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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 7th Quarter, we have concentrated our efforts in three areas: 1) preparation of single-cell and multiple-cell stacks, 2) understanding the origin of internal resistance in single-cell and multiple-cell stacks, and 3) measurements of the temperature characteristics of a single cell.

2. EXPERIMENTAL METHODS

2.1 Preparation of Electrode Materials

Electrode materials were prepared by the standard thermal process.

2.2 Preparation of M and Es

M and Es were prepared by procedures developed during the previous two quarters.

2.3 Cell Hardware

Titanium cell hardware was modified for temperature experiments by drilling a thermocouple well into the plates. Silicone heating pads were fastened to each plate and the temperature of the cell was controlled using a temperature controller.

We continued to use Teflon as a gasketing material. Both TFE and FEP materials have been used. Two methods of applying the gaskets have been used. In one method, the membrane is trimmed so that it is the same size as the electrodes. A single gasket surrounds the membrane and electrode assembly (M and E) and is used to seal the cell. The cell assembly resembles Figure 1 in the 6th Quarterly Report.

The second gasketing method uses three separate gaskets. For a 2 x 2 inch M and E, the membrane is cut to be 0.125 inch larger than the electrodes on all four sides. Two electrode gaskets (with 2" x 2" square holes) and one membrane gasket (with a 2 1/4" x 2 1/4" square hole) are used for each M and E assembly.

Multiple cell stacks were fabricated during the 7th Quarter. Each M and E for the multiple cell stack was fabricated individually. Figure 1 shows how the M and Es were assembled into a multiple cell stack. The M and Es were gasketed using the three gasket method. A 0.001" thick Pt-plated Ti bipolar separator element was placed between each M and E. The M and Es were stacked between the endplates and compressed together using insulated bolts.

2.4 Cell Testing

Single cells and multiple cell stacks were tested for capacitance, energy storage, and internal resistance using procedures described in the 5th and 6th Quarterly Reports.

2.5 Electrode Resistance Measurements

The DC resistance of electrode plaques was measured. Coupons of 5 mm diameter were punched from electrodes and their resistance measured between stainless steel rams.

3. RESULTS AND DISCUSSION

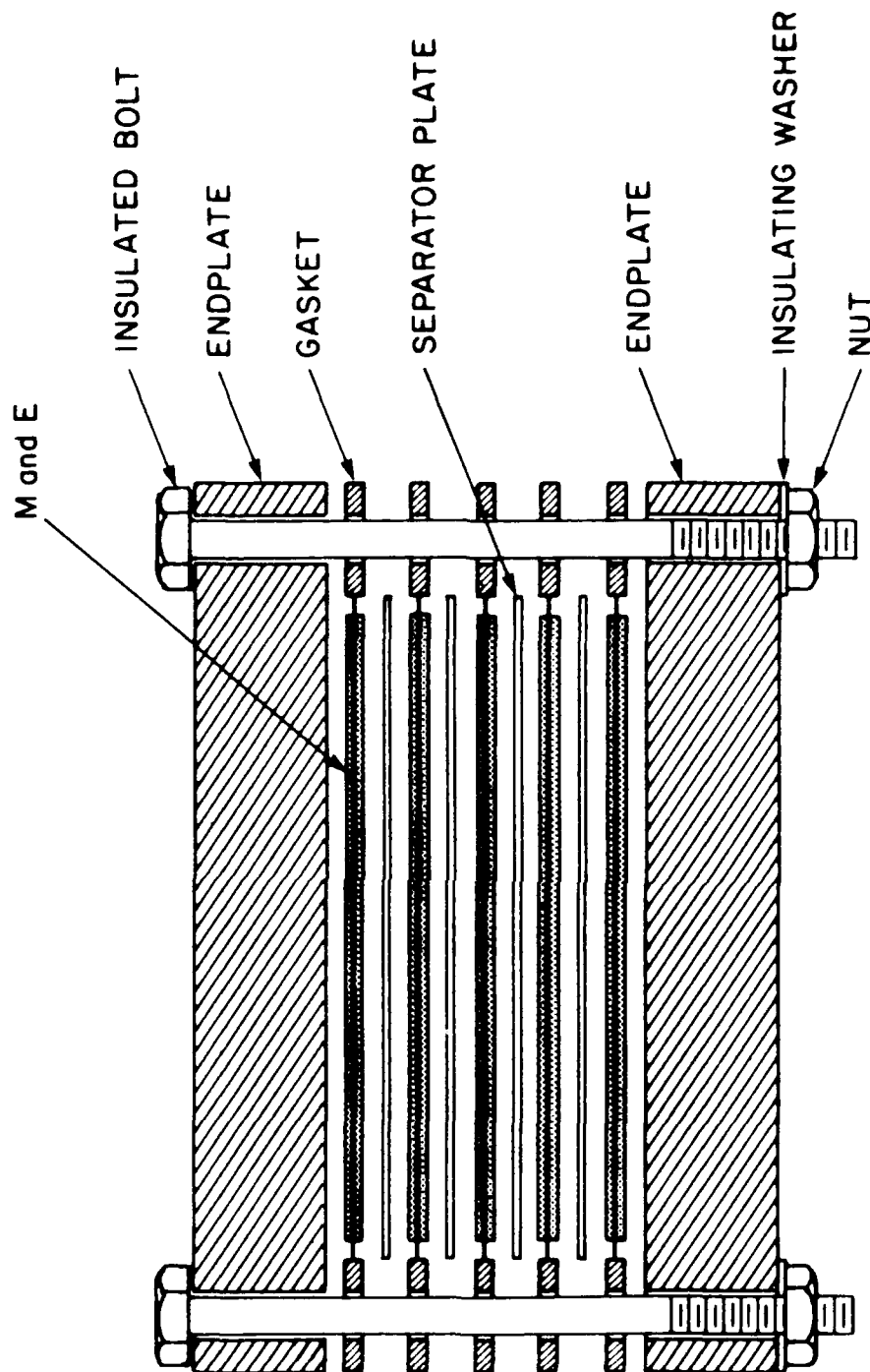
3.1 Multiple Cell Stacks

A three-cell and five-cell stack were built and tested during the 7th Quarter. The performance characteristics of these multiple cell stacks are given in Table I:

TABLE I: PERFORMANCE OF MULTIPLE CELL STACKS

Number of Cells	Membrane	Capacitance* (F/cm ²)	Internal Resistance (ohm-cm ²)
3	Nafion 117	0.253	0.900
5	DOW	0.17	0.625

*Discharge through a 10-ohm load



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Figure 1: Multiple Cell Stack Assembly

All electrodes were RuO_x -10% Nafion on a platinum-plated titanium/heat-treated Black Pearls substrate. M and Es were 25 cm² size. The stacks were assembled as shown in Figure 1. The cell stack was compressed to 80 in.-lbs. using insulated bolts.

Figure 2 shows the initial portion of the discharge curve for the 5-cell stack discharging through a 1-ohm load. During the first one second, the cell delivered over 14 joules of energy to the load.

The capacitance and internal resistance of the individual cells in the stacks were not measured. A comparison can be made with single cell performance by assuming that the cells act as capacitors and resistors in series and that each cell in the stack has identical characteristics. The individual cell capacitance can then be calculated as:

$$C_i = N \times C_t \quad [1]$$

and the individual cell resistance as:

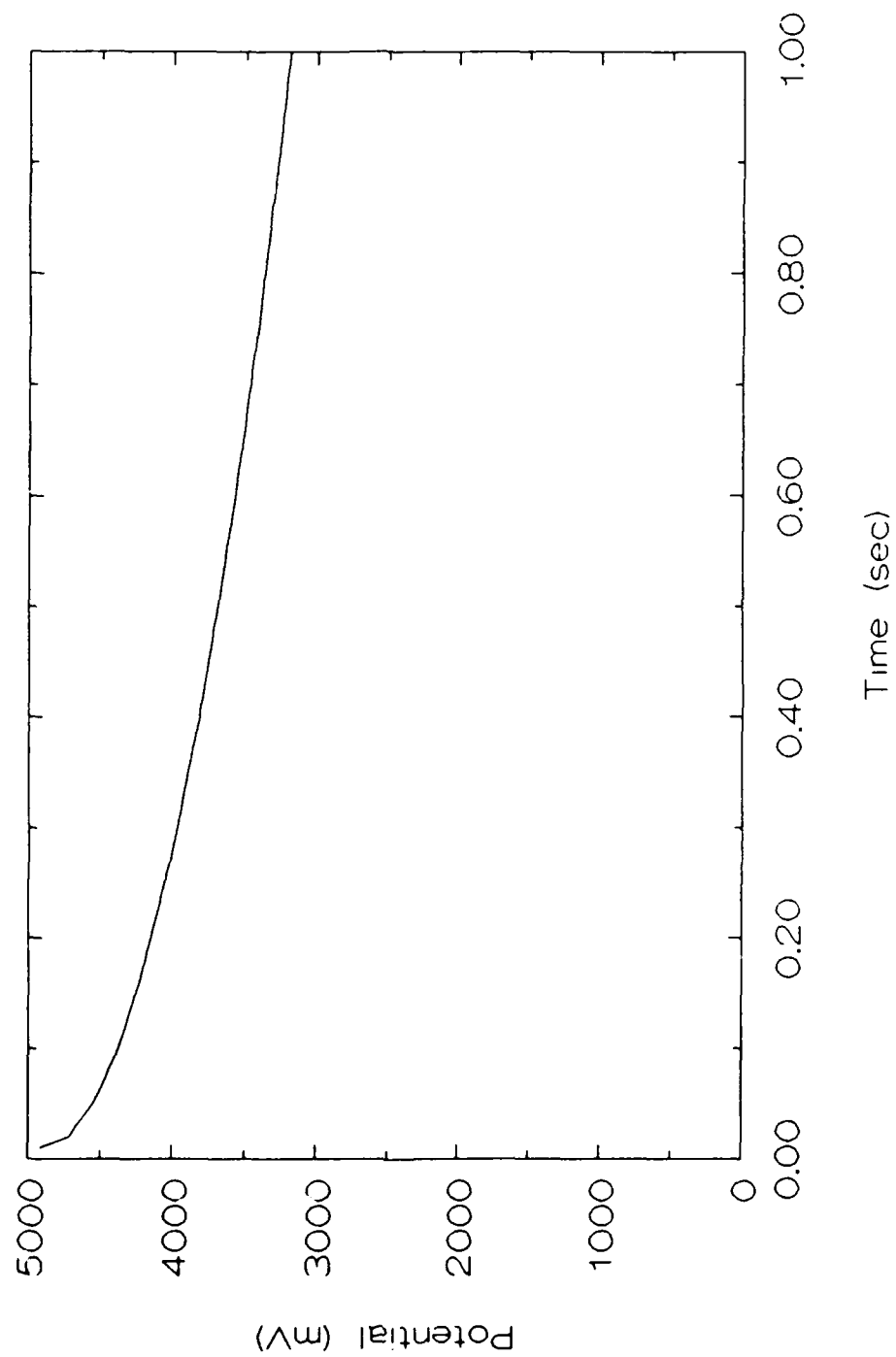
$$R_i = \frac{R_t}{N} \quad [2]$$

where N is the number of cells. Table II compares the calculated performance of the single cells in the multiple cell stacks with previously measured performance of a single cell.

TABLE II: COMPARISON OF PERFORMANCE (PER M and E)

Cell	Membrane	Capacitance (F/cm ²)	Internal Resistance (ohm-cm ²)
Single cell in 3-cell stack	Nafion 117	0.76	0.3
Single cell in 5-cell stack	DOW	0.85	0.125
377-49-1 single-cell stack	DOW	0.84	0.32

The capacitance of a single cell in the 5-cell stack is within 1.2% of the capacitance of a previously measured single cell, 377-49-1. The capacitance of the single cell in the 3-cell stack is



**Figure 2: Initial Portion of Discharge for 5-Cell Stack
Through a 1-ohm Load**

about 9.5% less than the capacitance of the previously measured single cell. This can be ascribed to variations in the loading of RuO_x on the electrodes. The resistance of each cell in the five-cell stack is less than the single cell tested previously. This is due to improvements in M and E production technique leading to a more uniform M and E which makes better contact with the cell and end plates.

Figures 3a and 3b and 4a and 4b show the time dependence of capacitance and internal resistance for the 3-cell and 5-cell stack respectively. Over an 80-day period, the capacitance and internal resistance of the 3-cell stack remained level. The same conclusions hold for the 5-cell stack over a 50-day period.

3.2 Temperature Effects

The capacitance and internal resistance of an M and E were studied as a function of temperature from 25 to 95°C. Figure 5a is a plot of logarithm of internal resistance versus reciprocal absolute temperature. The data points can be fit to the equation

$$R_{\text{cell}} = 0.010525 \exp \frac{2102}{RT} \quad [3]$$

with a high degree of correlation. The dotted line in Figure 5a shows the resistance of Nafion 117 which is represented as (LaConti, 1980)

$$R_{\text{Nafion}} = 0.00487 \exp \frac{2160}{RT} \quad [4]$$

The activation energy for Nafion 117 resistance is with 3% of the measured activation energy for cell resistance. Thus, cell resistance changes with temperature are dominated by the changes in electrolyte resistance with temperature. This is the same behavior as reported for electrochemical capacitors using a sulfuric acid electrolyte (Tong, et al., 1988). The higher resistance of the complete M and E as compared to the Nafion 117 electrolyte is due to contact resistances in the system.

The variation of capacitance with temperature is shown in Figure 5b. There is approximately a 100% increase in capacitance when going from 25°C to 95°C. The variation of capacitance with temperature can be written as:

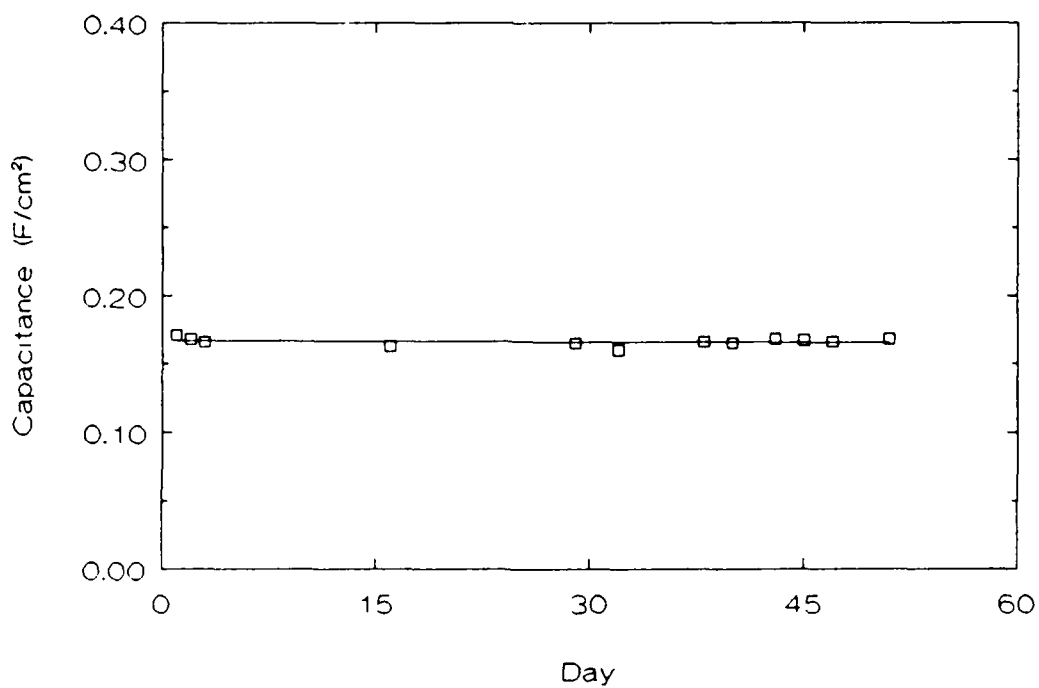
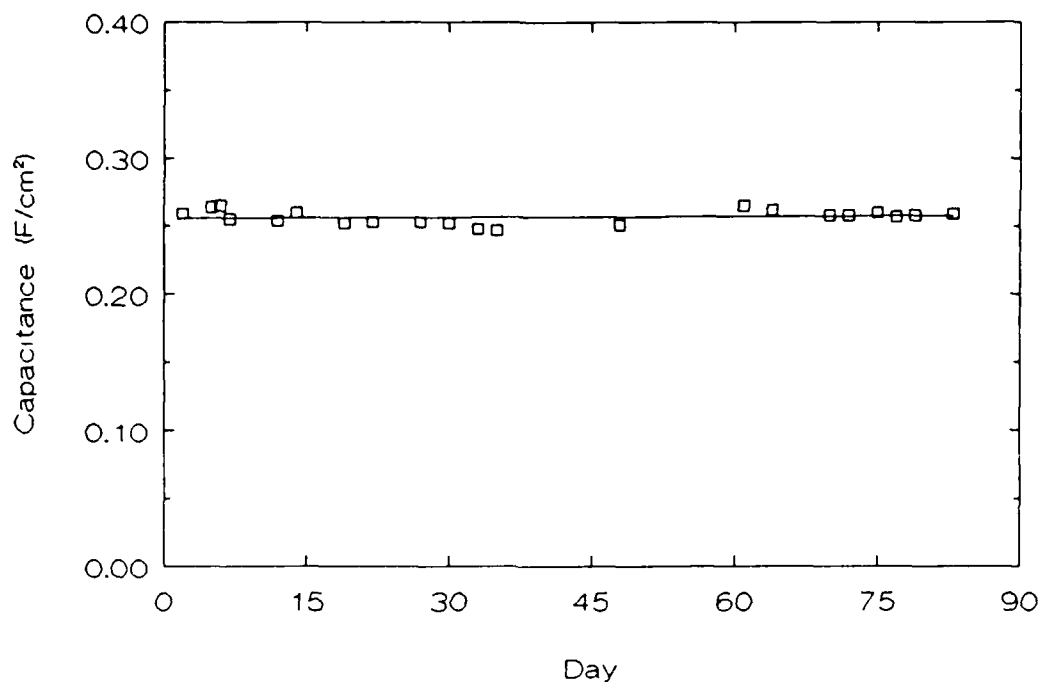


Figure 3: Capacitance as a Function of Time
a) 3-Cell Stack, b) 5-Cell Stack

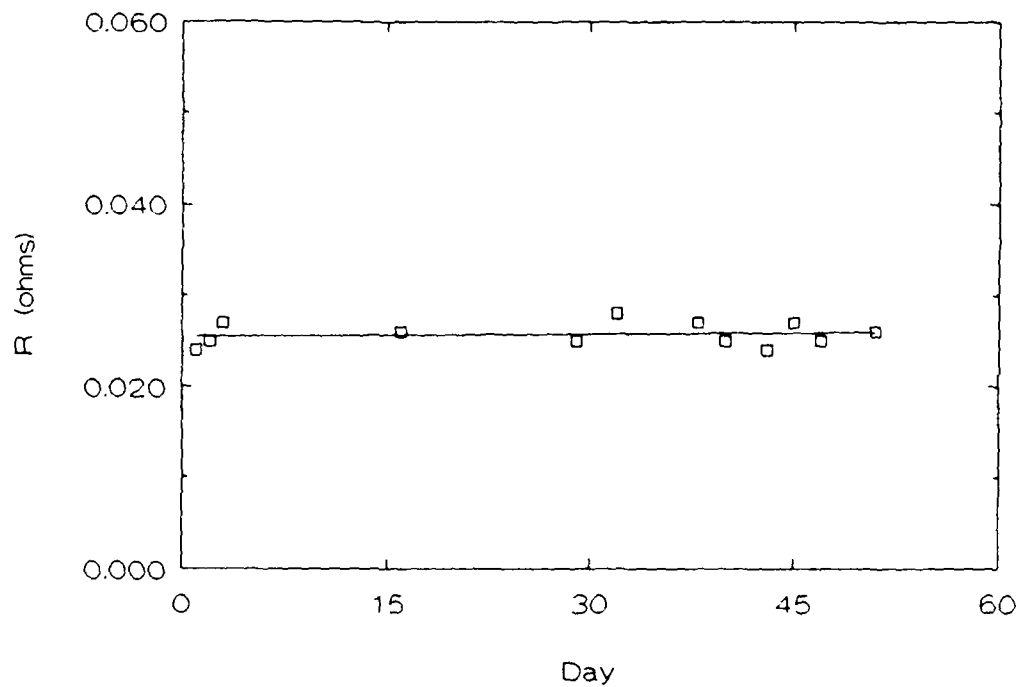
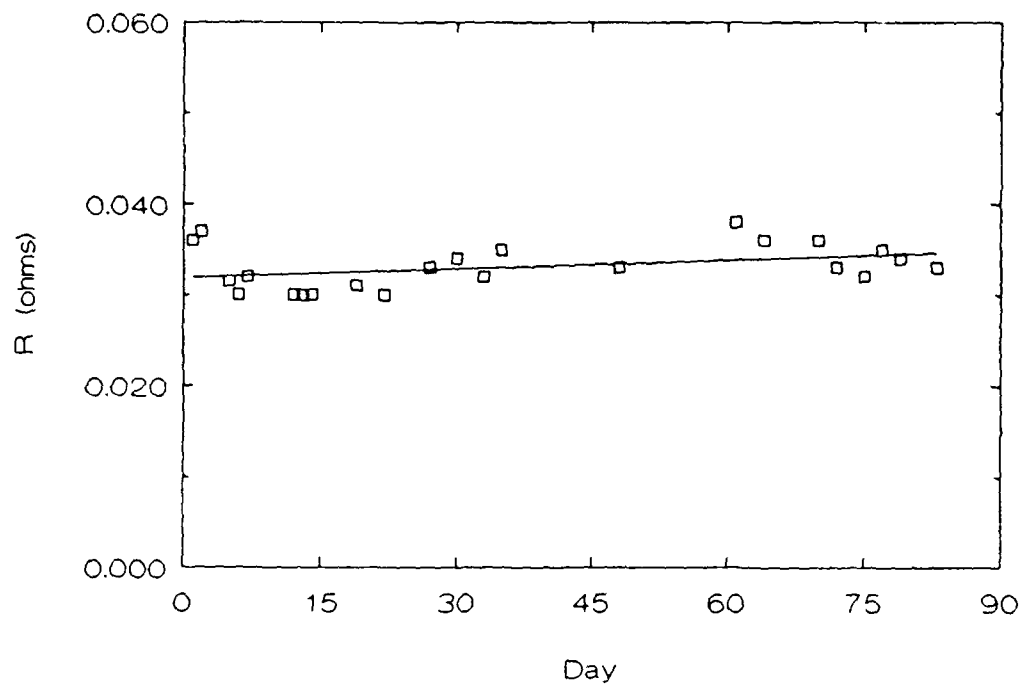


Figure 4: Internal Resistance as a Function of Time
a) 3-Cell Stack, b) 5-Cell Stack

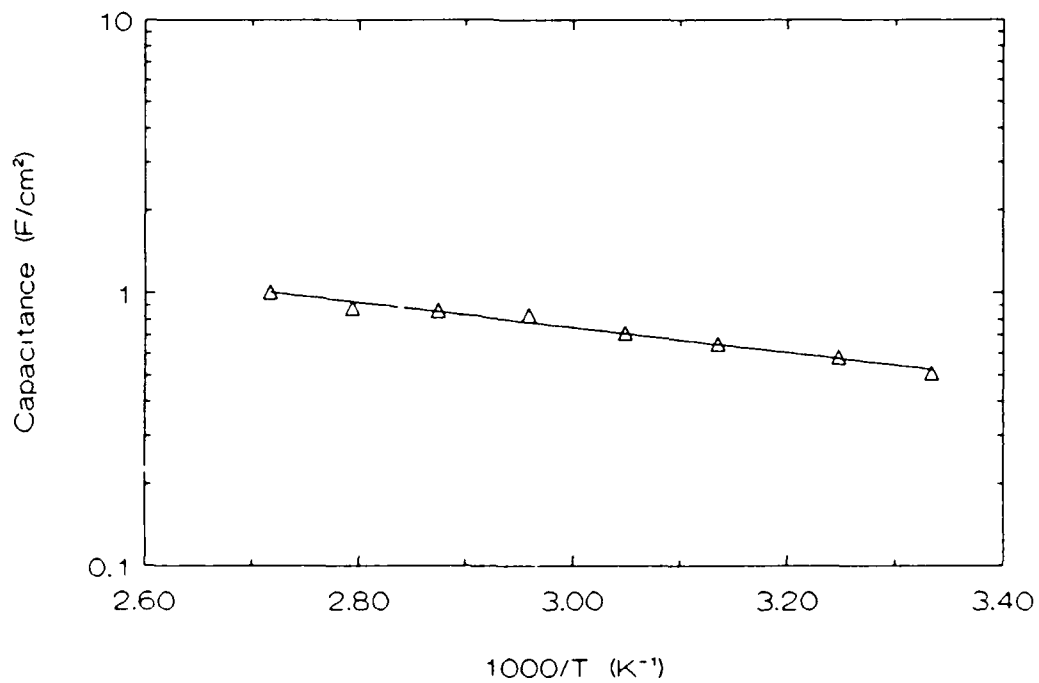
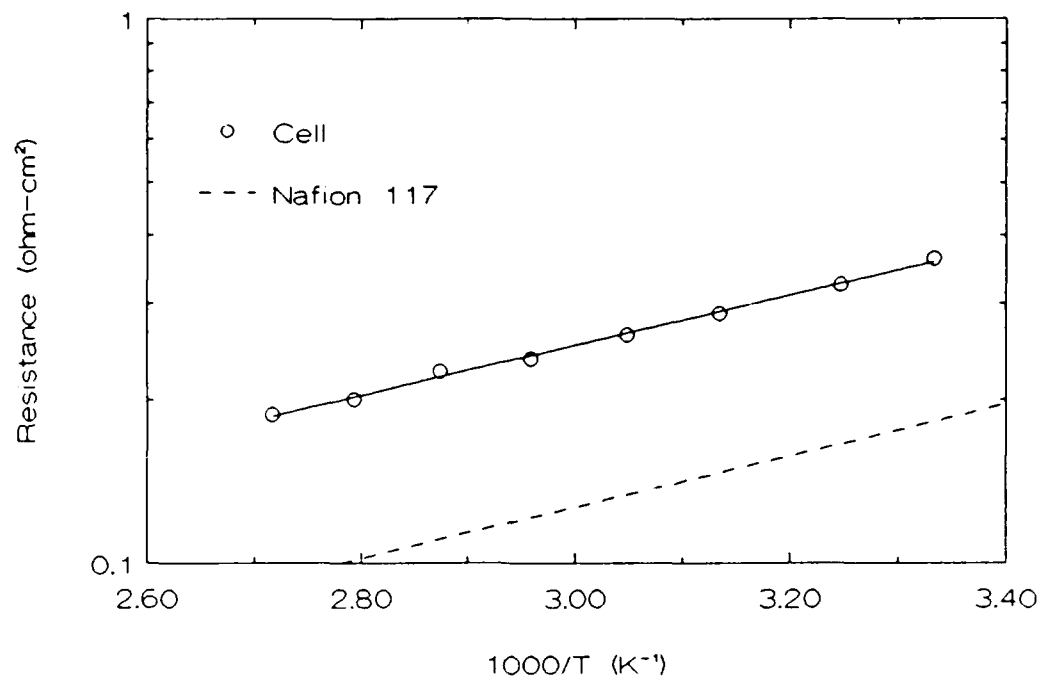


Figure 5: Temperature Effects on Capacitor Cell
a) Internal Resistance, b) Capacitance

$$C = 17.78 \exp \frac{-2099}{RT} \quad [5]$$

This variation of capacitance with temperature is much larger than that reported for sulfuric acid based systems. Pinnacle Research reports a less than 10% change in capacitance between 25 and 80°C (Tong, et al., 1988). The NEC SUPERCAP shows approximately a 12% change between 25 and 95°C (NEC SUPERCAP data sheet for FAOH105Z device). The larger variations in capacitance observed with the solid ionomer device is most likely due to a diffusional limitation on charge access. A diffusional limitation is suggested based on the activation energy of 2.1 kcal. Proton transport from the active RuO_x sites to the electrolyte may be the limiting step. There are not enough sulfonic acid groups to completely cover every RuO_x surface site. Therefore, when the RuO_x undergoes a redox reaction, the protons hop from the RuO_x surface site to the electrode-electrolyte interface.

The cell was held at 95°C for three days. Over that period, the cell resistance remained at 0.175 ohm-cm². The gasketing was therefore effective in preventing the cell from losing water at this elevated temperature.

3.3 Internal Resistance

RuO_x -10% Nafion (15-20 mg/cm²) on a heat-treated Black Pearls-platinum-plated titanium current collector has been adopted as a standard electrode. With these electrodes bonded to a Nafion 117 membrane, an internal resistance of 0.38 to 0.50 ohm-cm² for a single cell is obtained. With the 4-mil DOW membrane, the internal resistance ranged from 0.19 to 0.30 ohm-cm² for a single cell. When three M and Es made on Nafion 117 were assembled into a cell stack, the internal resistance of the stack was 0.90 ohm-cm² or 0.30 ohm-cm² per M and E. For a five-cell stack made with a Dow membrane M and Es, an internal resistance of 0.625 ohm-cm² was measured or 0.125 ohm-cm² per M and E. The M and E resistance varies over a range. The multiple-cell stacks show a lower resistance per M and E than a single cell. Changing the gasket thickness from 25 μm to 75 μm less than the M and E thickness results in a 28% decrease in cell resistance. The M and E assemblies show a variation in thickness over the area of the M and E. Since the gasketing (FEP or TFE, Teflon) is relatively incompressible, this may result in parts of the M and E

not being contacted by the end plates. We are beginning to make a systematic study of how these factors (number of cells, gasket thickness, etc.) affect the internal resistance of the capacitor module. The goal will be to develop a design in which the internal contact applied to the M and Es is not dependent on the thickness of the sealing gasket or the force applied to the external gaskets in the seal area.

Measured electrode resistance was less than 0.01 ohm-cm^2 . The resistance of the electrode plaque and support current collector, therefore, contributes negligibly to the cell internal resistance.

4. FUTURE WORK

Decreasing the internal resistance of the cells will continue as an active area of investigation. Methods to reduce contact resistance between the electrodes and membrane will be explored.

Charge retention and leakage current are important cell parameters. We are planning to obtain quantitative data on these next quarter.

5. REFERENCES

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