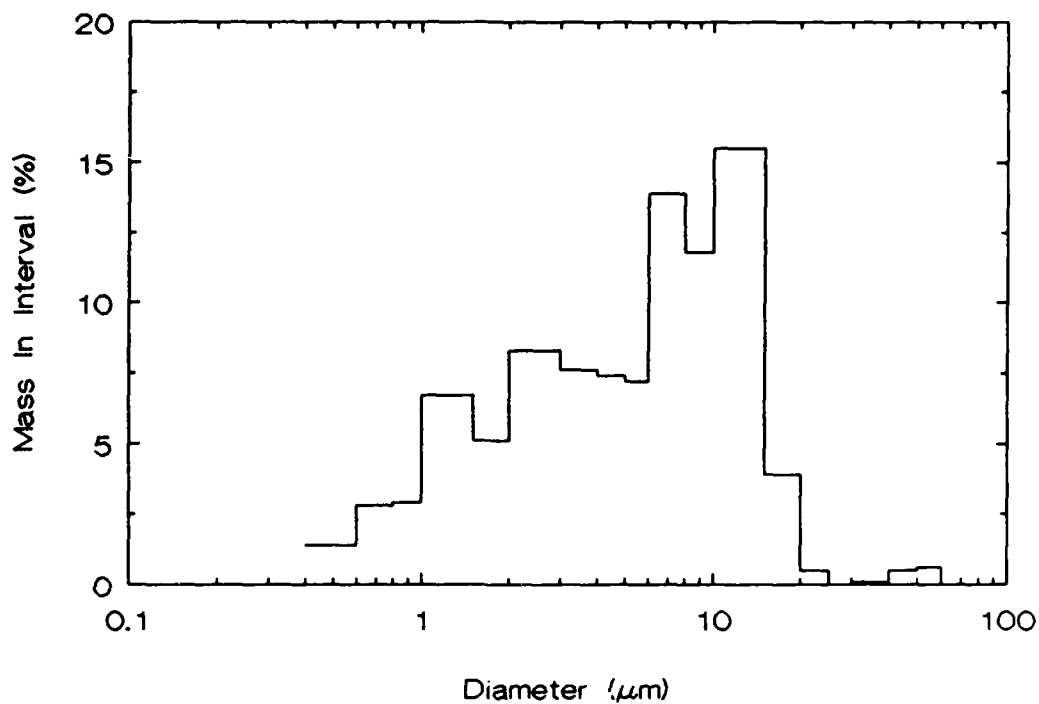


Figure 2: Mass Distribution of RuO_x Particulates Measured by Gravity Sedimentation

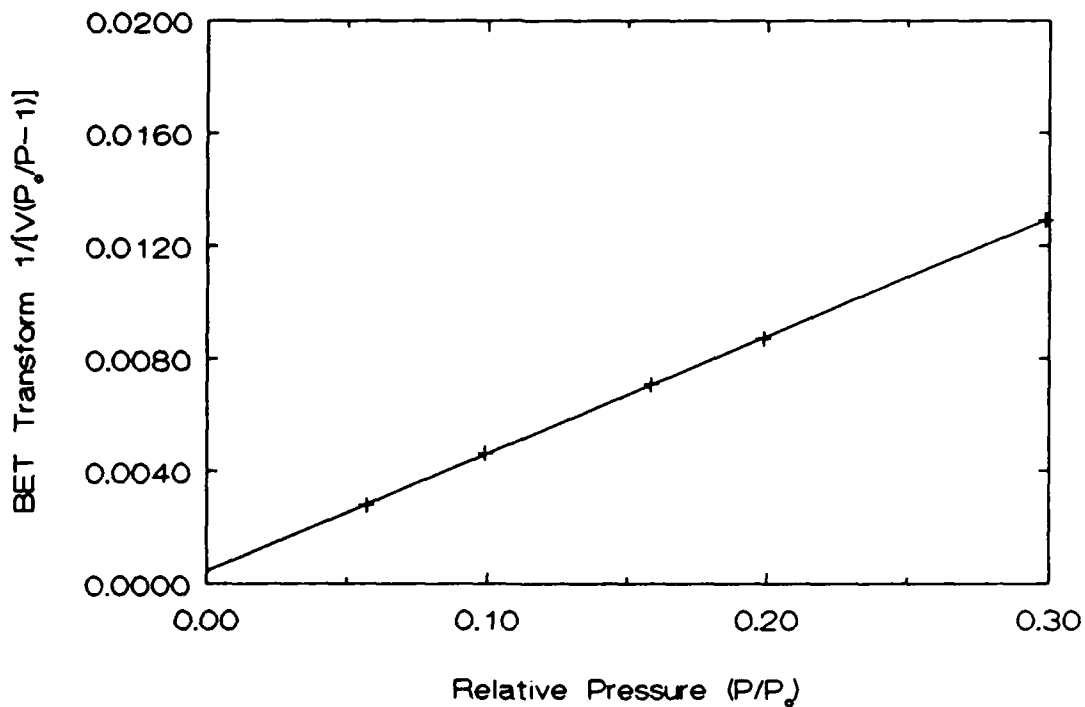


Figure 3: BET Transform vs. Relative Pressure for Nitrogen Adsorption on RuO_x

The total pore volume and pore size distribution were measured by the method of Barrett, Joyner, and Halenda (BJH method). Figure 4 is a plot of pore volume vs. pore diameter. The size range of pores accessible by nitrogen porosimetry is 17 to 3000 Å. The volume of pores in this range is 0.260 cm³/g. This is close to the 0.258 cm³/g measured by mercury porosimetry (30 Å to 120 μm diameter range) and is close to the 0.235 cm³/g measured by Balko, et al. (1980) for RuO_x similarly prepared.

Figure 5 is a plot of cumulative surface area vs. pore diameter. The surface area in pores greater than 200 Å in diameter is less than 10 m²/g. Most of the surface area is in pores less than 100 Å in diameter. The average pore diameter is about 100 Å.

The morphology of porous aggregates of RuO_x crystallites is expected from the synthesis of a dense material (6.67 g/cm² for RuO_x) from a less dense material (3.11 g/cm³ for RuCl₃). The measured pore volume of 0.26 cm³/g is about 30% greater than the difference in specific volumes of the two materials of 0.18 cm³/g. Oxides, when synthesized from their corresponding hydroxides, have pore volumes close to (or less when pores are closed off) the difference in specific volume between the precursor of the product. This means that the transformation is more complex than a simple pseudomorphic, topotatic transformation. This is not surprising because the transformation of RuCl₃ into RuO_x involves the incorporation of oxygen into the lattice and a change in oxidation state.

In order to make use of the surface area of the RuO_x electrode material, the electrolyte must penetrate into the pores. Small electrolytes such as H₂SO₄ and associated water molecules have effective diameters of less than 20 Å and could effectively contact all of the surface area of the RuO_x porous aggregates. The 1100 EW Nafion electrolyte is much larger; an effective size of over 200 Å has been reported for the solubilized form (Aldebert, et al., 1986). The Nafion electrolyte may not be able to penetrate into the RuO_x pores. This is the same conclusion as reached in the 4th Quarterly Report on the basis of the mercury porosimetry results.

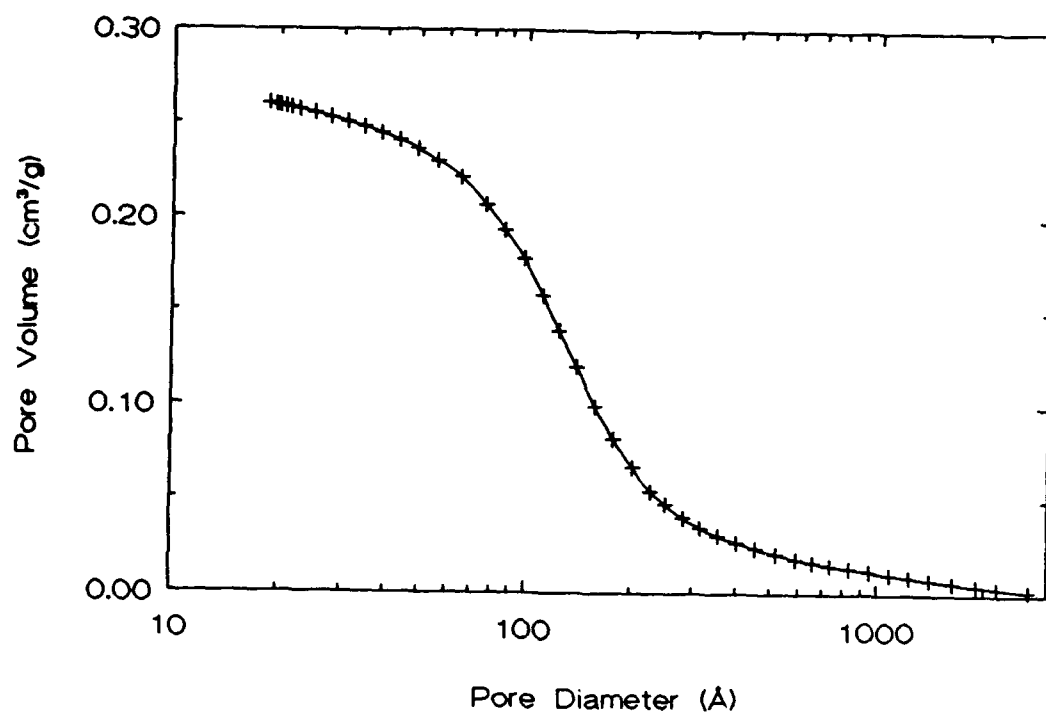


Figure 4: Cumulative Pore Volume vs. Pore Diameter for RuO_x Prepared by the Thermal Method

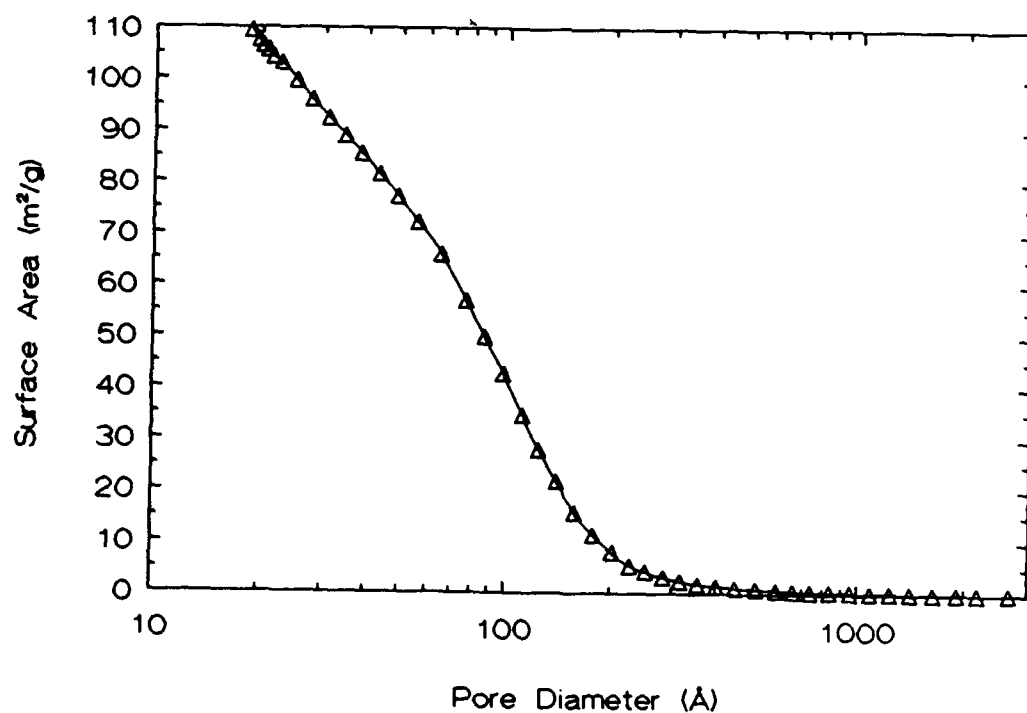


Figure 5: Cumulative Surface Area vs. Pore Diameter for RuO_x Prepared by the Thermal Method

3.2 Cell Testing

3.2.1 Capacitance

Capacitance of the M and Es made on the different backing layers, using the modified Giner, Inc. proprietary method, was measured by charging the M and E, discharging through at 10 ohm resistor, and dividing the total charge by the initial voltage (see the 5th Quarterly Report for a derivation) to obtain the capacitance. Table II lists the measured capacitances. M and Es fabricated using the RuO_x-Nafion mixture on Black Pearls carbon had significantly higher capacitance than those saturated with PANEX or Vulcan XC-72 backings. When Nafion 111 (0.001 inch thick) or a Dow membrane was substituted for the standard Nafion 117 membrane, the capacitance remained greater than 1 F/cm². A control M and E with Black Pearls electrodes painted with Nafion, but with no RuO_x had a capacitance of only 0.16 F/cm². Therefore, the RuO_x layer makes a significant contribution to the capacitance of the M and E. Heat treated Black Pearls also gave an M and E with high capacitance but not as high as plain Black Pearls.

Table II: Capacitance of M and Es Discharging Through a 10-ohm Resistor

M and E	Backing Layer	RuO _x Loading (mg/cm ²)	Membrane	Capacitance (F/cm ²)
369-62-1	Black Pearls	15,20	Nafion 117	1.20
369-69-1	Black Pearls	15,15	Nafion 117	0.57
377-32-1	Black Pearls	19.5,22.3	Nafion 117	1.15
377-32-5	Black Pearls	15,16.5	Nafion 117	1.33
369-92-1	Black Pearls	16.5,17	Nafion 111	1.17
377-38-4	Black Pearls	15,18.4	Dow	1.13
369-64-1	Black Pearls	0,0	Nafion 117	0.16
377-49-1	HT Black Pearls	13.3,18	Nafion 117	0.84
69-63-1	PANEX		Nafion 117	0.59
69-65-1	PANEX	10,12	Nafion 117	0.46
369-66-1	Vulcan XC-72 /PANEX	15,15	Nafion 117	0.57
369-65-2	Black Pearls ⁺	20,20	Nafion 117	0.90
369-65-3	Black Pearls [*]	15,15	Nafion 117	0.58

⁺ slurry cast

^{*} with Ru black layer on membrane

The origin of the higher capacitances of the Black Pearls M and Es is not well understood at this time. One idea that can be advanced is that painting on the Black Pearls carbon allows a

better dispersion of RuO_x aggregates and, therefore, better contact between the RuO_x and Nafion is achieved. This would be especially true if, as postulated in the previous section, the Nafion coats the outside of the porous aggregates and does not penetrate significantly into their interior.

Another area requiring explanation is the magnitude of the capacitances obtained with the M and Es. If we assume that the RuO_x powder has a surface area of $100 \text{ m}^2/\text{g}$ and the electrode loading is $15 \text{ mg}/\text{cm}^2$, then the electrode roughness factor is 15,000. The double layer and pseudo capacitance on RuO_x is on the order of $150 \mu\text{F}/\text{real cm}^2$ (Kleijn and Lyklema, 1987). This means the capacitance per electrode should be $2.25 \text{ F}/\text{geo-cm}^2$ or per M and E $1.125 \text{ F}/\text{geo-cm}^2$ (two electrodes in series). Since this is near the capacitances measured, either the surfaces of the pores of the RuO_x can charge up or bulk RuO_x is being utilized in charge storage. Both these explanations are consistent with the multiple time constants inferred from the AC impedance and resistive load discharge experiments reported previously.

3.2.2 Internal Resistance

The internal resistance of the cell (or cell stack) will ultimately limit the rate at which power can be delivered. Consider the circuit given in Figure 6. Here the device is considered to be a capacitor with capacitance C and internal resistance R_i . It discharges through a load with resistance R_L . The total resistance R_t is the sum of R_i and R_L . The power delivered to the load is the product of current and voltage:

$$P = iV = \frac{V_o^2 R_L}{R_t^2} \exp(-2t/R_t C)$$

This can be integrated to give the energy delivered to the load after a time t_p :

$$E_L = \frac{1}{2} V_o^2 C \frac{R_L}{R_t} [1 - \exp(-2t_p/R_t C)]$$

This equation demonstrates that the energy delivered in time t_p will be decreased due to R_t being greater than R_L .

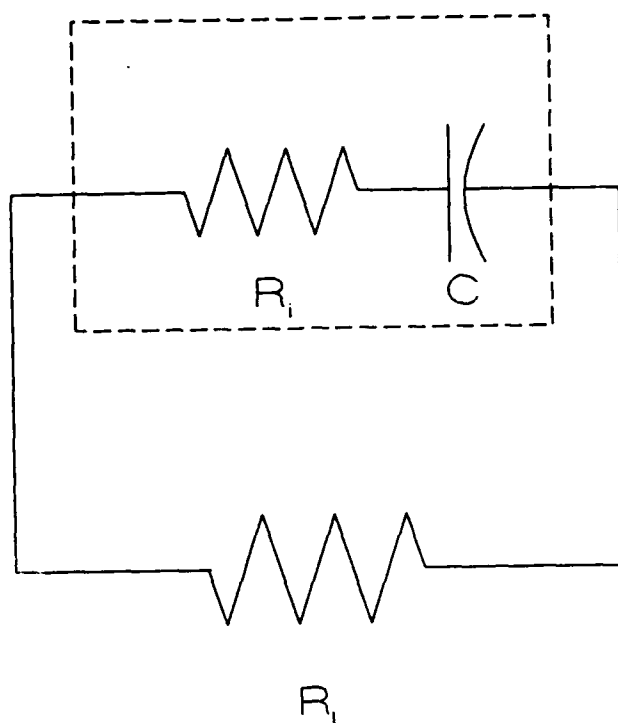


Figure 6: Equivalent Circuit of a Capacitor with Capacitance, C , and Internal Resistance, R_i , Discharging Across a Load Resistance, R_L

As a hypothetical example, consider the case where $C = 0.33\text{F}$, $V_o = 8\text{V}$, $R_L = 1\text{ ohm}$ and $t_p = 1\text{ sec}$. The DC energy storage of this capacitor is 10J and 9.98J can be delivered to this load in 1 second if $R_i = 0$. Figure 7 shows how the energy delivered to the load declines with increasing internal resistance. With a $100\text{ m}\Omega$ internal resistance only 9.06 J can be delivered, and if the internal resistance is doubled to $200\text{ m}\Omega$ then only 8.29 J can be delivered.

Table III lists the resistance of some M and Es made during this quarter. The acrylic cell hardware (Figure 1 of the 3rd Quarterly Report) was used to hold the M and Es and current interruption was used to measure the resistance. The resistance of an M and E with a Nafion 117 membrane ($178\text{ }\mu\text{m}$ thick) is 0.375 ohm-cm^2 . The membrane resistance (for a membrane equilibrated at 100°C with water) should be 0.22 ohm-cm^2 at 25°C . The resistance of the M and E with the Nafion 111 membrane ($25.4\text{ }\mu\text{m}$ thick) is 0.275 ohm-cm^2 which is far from the factor of seven reduction expected if the electrolyte resistance is the controlling factor.

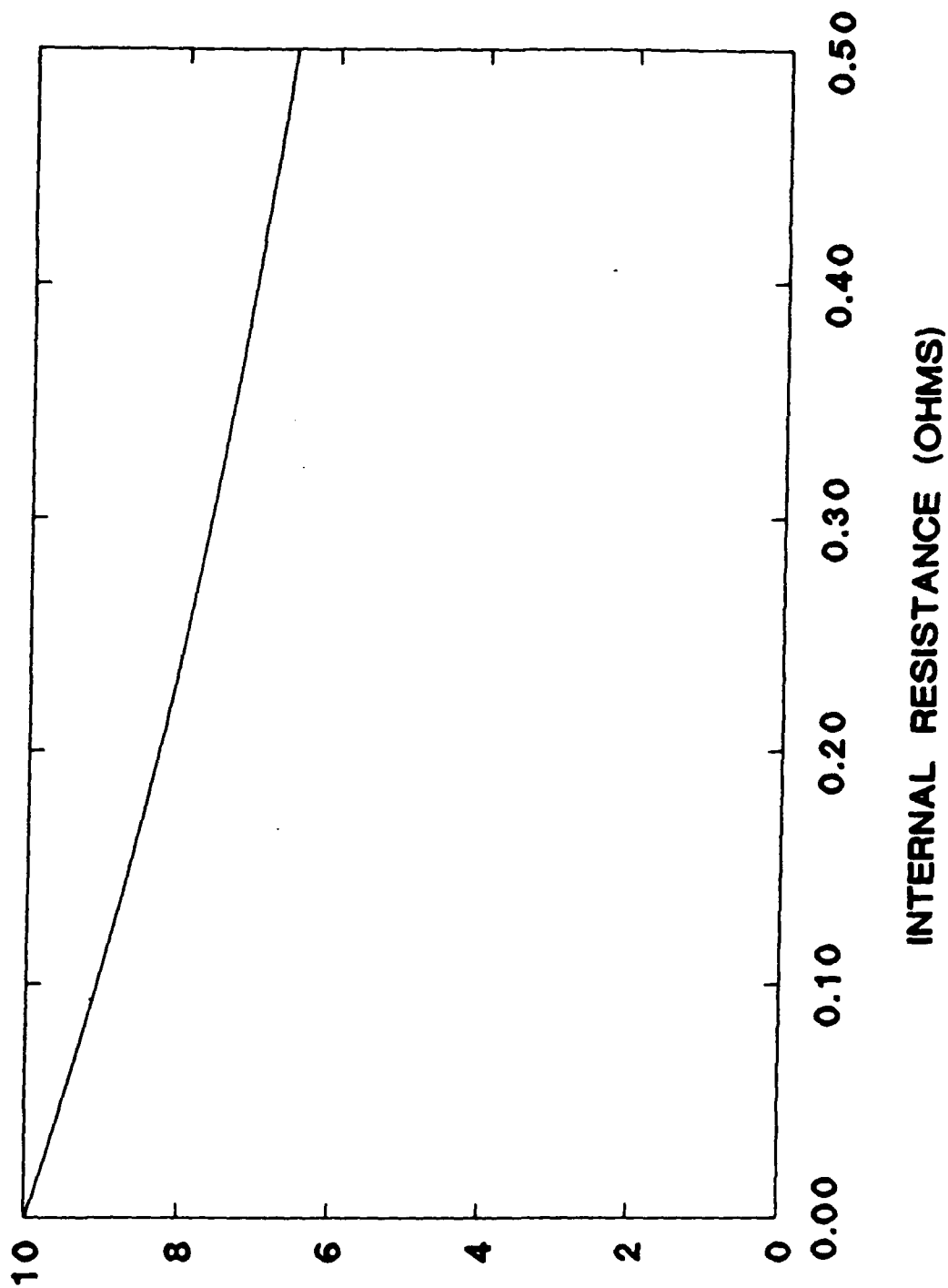


Figure 7: Energy Delivered vs. Internal Resistance for an 8 V, 0.33 F Capacitor

Table III: Resistance of M and Es

M and E	Backing Layer	Membrane	Resistance (ohm/cm ²)
369-32-1	Black Pearls	Nafion 117	0.375
369-32-5	Black Pearls	Nafion 117	0.375
377-92-1	Black Pearls	Nafion 111	0.275
377-38-4	Black Pearls	Dow	0.300

These results point to other factors other than the electrolyte membrane resistance as contributing to the resistance of the cell. These other resistances can include contact resistances between the electrode and cell plates, contact resistance between the electrode and membrane, and electrode resistance.

3.2.3 Long-Term Testing

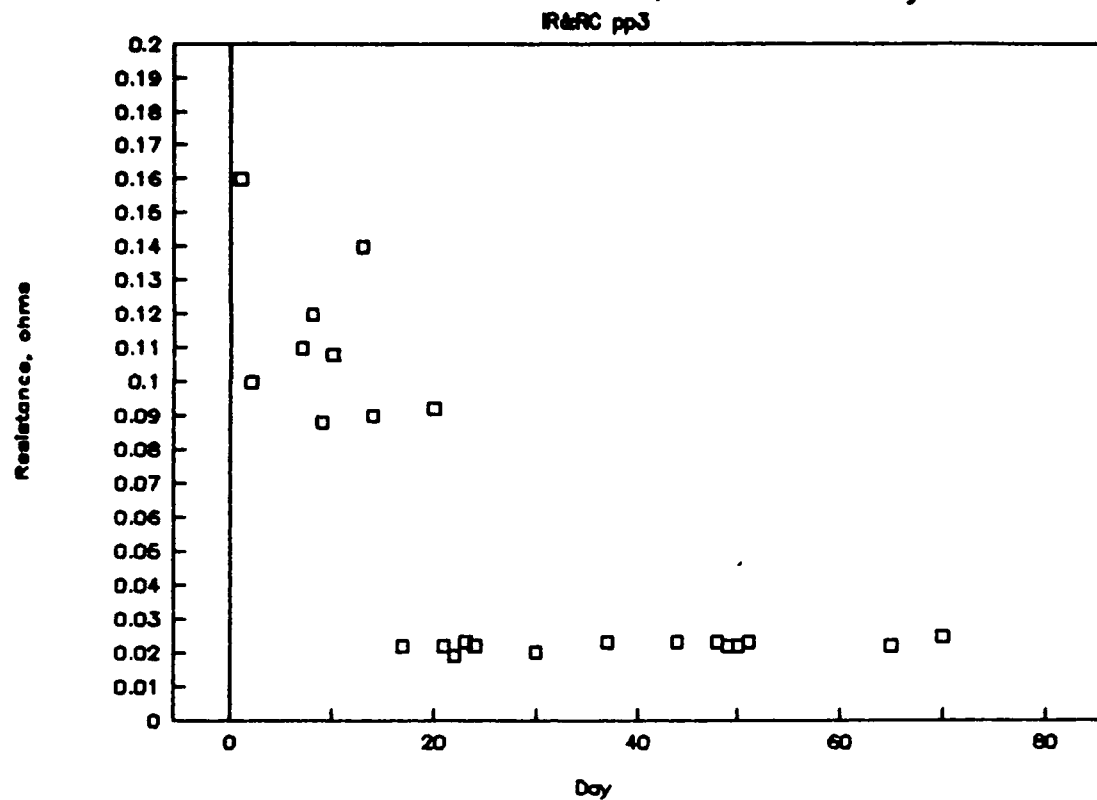
M and Es were tested for variation in capacitance and internal resistance with time using the cell hardware with polymeric end plates. Figure 8a is a plot of internal resistance vs. time for an M and E made by the transfer from metallic foil technique. The higher resistance of the first 20 days is due to using test clips that contributed to the measured resistance. After changing to spade lug connections, the resistance dropped to 0.02 ohms (0.5 ohm-cm²). It has remained stable near that value for over two months demonstrating that loss of water (by membrane dehydration), which would lead to higher resistance, is not taking place. The capacitance (Figure 8b) shows somewhat more scatter, but also remains nearby constant with time.

4. FUTURE WORK

Cell internal resistance has been identified as a factor that will limit useful power output of the capacitor cells. Studies are being conducted to determine how the different components and component interfaces contribute to the cell internal resistance. Internal resistance and capacitance will also be studied as a function of temperature.

The titanium cell hardware (Figure 1) is an appropriate vehicle for building multi-cell stacks. Multi-cell stacks will be fabricated and evaluated for capacitance, internal resistance and charge retention.

25cm² PP Cell – R,ohms vs Day



25cm² PP Cell – Capac, F/cm² vs Day

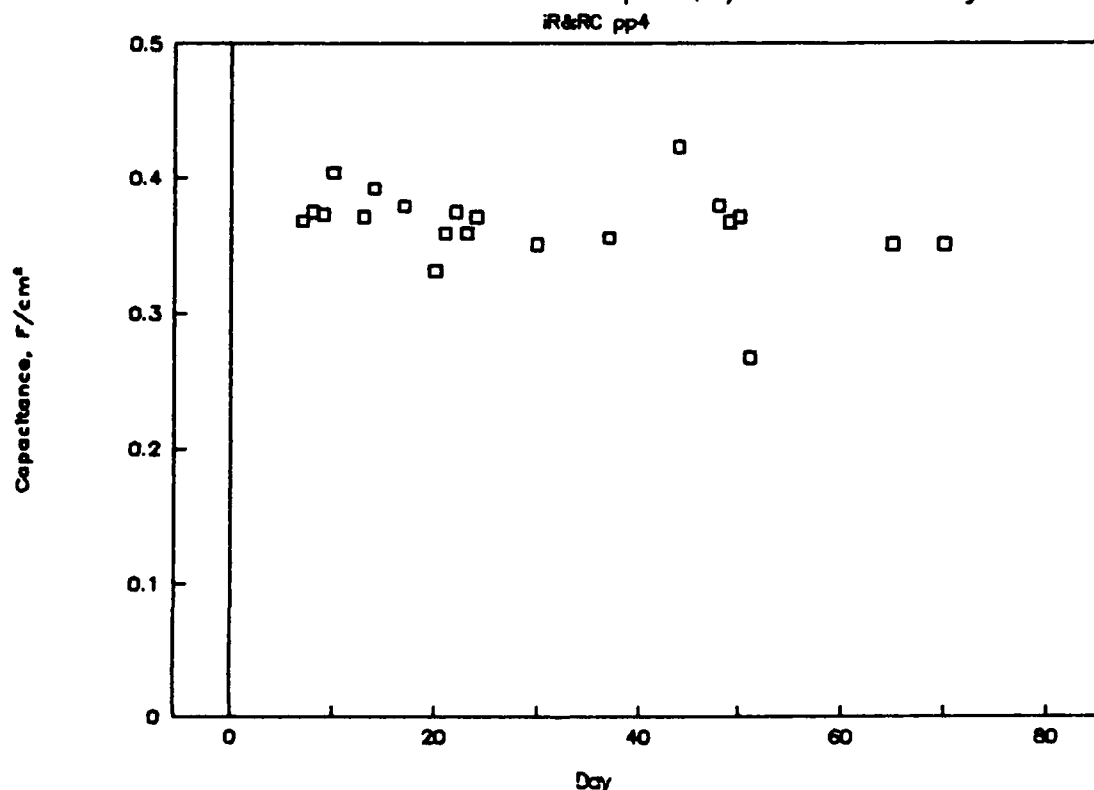


Figure 8: M and E in a 25 cm² Cell with Polypropylene End Plates
a) Internal Resistance vs. Time
b) Capacitance vs. Time

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