ADVANCED DOUBLE LAYER CAPACITORS

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Work has been conducted that could lead to a high energy density electro-chemical capacitor, completely free of liquid electrolyte. A three-dimensional RuO_x-ionomer composite structure has been successfully formed and appears to provide an ionomer ionic linkage throughout the composite structure. Capacitance values of approximately 0.6 F/cm^2 have been obtained compared 1 F/cm^2 when a liquid electrolyte is used with the same configuration.

INTRODUCTION

Electrochemical capacitors store energy by utilizing double layer and sur-face redox type processes. Table I compares energy density, power density, and cycle life figures for batteries, electrochemical capacitors, and conventional capacitors. The projected energy density for electrochemical capacitors are two orders of magnitude lower than that of batteries, but power densities (on the millisecond to second) time scale are three orders of magnitude higher. Energy density is much better than for conventional capacitors, but the nature of the electrochemical processes make the electrochemical capacitors suitable for rela-tively long pulses (milliseconds) and low to intermediate power applications.

Table I

Device	Wh/L	W/L	Cycle LIfe
Batteries	50-250	150	$<10^4$
Electrochemical Capacitors	5	$>10^5$	$>10^5$
Conventional Capacitors	0.05	$>10^8$	$>10^6$

Several applications of devices with the characteristics of electrochemical capacitors can be envisioned: lightweight electronic fuses, burst power for battery-powered vehicles and backup power for computer memory. The last appli-cation takes advantage of the high cycle life of electrochemical capacitors, instead of the high power density. Commercial devices, based on high surface area carbons and sulfuric acid and marketed by NEC under the SUPERCAP brand label, are already being sold for this application. Preliminary projections

indicate that the advanced electrochemical capacitors that are being developed will have an order of magnitude higher specific energy and energy density than these carbon-based capacitors.

A simplified equivalent circuit of a single electrochemical capacitor cell is shown in **Figure 1**. A device consists of two electrodes separated by an electrolyte. Capacitances for metals and carbons in contact with aqueous solutions are 10-40 microfarads/real cm^2. Certain noble metal oxides in contact with aqueous solutions have capacitances in the range of approximately 150 microfarads/cm^2 (Kleijn and Lyklema, 1987). Materials in contact with organic solvent-electrolytes may also have high capacities. In addition, pseudocapacity due to fast surface redox reactions can contribute to energy storage which is accessible on a similar time scale as double layer energy storage. High surface area porous electrodes can be used to give capacitances up to several farads per geometric cm^2.

The equivalent circuit also illustrates several resistances present in the system. The resistance in parallel with the capacitance represents a leakage path. It should be as high as possible. The series resistance between the electrodes ultimately limits the power that can be delivered by the system. The major contributor to this is the resistance of the electrolyte between the electrodes. In addition, for practical systems using porous electrodes, the distributed electrolyte resistance in the electrode contributes to the series resistance.

Because of the decomposition of water, aqueous-based devices are limited to about 1 V per cell; organic-based devices may have higher cell voltages because organic solvents have higher decomposition voltages. To build up the voltage, several cells need to be stacked in series.

These physical principles provide an explanation for some of the figures of merit listed in Table I. Energy density of electrochemical capacitors is lower than that of batteries because the capacitors use surface processes to store energy instead of bulk processes. However, these surface processes are accessible on a much shorter time scale than bulk processes giving the electrochemical capacitor a higher power density. Cycle life is greater than that of batteries because the surface processes result in no or small morphological changes in the material. In a sense, the electrochemical capacitor can be thought of as a specialized type of battery.

Some work has been conducted in the development of solvent-electrolyte-based electrochemical capacitors (Holleck,et al., 1988; Lee, et al., 1988). A problem with these systems is the possibility of electrolyte leakage. This can occur because of external pressure changes or gas evolution due to cell overcharge. The typical sulfuric acid electrolyte (3 to 4M H_2SO_4) is very corrosive and leakage could cause the module and ancillary equipment to be damaged or destroyed. This has led us to investigate devices where the liquid electrolyte is replaced by a solid ionomer electrolyte. Perfluorosulfonated ionomer electrolytes, such as Nafion[R], consist of a perfluoro polymer backbone to which sulfonic acid sites are permanently anchored. The only liquid or vapor present in these devices would be pure water.


(R) E.I. DuPont Trademark

The device concept is shown in **Figure 2**. The capacitor electrodes (high surface area metal oxides) are separated by thin sheets of ionomer membrane. Current collection is accomplished via lightweight foils or screens. The configuration allows the individual cells to be stacked into a module. The repeating element consists of the thin bipolar metal collector in intimate contact with a unitized particulate-solid ionomer composite structure.

The major challenge to be met when replacing the liquid electrolyte with the solid ionomer electrolyte is maintaining a high surface area electrode-electrolyte contact. A liquid electrolyte is sorbed into the macropores of the electrode and micropores down to about 100 Å by capillary action. An illustration of the type of composite that needs to be formed with the solid electrode-solid ionomer electrolyte structure is shown in **Figure 3**. A film of ionomer is needed from the face of the electrode in contact with the ionomer membrane separator extending back into the electrode toward the current collector. The electrode particulates must make intimate electronic contact with each other and with the current collector. Ideally, there is ionomer ionic linkage throughout the thin particulate-solid ionomer composite structure and extends from metal collector to metal collector.

There are several requirements for the electrode material to be used in the electrochemical capacitor. Most importantly, it should have a high double layer capacity and pseudocapacity on a real area basis. In order to have a high capacitance on a geometric area basis, the material should have a high surface area. The material should be able to be fabricated into a porous electrode forming a high surface area interface with the solid ionomer electrolyte and bonded to the ionomer membrane separator.

RuO_2 was selected as the electrode material to be studied initially because it meets all of these requirements. The oxide has a high double layer capacity of about 150 microfarads/real cm^2 (Kleijn and Lyklema, 1987). There is also a substantial pseudocapacity due to the surface reaction which can be written approximately as:

$$2RuO_2 + 2H^+ + 2e^- \longrightarrow Ru_2O_3 + H_2O \qquad [1]$$
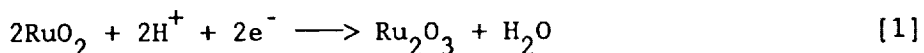
This type of surface reaction in combination with double layer processes has been shown to be capable of sustaining high current densities on the millisecond scale (Holleck, et al., 1988; Lee, et al., 1988). RuO_2 can be made into a high surface area coating (Trasatti and Lodi, 1980) or as high surface area particulates (Balko, et al., 1980). Bonding of particulates to an ionomer membrane has been demonstrated for RuO_2 anodes for use in chlor-alkali cells (Coker, et al., 1980) where membrane and electrode assemblies with active areas of up to 35 ft^2 have been prepared.

EXPERIMENTAL METHODS

RuO_2 was prepared by thermal decomposition of $RuCl_3$ in a $NaNO_3$ flux (Balko, et al., 1980). The resulting powder was characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD) and nitrogen surface area (BET method).

Two approaches were used to form the RuO_2-ionomer composite electrodes:
1) impregnation of a PTFE-bonded RuO_2 electrode with ionomer solution, and
2) mixing of ionomer solution with RuO_2 powder, followed by formation into an
electrode. In all cases, the ionomer solution was 5% Nafion 117 in an alcohol-
water mixture (Aldrich Chemicals).

The RuO_2-Nafion composite electrodes were hot-pressed to a Nafion 117
membrane. A diagram of the test cell is shown in **Figure 4**. The electrode
arrangement for testing consisted of two electrodes pressed on opposite sides
of the membrane. The membrane and electrode (M and E) assembly was held between
two acrylic plates which contained a water reservoir to keep the M and E wet.
A tail of the Nafion 117 membrane dips into a beaker of H_2SO_4 which contains a
Hg/Hg_2SO_4 reference electrode. Some of the M and E assemblies had an integrally
bonded Pt/air reference electrode.

The effectiveness of forming the extended RuO_2-ionomer interface and the
maximum electrochemical limits of operation were assessed by using cyclic
voltammetry. The electrode was cycled between voltage limits where only double
layer and reversible surface redox processes occur. For double layer or surface
processes, the current is related to sweep rate by:

$$i = C \frac{dV}{dt} \qquad [2]$$

where C is the capacitance of the electrode.

RESULTS AND DISCUSSION

Powder X-ray diffraction showed the material to be substantially RuO_2.
There was some undecomposed $RuCl_3$ present. Nitrogen adsorption measurements
gave surface areas near 50 m^2/g. The SEM photograph in **Figure 5** shows the
particles to be pyramid-shaped and on the order of 0.1 to 5 microns in size.
Clearly these surface areas cannot be explained on the basis of impermeable
particles of this size. TEM examination of a 50 m^2/g powder (**Figure 6**) shows
that the particles have considerable internal porosity with crystallites on the
order of 200 Å. Assuming spherical particles of this diameter, the calculated
specific surface area is about 40 m^2/g, which is in good agreement with the
measured BET surface area. This powder was heat treated which reduced its
surface area to 3 m^2/g. **Figure 7** shows that this surface area loss was due to
the loss of the small size particles by sintering. This type of morphology in
the oxide is not unexpected. The density of $RuCl_3$ is 3.1 g/cm^3, while RuO_2 has
a density of 7 g/cm^3. When the decomposition reaction is accompanied by a large
decrease in specific volume (as is the case here) the final products tend to
have the external shape and dimensions of the precursor, but with many small
voids (Volpe and Boudart, 1985). This appears to be the case here.

Voltammograms of a RuO_2 electrode bonded to a Nafion 117 membrane are shown
in **Figure 8**. At potentials more negative than -0.4 V vs. $Hg/HgSO_4$, RuO_2 is
irreversibly reduced to lower oxides (shown as the beginning of a reduction wave
in Figure 8). Above about 0.5 V, oxygen evolution is possible. This gives a
single cell a usable voltage of 0.9 V. In the intermediate region, the voltam-
mogram is fairly flat with peaks due to reversible surface conversion of oxides

as in Reaction 1. Trassati and Lodi (1980) have stated that the oxide cycles between the +3 and +4 states in the region of -0.3 to 0.3 V. The current in the potential region near 0.15 V was plotted against sweep rate to obtain capacitance.

The capacitances of 50 m^2/g powder bonded to the Nafion 117 membrane with no ionomer impregnation are about 0.15 F/cm^2. This capacitance is independent of RuO_2 loading. This is approximately one order of magnitude lower than the capacitance if the electrode was completely flooded with sulfuric acid.

Our most successful attempts to extend the area of electrode-electrolyte contact has been via the technique of suspending RuO_2 in a Nafion solution and spreading it onto the Nafion 117 membrane, followed by evaporation of the solvent. **Figure 9** shows the results obtained by using this technique with a low surface area powder and 5 wt% Nafion in the final electrode. Although the absolute values of capacitances are low, a clear correlation is seen between RuO_2 loading and capacitance. **Figure 10** shows that with a higher surface area powder, similar results can be achieved. Another technique is to form the electrode on a separate thin sheet, followed by transfer to the membrane. Figure 10 shows that this method gives similar results; it is also more amenable for making larger electrodes. Electrodes up to 25 cm^2 have been made with this technique.

SUMMARY

The all-solid electrochemical capacitor concept offers the advantage of greater reliability and safety. If the electrode-ionomer structure can be optimized further and sufficiently thin ionomer membrane separators can be developed, then the energy and power density for the all-solid capacitor should be comparable to other advanced electrochemical capacitors being developed (Lee, et al., 1988 and Table I). The techniques of sealing/water management, thermal management and power transfer/control are expected to be similar to scaled-up all-solid-state proton exchange membrane bipolar electrolysis devices (Coker, et al., 1982). These devices containing up to 100 bipolar elements (0.3 ft^2) have been marketed as reliable devices for over 5 years.

ACKNOWLEDGEMENT

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Volpe, L. and M. Boudart. 1985. Topotactic Preparation of Powders with High Specific Surface area. Catal. Rev. Sci. Eng. 27:515.
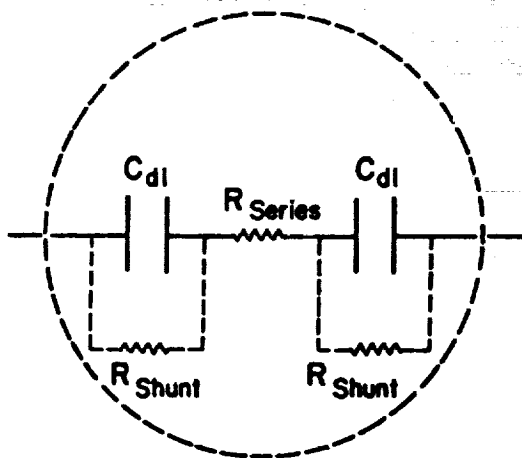
Figure 1. Simplified Equivalent Circuit of Electrochemical
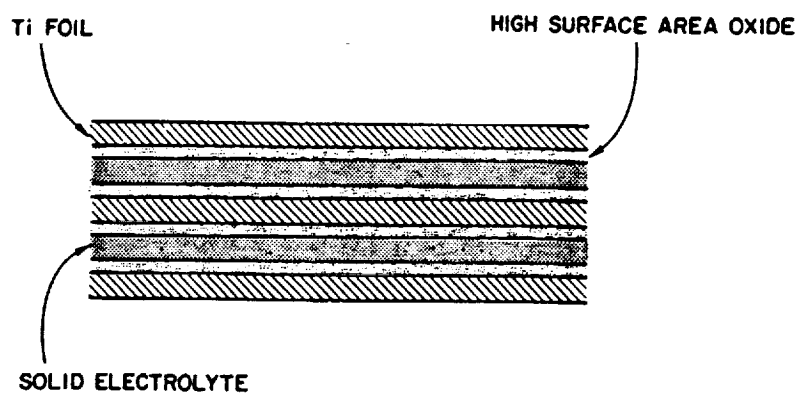   Capacitor Single Cell.

TI FOIL HIGH SURFACE AREA OXIDE

SOLID ELECTROLYTE

Figure 2. Unitized Electrochemical Capacitor Module.

METAL OXIDE
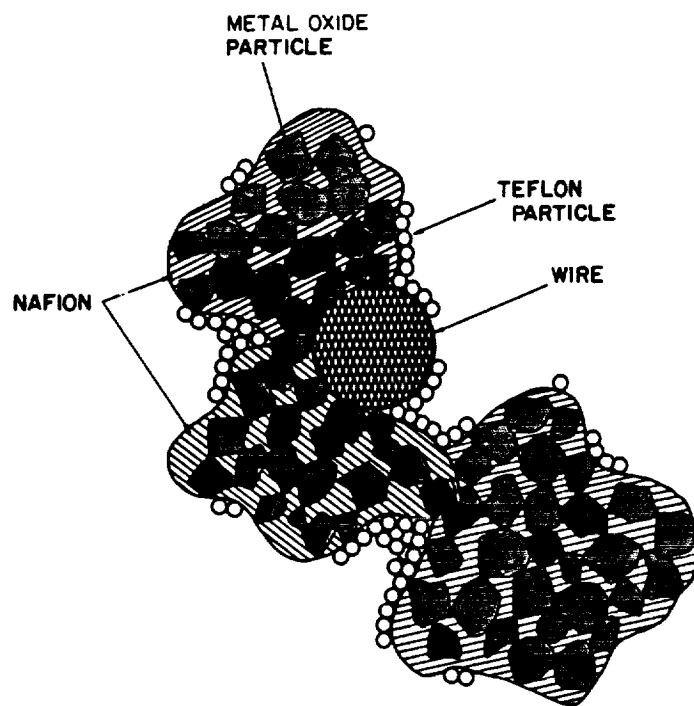PARTICLE

TEFLON
PARTICLE

WIRE

NAFION

Figure 3. Structure of Ionomer-Metal Oxide Composite Electrode.

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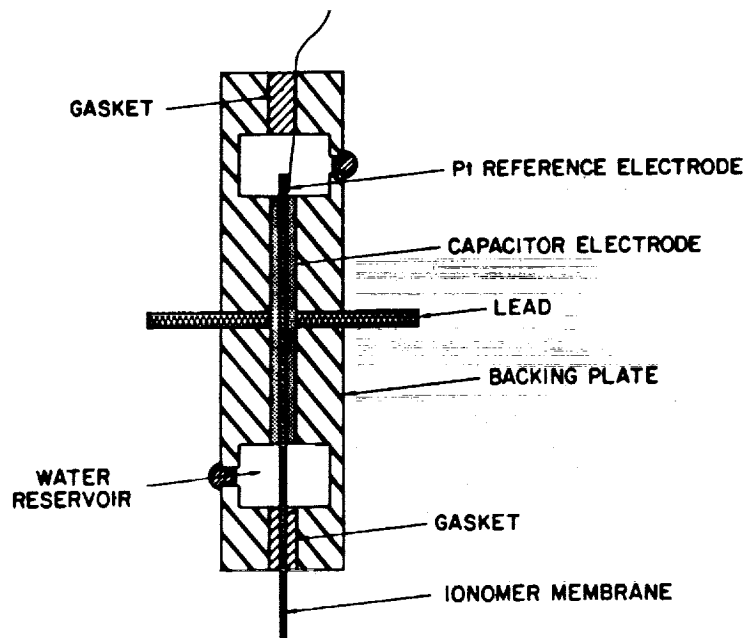
Figure 4. Test Fixture for All-Solid Capacitor Cell.

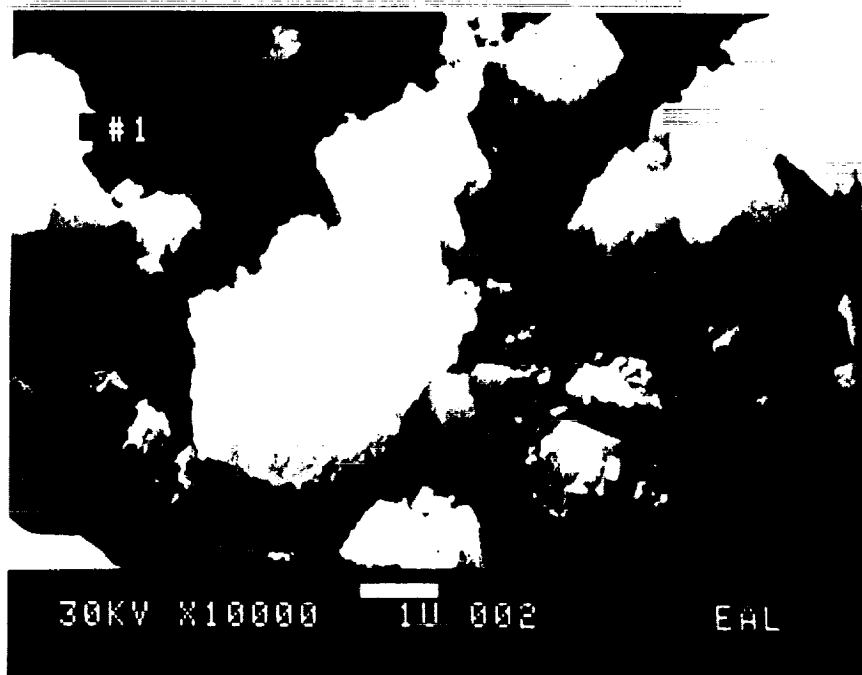Figure 5. SEM Photograph of RuO_2 Particulates.
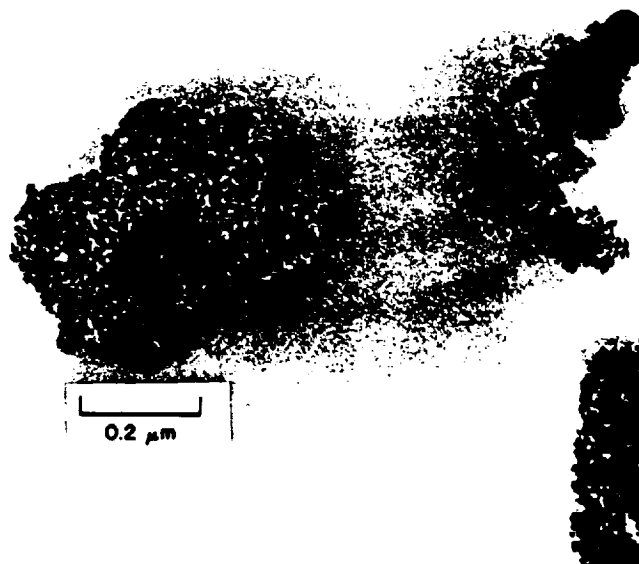
Figure 6. TEM Photograph of 50 m^2/g RuO_2 Particulates.
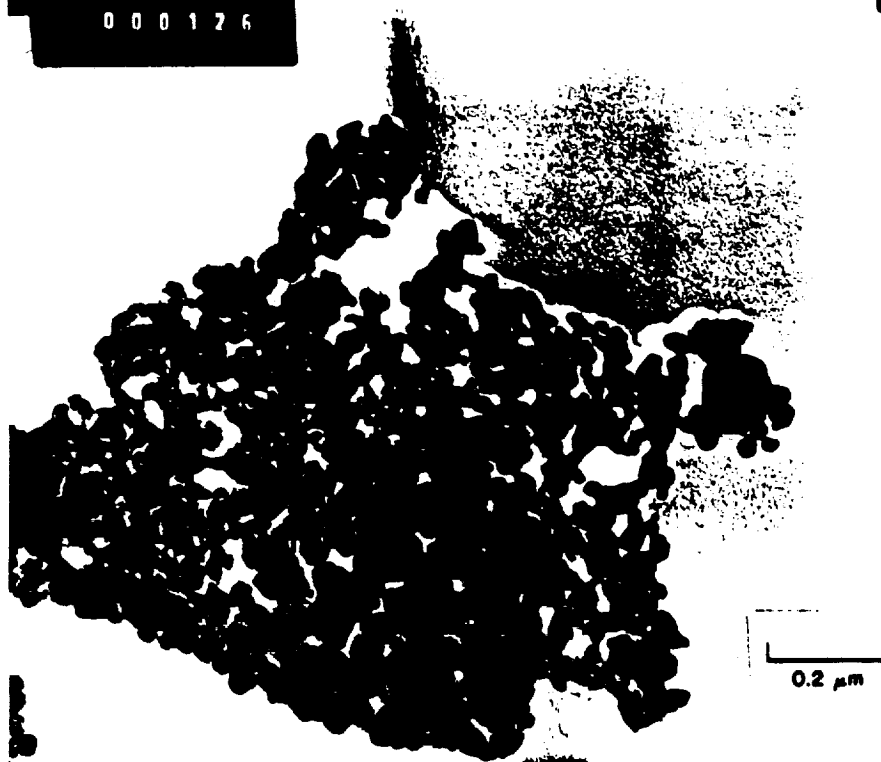
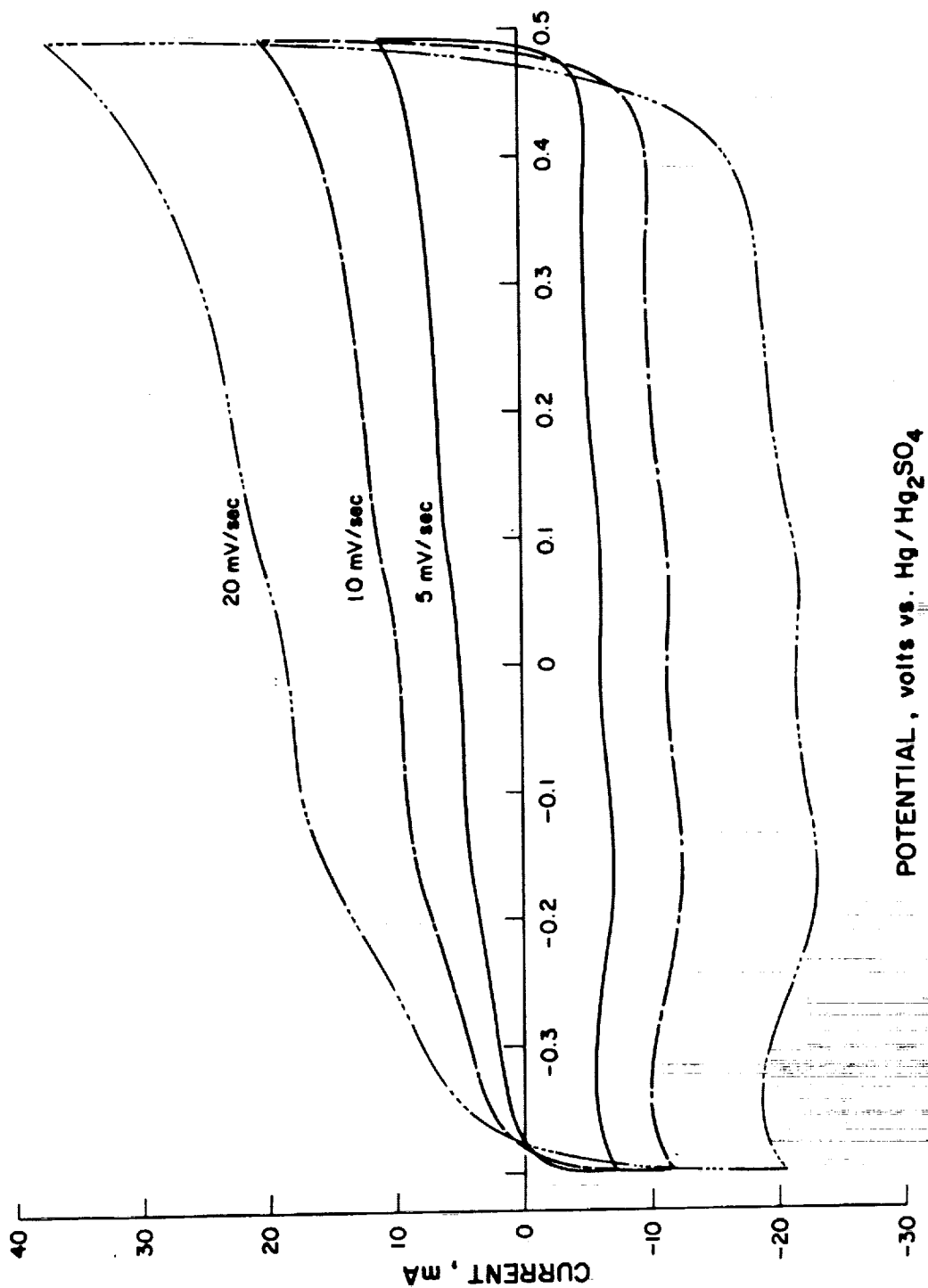Figure 7. TEM Photograph of 3 m^2/g RuO_2 Particulates.

Figure 8. Voltammogram of RuO_2 Bonded to Nafion 117 membrane; 6.45 cm^2 Electrode.
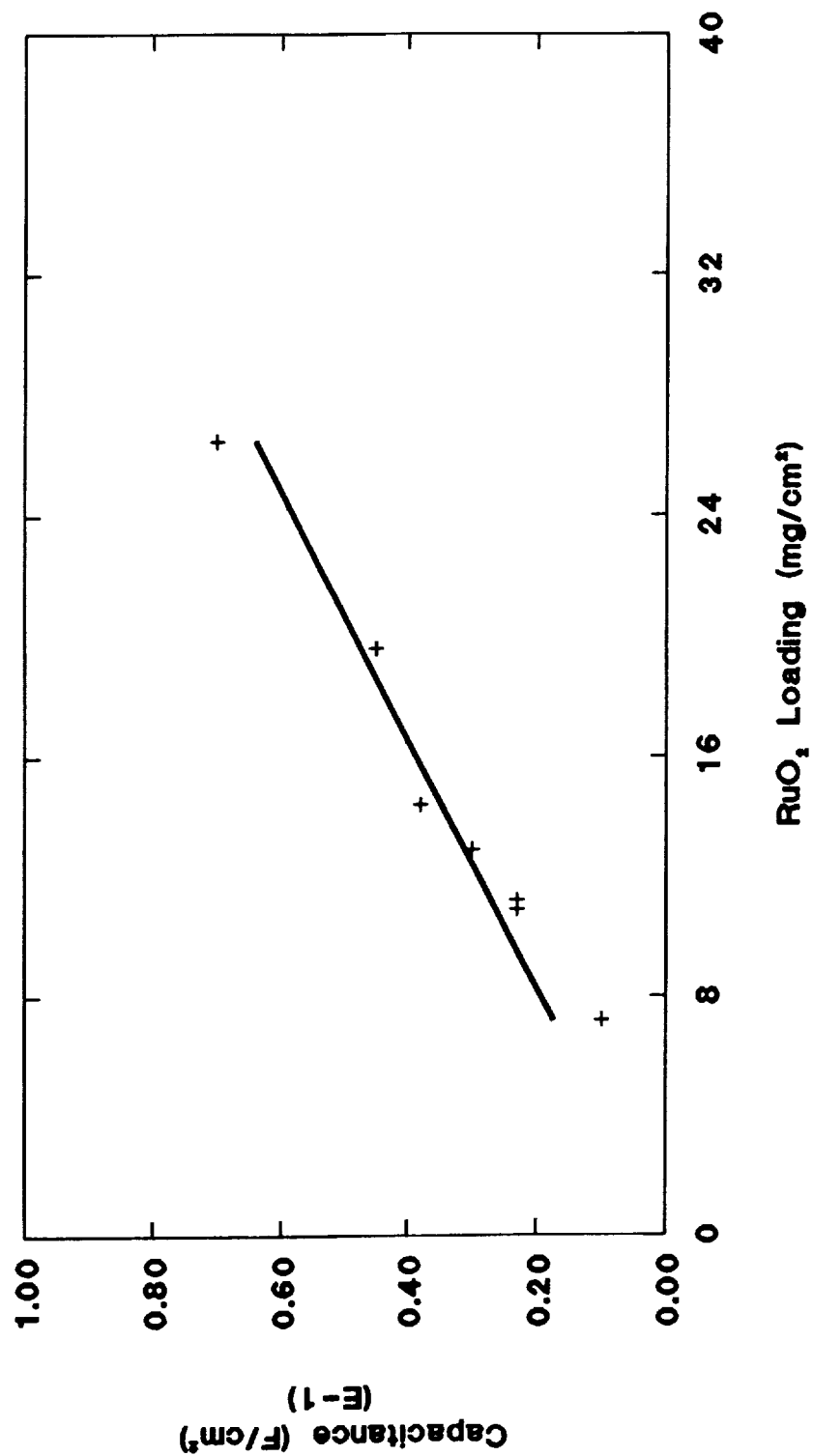
Figure 9. Capacitance Versus Loading for RuO_2 (Low Surface Area)-Nafion Electrodes Bonded to a Nafion 117 Membrane.
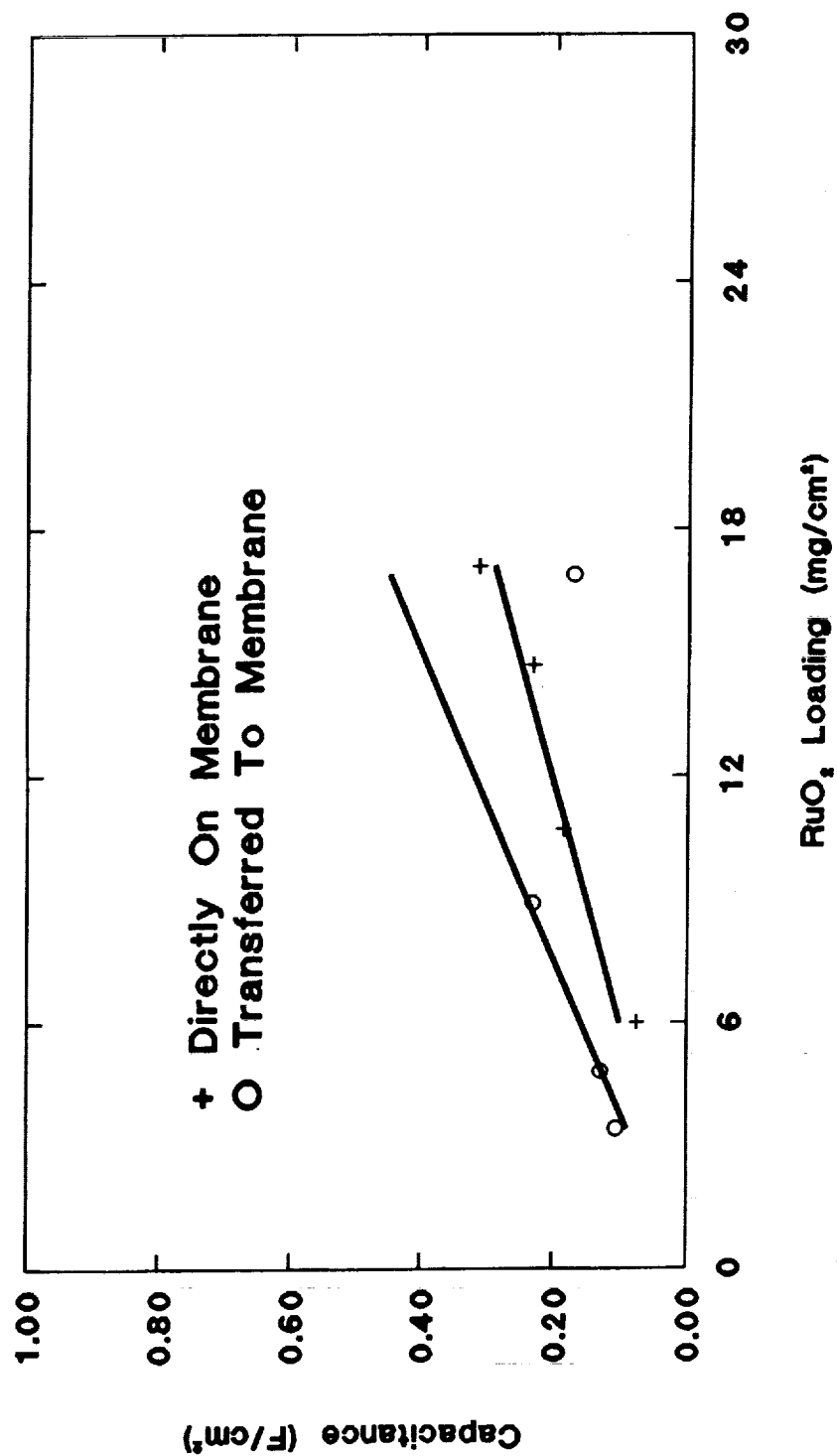
Figure 10. Capacitance Versus Loading for RuO_2 (High Surface Area)-Nafion Electrodes Bonded to a Nafion 117 Membrane.