PROPERTIES AND PERFORMANCE OF HYBRID ALUMINUM ELECTROLYTIC / ELECTROCHEMICAL CAPACITORS

John R. Miller
JME, Inc.
17800 Parkland Drive
Shaker Heights, Ohio 44122
216-751-9537

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

SUMMARY

Test data was recently presented for a hybrid electrolytic/ electrochemical capacitor having sintered tantalum anodes and RuO_2 cathodes. A 50-V, 18-mF capacitor of this design had electrical performance that was comparable to an advanced aluminum electrolytic capacitor but with only one-tenth the volume and just one-half the mass. This design, however, is very expensive because of the tantalum anode. RuO_2 cathode costs are negligible.

Here, for the first time, we report test results for aluminum hybrid capacitors. These were fabricated with etched aluminum anodes, RuO_2 cathodes, and electrolytes that are compatible with aluminum and its oxide. Anodes rated at 6.3 to 250 V were used. Although cathode pseudocapacitance was diminished using the aluminum-compatible electrolytes, test data confirms that the aluminum hybrid concept is viable. Impedance data of these test devices is almost identical to those of controls fabricated with the same anodes but with aluminum cathodes. Hybrids having a more optimum aluminum anode structure should maintain the attractive performance, weight, and size advantages of the hybrid approach at a more affordable cost than tantalum.

INTRODUCTION

The Evans hybrid capacitor exploits the best features of two capacitor technologies. It uses the anode from an electrolytic capacitor and the cathode from an electrochemical capacitor. This combination provides a working voltage and a frequency response very similar to those of an electrolytic capacitor but with a greatly augmented capacitance density.

Reported test data from several hybrid capacitors includes results from a 215-V prismatic design that stored more than 4 J/ml [1], a tubular military- style capacitor (CLR-81) that stored four times more energy than previous versions [2], and a 50-V prismatic capacitor having electrical performance comparable to that of an advanced aluminum electlolytic capacitor but with only one-tenth the volume and just one half the mass [3].

Figure 1 shows a Bode plot of the impedance of an 18-mF, 50-V Evans hybrid and an 18-mF, 50-V Nippon Chemicon series 36DA aluminum electrolytic capacitor (from reference [3]). As shown in this figure, the hybrid has electrical properties that are very comparable to that of a conventional aluminum electrolytic capacitor.

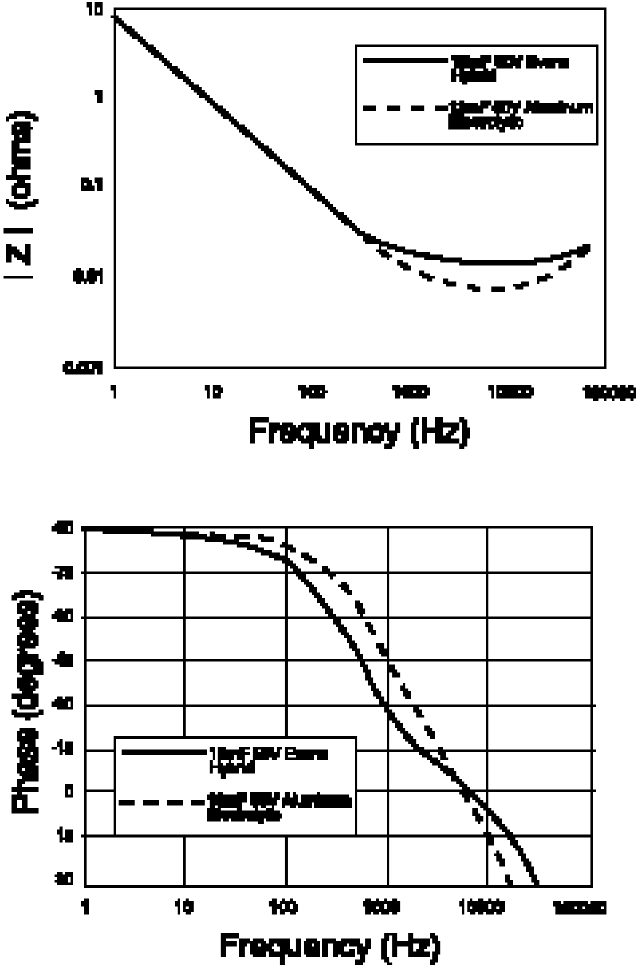

Figure 1. Bode plots of a tantalum hybrid and a commercial aluminum electrolytic capacitor. Each stores -18 mF and is rated at 50 V.

Each of the above hybrid capacitors used an anodized, porous tantalum anode that was fabricated using powder-sintering processes. And each had a pseudocapacitor cathode composed of an adherent ruthenium oxide coating on either tantalum or titanium [4]. Phosphoric or sulfuric acid electrolyte was used.

These embodiments of the Evans hybrid capacitor offer exceptional advantages in performance and/ or energy density over other electrolytic and electrochemical capacitors. But tantalum and ruthenium are very costly materials, and tantalum has a low gravimetric capacitance density compared to aluminum. The objectives of this work were to examine Evans hybrid capacitor material costs and to evaluate aluminum as a potential hybrid capacitor anode material.

Important questions include the following: (1) Does ruthenium or does tantalum dominate the cost in the present configuration?; (2) Will aluminum function like tantalum in a hybrid capacitor?; and (3) What performance is provided when aluminum anodes are used instead of tantalum? This paper attempts to answer these three questions.

TANTALUM HYBRID COST ISSUES

Electrolytic capacitors are actually two dielectric capacitors in series. The Evans hybrid is different in that it uses a pseudocapacitor instead of a dielectric capacitor in the cathode. This substitution can be made, provided that the voltage across the cathode capacitor V_C does not exceed the breakdown potential of the electrolyte, about 1.2 V for aqueous electrolytes.

The relationship between V_C and the voltage across the anode capacitor V_a is determined by their capacitance ratio

$$V_C / V_a = C_a / C_c,$$

where C_a is the anode capacitance and C_c is the cathode capacitance. Fixing V_C well below one volt, say at 0.25 V, and noting that the device capacitance C_0 will be approximately equal C_a when the device voltage V_0 is greater than a few volts, then the capacitance needed in the cathode to establish the necessary voltage relationship is

$$C_c = 4 * C_0 * V_0$$

Cathode costs can be calculated by assuming a specific capacitance of 100 F/g for the RuO_2 material and a price of $5.00/g, both very conservative estimates. Thus, cathode costs for the hybrid are \$0.20* $C_c * V_0$, where C_c is in Farads and V_0 is in volts.

Capacitor-grade tantalum powders have specific capacitance values in the range of 5,000 to 50,000 μF*V/g depending on powder source, sintered density, operating voltage, etc. Presently, the price for these materials is about $200/lb. Using a specific capacitance value of 20,000 μF*V/g, anode costs for the Evans hybrid are \$22* $C_c * V_0$, where C_c is in Farads and V_0 is in volts.

The above estimates are applicable only up to the maximum voltage to which the anode can be formed. Although tantalum foils have been formed to voltages greater than 500 V [5], sintered anodes are very difficult to form at such high voltages. A more practical maximum formation voltage for sintered tantalum is 200 V.

Tantalum hybrid capacitors can be series-connected to operate at voltages above the maximum formation voltage. Then at these voltages, material costs have a quadratic rather than a linear dependence on voltage. This cost behavior is followed by both the anode and the cathode at these elevated voltages.

Figure 2 shows cost estimates for the anode and the cathode using the above equations. Costs are proportional to the voltage up to 200 V and then are proportional to the square of the voltage. RuO_2 costs are a constant 110 times less than the tantalum costs--effectively they can be ignored.

It is informative to examine capacitor material costs using a specific example. For a 20,000 µF, 50-V hybrid capacitor, tantalum costs are estimated at \$22.00. R-102 costs are estimated at \$0.20.

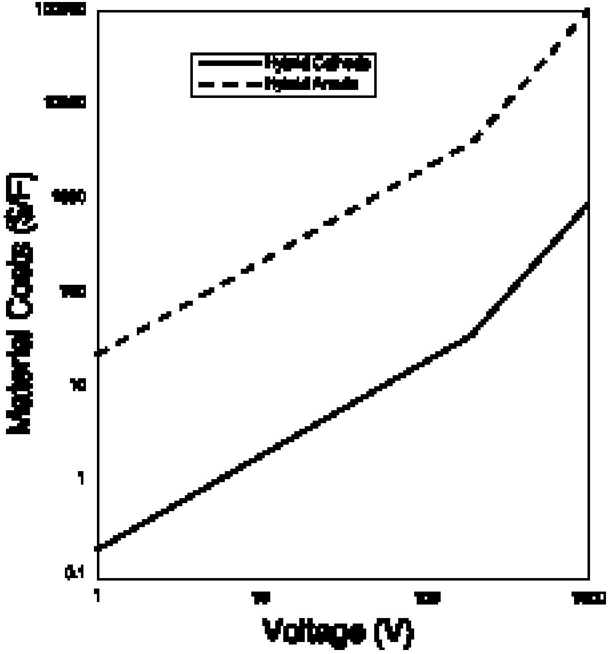

Figure 2. Material cost estimates for the anode and the cathode in a tantalum hybrid capacitor. RuO_2 *costs can effectively be ignored.*

As an aside, consider the material costs for a symmetric RuO_2 pseudocapacitor. Such devices have been under development for many years but have not become available commercially [6]. High material costs have been suggested as one reason for this situation [7]. Assuming a cell voltage of 1.0 V, the total capacitance C_t contained in a symmetric pseudocapacitor is

$$C_t = 4\ C_c{*}V_0^2$$

Using the same specific capacitance and price as before, RuO_2 costs for the symmetric capacitor are $\$0.2{*}\ C_c\ {*}\ V_0^2$, where C_c is in farads and V_0 is in volts. Note the quadratic dependence on the voltage.

Material costs for the same 20,000-µF 50-V capacitor, if constructed using symmetric RuO_2 electrodes, would be \$10.00, one-half the material costs of the hybrid. And these costs could possibly be still lower if hydrated RuO_2 were used [8]. But a symmetric pseudocapacitor does not have comparable frequency response to the hybrid capacitor [3], nor has it immunity from voltage-imbalance problems in high-voltage applications [9]. These performance issues, along with higher anticipated manufacturing costs due to the need to series-connect many cells, may negate apparent cost advantages.

In summary, the dominant cost in the Evans hybrid capacitor described in references [1] to [3] is attributable to the use of a tantalum anode. Costs associated with the RuO_2 cathode comprise less than 1% of the total. Consequently, substitute anode materials are needed in order to reduce the overall cost of the hybrid capacitor.

ALUMINUM HYBRID CAPACITOR

Aluminum is the obvious substitute material in the Evans hybrid. It has low cost and is proven in aluminum electrolytic capacitors. Such devices use etched foil for both their anodes and their cathodes. Anode foils are readily available with voltage ratings up to 550 V.

Electrolytes used in aluminum electrolytic capacitors have near-neutral pH and no aggressive species that might attack aluminum or its oxide. Typical solvents include ethylene glycol, dimethylformamide and γ-butyrolactone. Mixtures of these are often used. Common solutes include ammonium, quaternary ammonium, and tertiary amine for cations, and borate or dicarboxylate for anions. Some water is usually present in the electrolyte (1-3%) to support formation of the anodic aluminum oxide dielectric after capacitor assembly [10].

Ruthenium oxide offers good performance with tantalum anodes in the Evans hybrid. It is a pseudocapacitor that stores charge in the double layer as well as through Faradiac charge-transfer processes of adsorbed protons. In strong acids, like those used with the tantalum anode, the majority of the stored charge is due to the charge transfer reaction [11]. Near a pH value of 7, the stored charge is approximately one-half that measured at higher or lower pH values [12]. Then a major issue becomes how well RuO_2 works with electrolytes that are suitable for aluminum anodes.

This issue was investigated using four aluminum electrolytic capacitor electrolytes. Each of these was optimized for a specific operating voltage. Sulfuric acid (38% by weight), an electrolyte used with the tantalum anodes, was included as a control. An anhydrous electrolyte was also included in this study. It was composed of 89% propylene carbonate, with the balance tetraethylammonium tetrafluoroborate. Its specified water content was below 10 ppm. The anhydrous electrolyte was included in this study to measure the relative amount of charge stored in the double layer compared to charge stored via charge-transfer processes.

The capacitance of a single RuO_2 cathode was measured at 120 Hz in each of the electrolytes. This was done at ambient conditions except for the anhydrous electrolyte, which was evaluated in a Vacuum Atmospheres Company drybox having a water concentration below 15 ppm. Capacitance values were obtained using a 1250 Solartron frequency response analyzer with a PAR EG&G 273 potentiostat/galvanostat. Tests were performed in flooded conditions with a platinized-platinum reference electrode and an etched and formed aluminum counter electrode. Electrolyte conductivity was measured using a Beckman conductivity cell and the same impedance measurement equipment. Table I lists these results.

All of the electrolytes formulated for aluminum electrolytic capacitors (A through D) had conductivities more than 100 times below the sulfuric acid value. Capacitance of the RuO_2 cathode with these electrolytes ranged from 14 to 36% the sulfuric acid value. There does not appear to be a correlation between electrolyte conductivity and cathode capacitance.

Cathode capacitance with the anhydrous electrolyte, presumably due strictly to double layer charging, was 11% the sulfuric acid value, consistent with the reported pseudocapacitance--double-layer capacitance ratio [13]. Thus, electrolytes B, C, and D allowed the cathode to store a considerable amount of its total charge through pseudocapacitive processes.

Table I Capacitance of One RuO_2 Cathode in various Electrolytes

Electrolyte	Cond. (mS/cm)	Cap.[a] (mF)	Cap as % of H_2SO_4
A	0.80	2.6	14
B	1.2	6.4	36
C	4.5	5.7	32
D	6.7	3.6	20
Anhydrous	11	1.9	11
H_2SO_4	750	18	100

[a] 120-Hz value

It is straightforward to estimate RuO_2 cathode costs for an aluminum hybrid. Electrolytes B and C offer one-third the capacitance that is provided by sulfuric acid. Then cathode costs for these electrolytes will be three times the tantalum hybrid value, i.e., $\$0.60 * C_c * V_0$. This linear relationship will be followed up to the maximum formation voltage of aluminum, possibly 500 V or more.

Using the same example as before, a 20,000-µF, 50-V aluminum hybrid capacitor would have an estimated cathode cost of $0.60. This is higher than for the tantalum hybrid, but still very attractive provided a significant reduction in the anode cost results.

ALUMINUM HYBRID PERFORMANCE

The performance of aluminum hybrid capacitors was examined by assembling simple test capacitors. The anodes were foils taken from United Chemicon aluminum electrolytic capacitors (series 36DA). The cathodes were either RuO_2 or aluminum cathodes extracted from these same devices. Flag-shaped samples were cut from three different capacitors, with voltage ratings of 6.3, 50, and 250V.

One side of each aluminum electrode was masked with a hot-melt adhesive. The exposed geometrical area on the other side was one square inch. These anode foils were reformed in electrolyte C at 125% of the rated voltage to repair damage in the dielectric caused by the cutting and masking operations.

Six test capacitors were assembled and evaluated, three using the anode and cathode from each of the dissected capacitors and three using these exact same anodes but with RuO_2 cathodes. Anode and cathode, separated by a non-woven glass separator, were clamped in a fixture and immersed in electrolyte C for testing. This electrolyte was selected because it had relatively high conductivity and provided high cathode capacitance.

The complex impedance of these test capacitors was measured at 5-V bias using the apparatus previously described. Figure 3 shows Bode plots for devices having the 6.3-V foil anodes and both aluminum and RuO_2 cathodes.

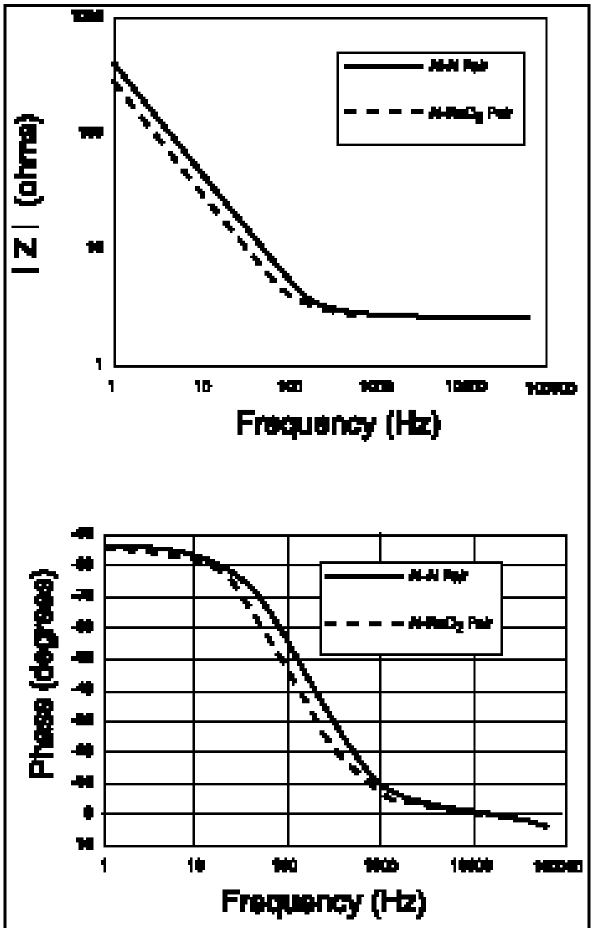

Figure 3. Bode plots for 6.3-V test capacitors using electrolyte C. One device has an aluminum anode and cathode. The second has an aluminum anode and a RuO_2 cathode.

The magnitude of the impedance is lower for the Al- RuO_2 pair than for the Al-Al pair at frequencies below ~200 Hz, indicating higher capacitance. This is indeed the case since the RuO_2 cathode has orders of magnitude more capacitance than the aluminum cathode, causing the device capacitance to approach the anode capacitance. Series resistances are comparable. The phase of the Al- RuO_2 pair approaches -90° at a somewhat lower frequency than the Al-Al pair. This result is consistent with the larger capacitance and consequent greater RC-time-constant of the Al- RuO_2 pair.

Bode plots for the 250-V test capacitors are shown in Figure 4. The Al-Al and the Al- RuO_2 pairs show no discernible differences over the measured frequency range. In short, their electrical behaviors are identical.

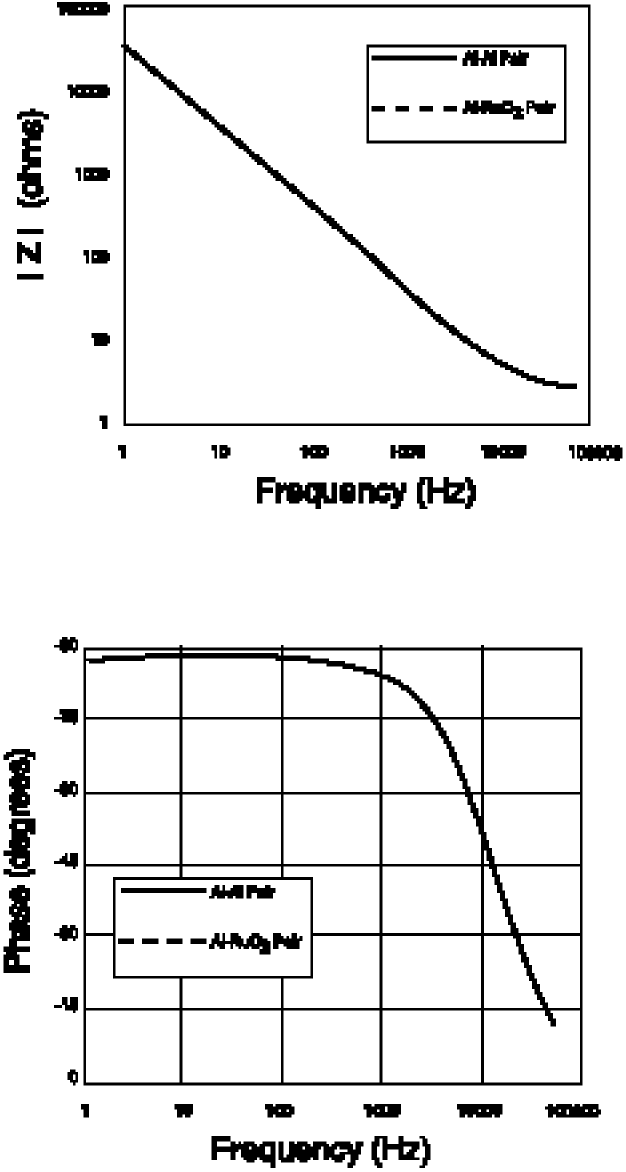

Figure 4. Bode plots for 250-V test capacitors. One device has an aluminum anode and an aluminum cathode. The aluminum hybrid device has an aluminum anode and a RuO_2 cathode. Measurements were made using electrolyte C under ambient conditions.

CONCLUSIONS

Major conclusions from this initial activity include the following.

1. The dominant cost of the tantalum hybrid capacitor is attributable to the use of a tantalum anode. Cathode material costs (RuO_2) constitute less than one-percent of the anode material costs.
2. Electrolytes presently used in aluminum electrolytic capacitors allowed the RuO_2 cathode to store a considerable amount of its total charge via pseudocapacitive processes. An optimized electrolyte should further increase cathode specific capacitance.
3. Aluminum hybrid test capacitors functioned very similar to standard aluminum electrolytic capacitors having the same geometry. A more optimum anode structure, for instance a pellet, should allow devices with much higher capacitance density.

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