High Energy Density Electrolytic-Electrochemical Hybrid Capacitor

David A. Evans
Evans Company
72 Boyd Avenue
East Providence, RI 02914
(401) 434-5600

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Abstract

A novel electrolytic/electrochemical capacitor has been developed that has five-times higher capacitance density than standard electrolytic devices. The capacitor is comprised of a pressed-sintered tantalum anode, formed Ta_20_5 dielectric, aqueous electrolyte, and a metal oxide ceramic cathode. The properties of each constituent are discussed.

Electrical characteristics of a 480 µF, 200 V, 2.5 cc prototype capacitor are reported. Data presented include discharge capacitance, ac impedance, and frequency analysis. A volumetric energy density of 4 J/cc was obtained for prototype devices.

Background

Electrolytic capacitors enjoy wide popularity because they are inexpensive, exhibit good electrical performance, and have high specific energy compared to other capacitor types in similar applications. For example, the energy density of high CV aluminum electrolytic capacitors (Mallory CGH) is on the order of 1 J/cc.

As the density and performance of active electronic devices increased, motivation developed to reduce the size of associated passive components. During the period which saw orders-of-magnitude reductions in size for active components, the energy density of electrolytic capacitors remained constant.

The first electrochemical capacitors, introduced by Sohio in the 1970s had an energy density of just over 2 J/cc (1.0 F, 5.5 V). Although this was a dramatic increase over electrolytic capacitors, applications of these devices have been limited by their relatively poor frequency response and low working voltage. These devices exploited the double-layer capacitance on high surface area carbon electrodes. Unlike capacitors using a dielectric, electrochemical capacitors with aqueous electrolyte have a maximum operating voltage limited to about 1 V/cell. This complicates the construction of practical high-voltage devices.

Other types of electrochemical capacitors have been described in the literature. One such capacitor, based on the pseudocapacitance found on symmetric pairs of mixed-metal-oxide electrodes, promised further increases in energy density (perhaps to 5 or 10 J/cc), though it was bothered by the same problems of the carbon types. Additionally, the active materials were very costly. As a consequence, this technology has had little commercial impact.

The needed device was a higher energy density capacitor which had increased voltage capability and improved frequency response. The objective of this work was to develop, build, and test such a device. The resulting device, combining the characteristics of both electrolytic and electrochemical capacitor types, met the objective.

Figure 1. Electrolytic capacitor circuit model.

Discussion

An electrolytic capacitor can be simply modeled by the circuit shown in Figure 1. It is equivalent to distinct anode and cathode capacitors connected in series by the electrolyte. The dielectric is usually a non-conductive oxide of the metal which forms the electrode. These devices are usually asymmetric, that is, they have a preferred arrangement of anode and cathode. The thickness of the dielectric on the anode sets the working voltage of the device. The thickness of the cathode dielectric sets the reverse voltage capability, but does not contribute to the device working voltage.

In commercial aluminum and tantalum electrolytic capacitors, the dielectric is thinner on the cathode than the anode. Most manufacturers use the highest specific surface area aluminum foils or tantalum powders available for the cathode because these materials are capable of the low voltage formations needed for the cathode dielectric. Typically, lower specific surface area materials are used for the anode because they are capable of the much higher voltage formations needed for the anode dielectric. The thinner dielectric and increased surface area of the cathode cause the cathode capacitance to be higher than the anode capacitance. The effect of changing the relative capacitances of the anode and cathode on device capacitance is readily apparent remembering that

$$\mathbf{l/Ct = l/Ca + l/Cc \quad (1)}$$

where Ct is device capacitance, Ca is anode capacitance, and Cc is cathode capacitance. If Ca = Cc, then Ct = 0.5 * Ca. If either Ca >> Cc or Cc >> Ca, the device capacitance, Ct, will approach the smaller of Ca or Cc.

Mixed-metal-oxide (MMO) electrochemical capacitors have high surface area electrodes characterized by very high specific capacitance, on the order of 200 to 500 $\mu F/cm^2$ of real surface area [1]. Because they employ no dielectric, the working voltage of the capacitor cannot exceed the breakdown potential of the electrolyte, which is about 1.2 volts for aqueous systems. This is a real disadvantage because high-voltage devices need multiples of cells stacked in series. This series arrangement by extension of equation (1) results in a severe capacitance penalty.

Figure 2 compares the volumetric energy density predicted for the new capacitor (HI-Q) with actual values for commercial aluminum foil and tantalum wet slug devices. As shown, significant improvements in energy density are

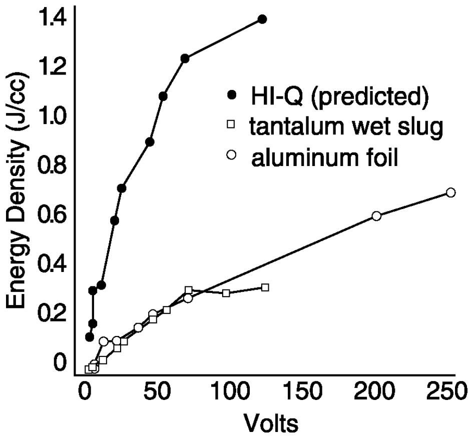

Figure 2. Energy density vs. Voltage for various capacitor types.

expected for the HI-Q device. At 100 V for example. the HI-Q energy density is five-times greater than the aluminum electrolytic value.

In order to fully exploit the capability of the MMO electrode materials, it is essential to eliminate the voltage limitation caused by electrolyte breakdown. This can be accomplished by limiting the voltage drop across the electrolyte/MMO interface to less than the breakdown voltage. Our approach was to add a dielectric in series with the electrolyte. The resulting cell voltage profile is shown in Figure 3. This keeps the voltage drop at the cathode electrolyte interface below the electrolyte breakdown potential.

When composed of a non-conductive metal oxide, this dielectric is most stable on the anode of the cell. Substituting a MMO electrode deposited on foil for the aluminum or tantalum foil cathode in those capacitors would provide some improvement in energy density because the cathode capacitance would be increased without requiring additional volume. Significant improvement in capacitance density can be gained by changing from a foil to a sintered powder anode.

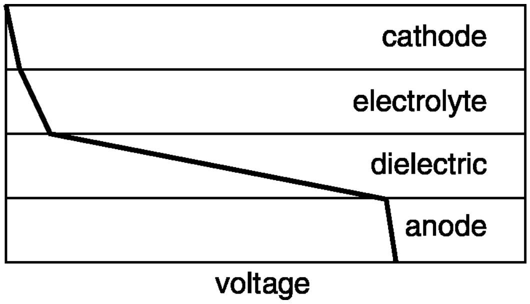

Figure 3. Schematic of cell voltage profile.

Prototype Construction

The prototype was targeted for an application requiring an energy density of 4J/cc and a working voltage of 215 V/cell. The device design had a total of four series-connected cells, each with a capacitance of 480 µF The total volume available for the packaged, high-reliability device was only 11 cc.

The anode was made from high-capacitance-density, high-purity, commercially available tantalum powder, pressed and sintered using standard methods. Formation of the tantalum pentoxide dielectric was done electrochemically in the usual way. This yielded a high-specific-surface-area porous electrode pellet with integral dielectric coating.

The MMO cathode was prepared on titanium foil according to a specific recipe developed to yield electrodes with a capacitance of about 6,000 µF/cm^2 of geometric area. The separator was a commercially available paper-based material. A suitable aqueous electrolyte was used.

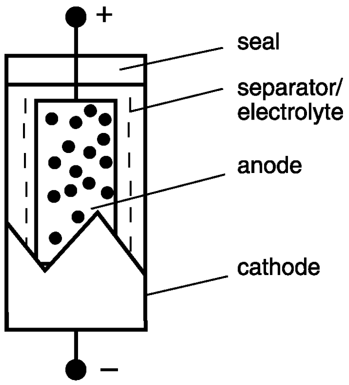

Figure 4. Schematic view of the prototype.

Tests and Results

Several of the 215 V, 480 µF cells were constructed as described. Electrical properties were evaluated by fixed-resistance discharging, constant current charging. ac impedance spectroscopy, and ac bridge measurements.

For an ideal capacitor discharged into a fixed resistance, the capacitance can be derived from the formula

$$\mathbf{V(t) = V_0\, e^{-t/RC}\ (2)}$$

where V_0 is the initial capacitor voltage, R is the fixed resistance, C is the capacitance, and V(t) is voltage as a function of time, t.

When t = T = RC, the voltage V(t) = 0.368 V_0. Capacitance taken at this time is referred to as the one-time-constant capacitance. 1 T and .25 T capacitance values are reported in Table 1. The difference in values reported at 1 T and .25 T indicate non-ideal behavior. Capacitance is less than ideal for shorter discharge times.

For an ideal capacitor charged at a constant current, the capacitance is

$$\mathbf{C = It/V(t)\ (3)}$$

where I is the current, V(t) is the voltage as a function of time, t. These numbers, for I = 10 mA, and t = 5 s. are reported in Table 1.

Table 1. Property Measurements

Part	Capacitance and method (μF)					ESR and method (Ω)			Il (μA)	Energy (joules)
	A	B	C	D	E	D	E	F		
1	606	514	313	250	469	0.92	1.29	.238	114	11.3
2	541	470	249	226	429	0.99	1.37	.287	52	10.3
3	575	502	249	241	445	0.94	1.30	.287	82	11.0

Key to methods:

A. Constant-current charge
B. 10Ω discharge, 1 T
C. 10Ω discharge, .25 T
D. ac bridge, 1 kHz
E. ac bridge, 120 Hz
F. 10Ω discharge

*energy calculation based on method B capacitance

The values for leakage current (Il) listed in Table 1 were measured after a charge time of 15 m at 215 V with an ammeter in series with the charging circuit.

Measurements of ESR and capacitance were made with a GenRad model number 1658 Digibridge. Results are shown at 120 Hz and lkHz. Again, differences in the values between one fre uency and the other are due to non-ideal behavior.

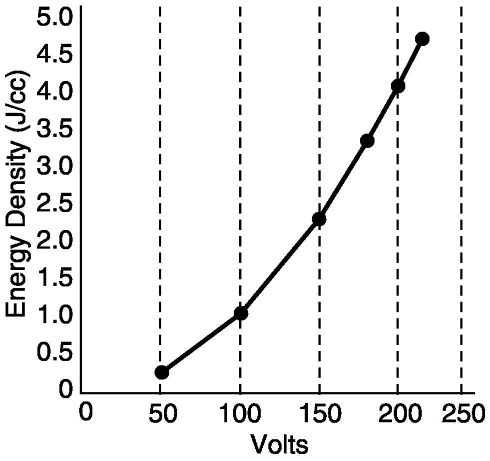

Figure 6. Energy density vs. Voltage for the HI-Q prototype.

Figure 6 shows the measured energy density of a single prototype device constructed for a working voltage of 215 V. The data were collected at various points by charging the device. then discharging into a 10 Ω resistor. calculating a 1 T capacitance, and using that in figuring the energy density. This proce dure was repeated at each voltage reported.

The capacitance of this proto type did not vary significantly with voltage, as shown in Figure 7.

The non-ideal behavior can be examined in further detail using ac impedance spectroscopy. Figure 8 is a Nyquist plot giving the reactance vs. resistance over the frequency range of 79 Hz to 63 kHz for one of the prototype capacitors. This data was obtained using a Schlumberger Solartron 1260 frequency response analyzer with a 1.5 V bias and a 10 mV ac signal. The plot for an ideal capacitor is a straight vertical line intersecting the x-axis at the ESR value. The non-ideal 45° angle in the high frequency region is typical of devices with porous electrode structures, and was expected on this prototype.

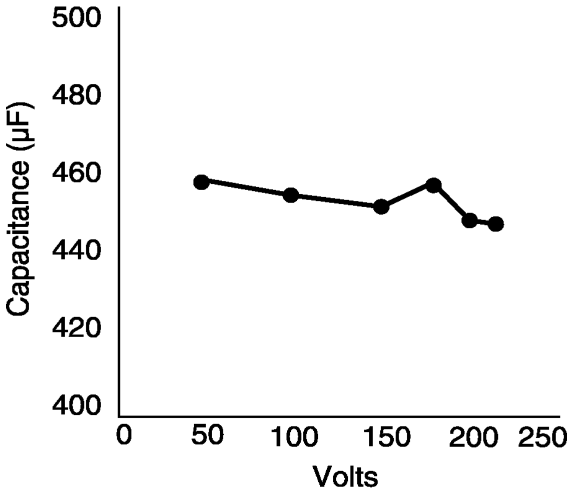

Figure 7. lT Capacitance vs. Voltage for the prototype

Figure 9 presents the same impedance data in a different format, that is, a resistor capacitor series combination. Electrical properties over the range in frequency of 1 Hz to 10 kHz are shown. The capaci tance was flat within 10% to a frequency of about 200 Hz, where it rolls off sharply.

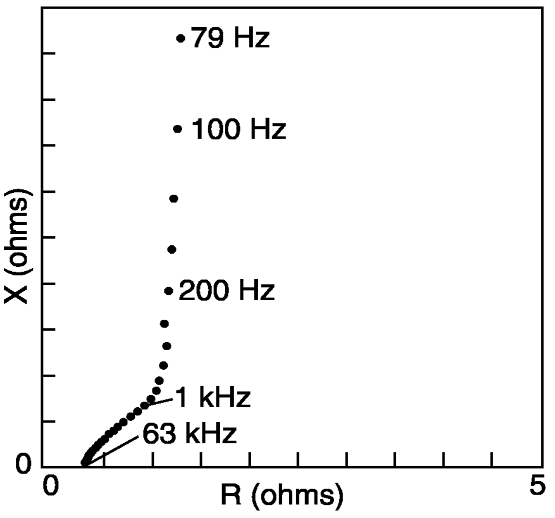

Figure 8. Nyquist Plot for the HI-Q prototype.

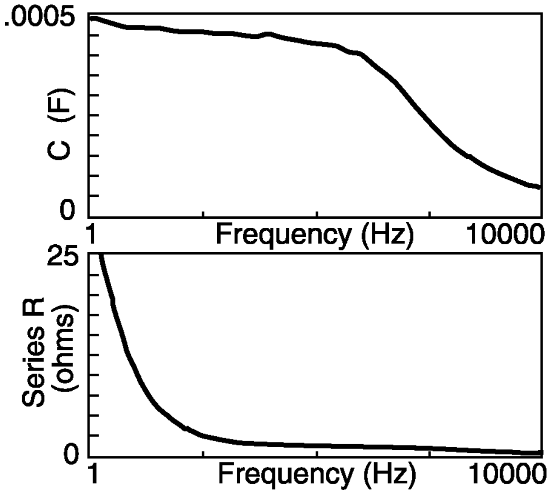

Figure 9. Electrical performance vs. Frequency.

Conclusion

The combination of mixed metal oxide cathodes and tantalum pellet type anodes yielded a device with very high energy density. The energy density of the prototype device was in excess of 4 J/cc at 215 V. This exceeds that of commercial electrolytic capacitors by a factor of five.

Work needs to be done and is ongoing to optimize the performance of these hybrid devices by improving their frequency response. Improved tantalum powders are being investigated, and modifications to the basic cathode recipe explored.

Reference

[1] B.E. Conway, “Some Basic Principles Involved in Supercapacitor Operation and Development”, Proc. 3rd Int. Seminar on Double Layer Capacitors and Similar Energy Storage Devices, Deerfield Beach, Florida (Dec. -8, 1993)