

ADVANCED DOUBLE LAYER CAPACITORS

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Summary

Work has been conducted that could lead to a high-energy-density electrochemical capacitor, completely free from 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 with 1 F cm^{-2} when a liquid electrolyte is used with the same configuration.

Introduction

Electrochemical capacitors store energy by utilizing double layer and surface redox type processes. Table 1 compares energy density, power density, and cycle life figures for batteries, electrochemical capacitors, and conventional capacitors. The projected energy density for electrochemical capacitors is 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 makes the electrochemical capacitors suitable for relatively long pulses (ms) and low-to-intermediate power applications.

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

TABLE 1

Device	Wh l^{-1}	W l^{-1}	Cycle life
Batteries	50 - 250	150	$< 10^4$
Electrochemical capacitors	5	$> 10^5$	$> 10^5$
Conventional capacitors	0.05	$> 10^8$	$> 10^6$

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memory. The last application 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 Fig. 1. A device consists of two electrodes separated by an electrolyte. Capacitances for metals and carbons in contact with aqueous solutions are 10 - 40 $\mu\text{F}/\text{real cm}^2$. Certain noble metal oxides in contact with aqueous solutions have capacitances in the range of approximately 150 $\mu\text{F cm}^{-2}$ [1]. 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 .

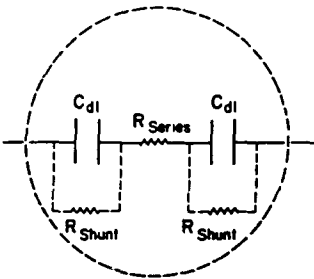


Fig. 1. Simplified equivalent circuit of electrochemical capacitor single cell.

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 1. The 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 [2, 3]. 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 - 4 M 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[®]*, consist of a perfluoro carbon polymer backbone to which sulfonic acid sites are permanently anchored. The only liquid or vapor present in these devices would be pure water.

The device concept is shown in Fig. 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.

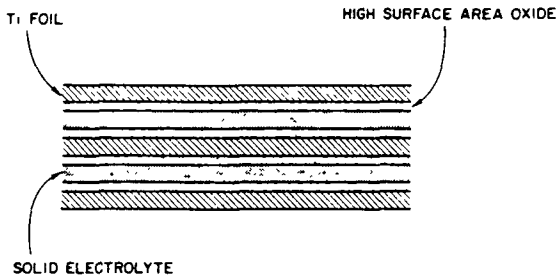


Fig. 2. Unitized electrochemical capacitor module.

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 Fig. 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

*Nafion[®], E.I. DuPont Trademark.

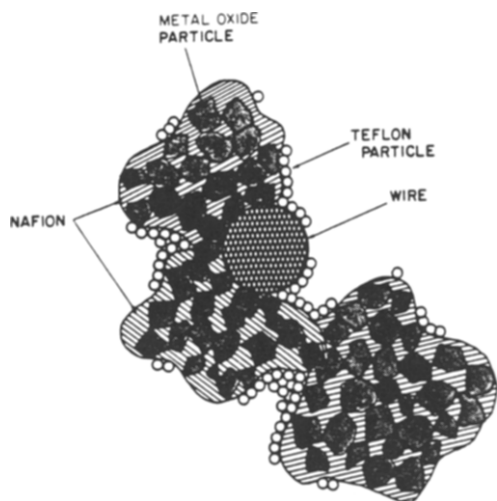


Fig. 3. Structure of ionomer-metal oxide composite electrode.

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 extending 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. It should be capable of being fabricated into a porous electrode forming a high surface area interface with the solid ionomer electrolyte and bonded to the ionomer membrane separator.

Initially, RuO_2 was selected as the electrode material to be studied because it meets all the requirements. The oxide has a high double layer capacity of about $150 \mu\text{F}/\text{real cm}^2$ [1]. There is also a substantial pseudocapacity due to the surface reaction, which can be written approximately as:



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 [2, 3]. RuO_2 can be made into a high surface area coating [4] or as high surface area particulates [5]. Bonding of particulates to an ionomer membrane has been demonstrated for RuO_2 anodes for use in chlor-alkali cells [6] where membrane and electrode assemblies with active areas of up to 35 ft^2 have been prepared.

Experimental

RuO_2 was prepared by thermal decomposition of RuCl_3 in an NaNO_3 flux [5]. 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: (i) impregnation of a PTFE-bonded RuO_2 electrode with ionomer solution; (ii) 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 Fig. 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 an $\text{Hg}/\text{Hg}_2\text{SO}_4$ reference electrode. Some of the M and E assemblies had an integrally bonded Pt/air reference electrode.

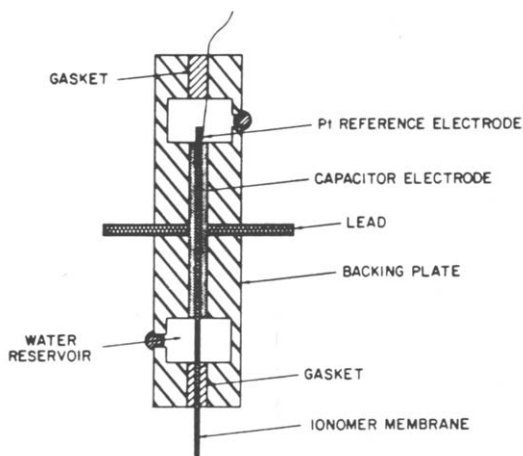


Fig. 4. Test fixture for all-solid capacitor cell.

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:

$$i = C \frac{dV}{dt} \quad (2)$$

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 $50 \text{ m}^2 \text{ g}^{-1}$. The SEM photograph in Fig. 5 shows the particles to be pyramid-shaped and of the order of $0.1 - 5 \mu\text{m}$ in size. Clearly, these surface areas cannot be explained on the basis of impermeable particles of this size. TEM examination of a $50 \text{ m}^2 \text{ g}^{-1}$ powder (Fig. 6) shows that the particles have considerable internal porosity, with crystallites of the order of 200 \AA . Assuming spherical particles of this diameter, the calculated specific surface area is about $40 \text{ m}^2 \text{ g}^{-1}$ which is in good agreement with the measured BET surface area. This powder was heat treated, which reduced its surface area to $3 \text{ m}^2 \text{ g}^{-1}$. 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



Fig. 5. SEM photograph of RuO_2 particulates.

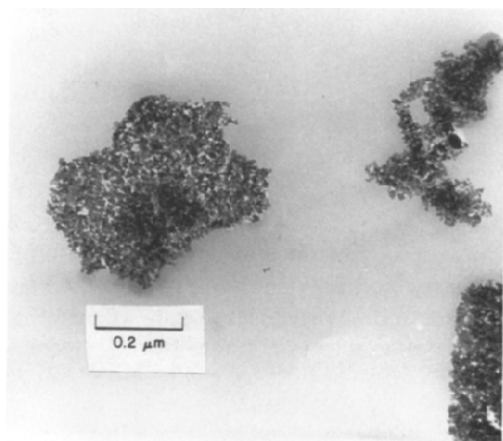


Fig. 6. TEM photograph of $50 \text{ m}^2 \text{ g}^{-1}$ RuO_2 particulates.

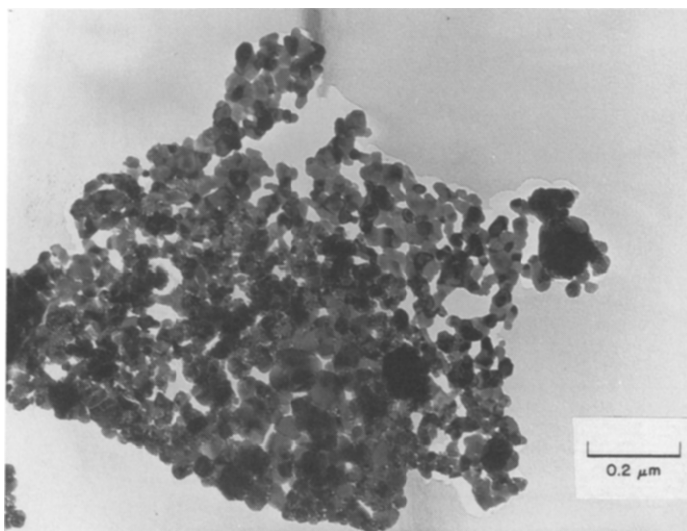


Fig. 7. TEM photograph of $3 \text{ m}^2 \text{ g}^{-1}$ RuO_2 particulates.

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 [7]. This appears to be the case here.

Voltammograms of an RuO_2 electrode bonded to a Nafion 117 membrane are shown in Fig. 8. At potentials more negative than -0.4 versus Hg/HgSO_4 , RuO_2 is irreversibly reduced to lower oxides (shown as the beginning of a reduction wave in Fig. 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 voltammogram is fairly flat with peaks due to reversible surface conversion of oxides as in reaction (1). Trassati and Lodi [4] 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 $50 \text{ m}^2 \text{ g}^{-1}$ 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 is 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

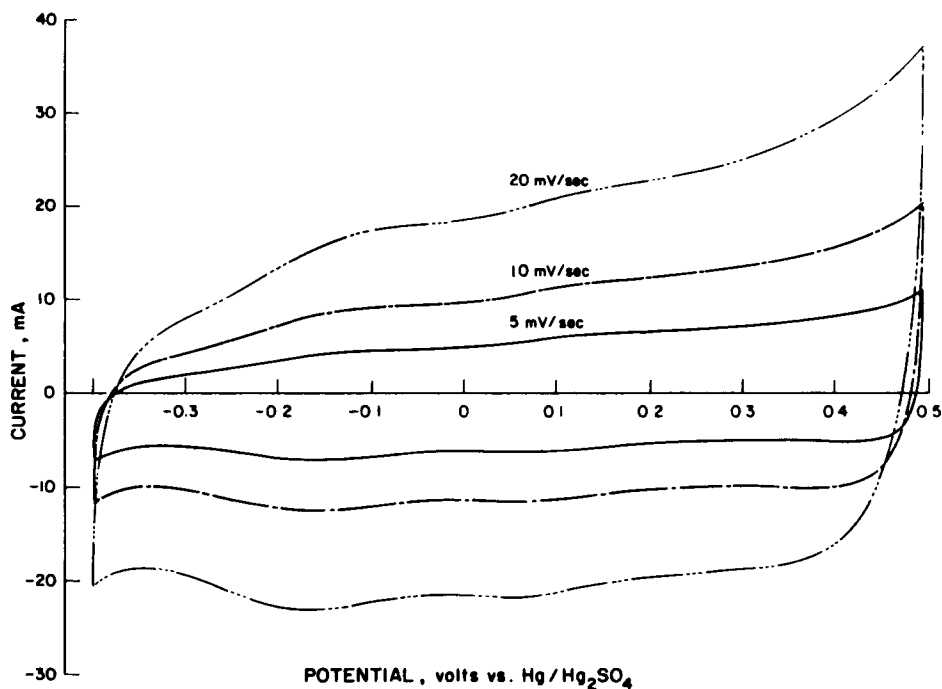


Fig. 8. Voltammogram of RuO_2 bonded to Nafion 117 membrane; 6.45 cm^2 electrode.

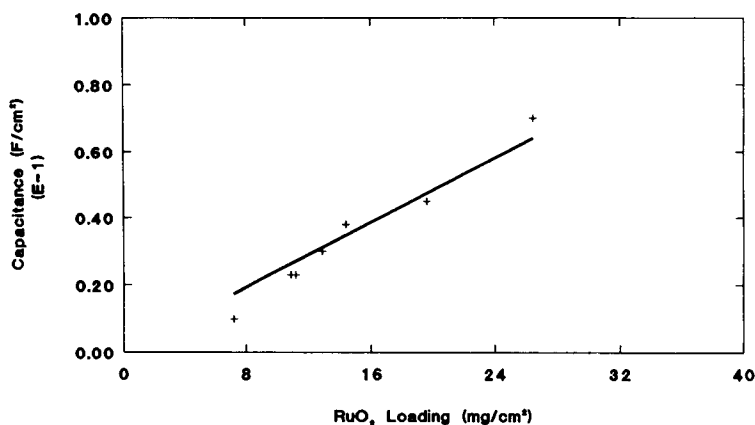


Fig. 9. Capacitance vs. loading for RuO_2 (low surface area)-Nafion electrodes bonded to a Nafion 117 membrane.

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.

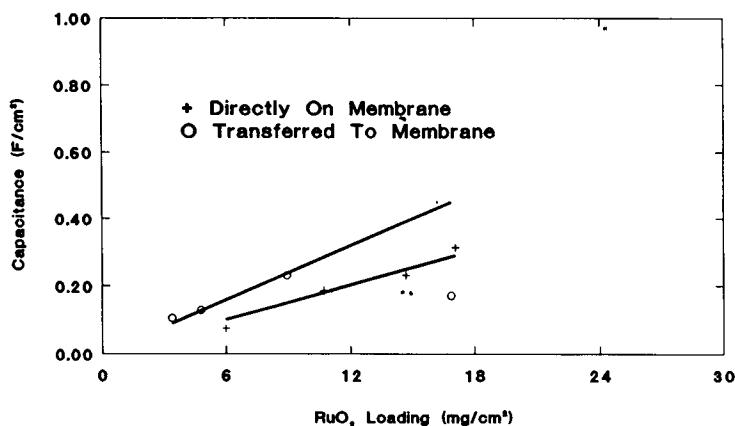


Fig. 10. Capacitance vs. loading for RuO₂ (high surface area)-Nafion electrodes bonded to a Nafion 117 membrane.

Conclusions

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 with other advanced electrochemical capacitors being developed [3], Table 1. 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 [8]. These devices, containing up to 100 bipolar elements (0.3 ft²), have been marketed as reliable devices for over 5 years.

Acknowledgement

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