

# Tantalum Hybrid<sup>®</sup> Capacitors for High- Volume Applications

David A. Evans  
Evans Capacitor Company  
33 Eastern Avenue  
East Providence, RI 02914  
401-435-3555  
snavedivad@aol.com

## Abstract

A new tantalum Hybrid capacitor, having a thickness of just 1.4mm has been developed. The new capacitor has innovative packaging features that minimize non-active components and allow simple, reliable assembly. The thin, flat package also tends to minimize electrical resistance. This unique capacitor combines the high cell voltage capability and low resistance of an electrolytic capacitor with the increased energy density of an electrochemical capacitor.

Electrical impedance spectroscopy was used to characterize capacitor electrical properties. The new capacitor has 10X the energy density of a tantalum electrolytic capacitor with similar electrical performance. The frequency response of this capacitor suits it for avionics, communications electronics, air- and surface- based radar systems, power supply, computer, and electronics applications.

## Introduction

The tantalum Hybrid capacitor (Patent No. 5,369,547) is a series combination of a dielectric oxide film capacitance, Ta<sub>2</sub>O<sub>5</sub>, and a high electrochemical capacitance, a film of the conductive metal oxide, RuO<sub>2</sub>. The result is a polar capacitor; with the Ta<sub>2</sub>O<sub>5</sub> film, the positive and the RuO<sub>2</sub> film the negative electrodes. A high potential can be maintained across the thin electrochemically formed Ta<sub>2</sub>O<sub>5</sub> film, while the RuO<sub>2</sub> film remains at low potential. This allows high cell voltage without fear of reaching the electrolyte breakdown potential.

The advantages of the Hybrid capacitor can be considered with an understanding of common electrolytic capacitors. These devices employ thin oxide films on the both electrodes, but they are usually asymmetric, using a material of higher surface area at the negative electrode. The film on the positive electrode is thicker than the negative electrode film, and sets the working voltage of the capacitor. The negative electrode has a higher capacitance, but the two electrodes often have similar physical sizes. [1]

The overall capacitance, C, can be determined by analysis of the equivalent series circuit for an electrolytic capacitor, shown in Figure 1. For series capacitors,

$$C = 1/C_a + 1/C_c,$$

where C<sub>a</sub> and C<sub>c</sub> respectively are the positive and negative electrode capacitances.

In the Hybrid capacitor, since  $C_c \gg C_a$ , the overall capacitance is determined by  $C_a$ . Because the  $\text{RuO}_2$  negative electrode requires little volume, available space can be used to enlarge the positive electrode. The result is a capacitor with at least four times the energy density of a tantalum electrolytic capacitor.

The tantalum Hybrid capacitor positive electrode is a pressed, sintered pellet of high capacitance density tantalum powder. Formation of the  $\text{Ta}_2\text{O}_5$  film is done electrochemically in aqueous electrolyte until a thickness corresponding to a certain voltage is reached. This determines the working voltage of the capacitor, which is in the range of 3 to 125 volts.

The negative electrode is a high capacitance density film of  $\text{RuO}_2$  bonded to a thin tantalum foil. The bulk capacitance of the  $\text{RuO}_2$  electrode material is approximately 50F/g. The capacitance density of the  $\text{RuO}_2$  film is approximately 50mF/cm<sup>2</sup>. Therefore, only a small amount of  $\text{RuO}_2$  is required.

Hybrid capacitors are capable of high working voltages without resorting to series connected cells. Low cell voltage, limited to the electrolyte breakdown potential (ca. 1.2 volts, aqueous, 3.5 volts, nonaqueous) is a consideration of practical importance in applying symmetric electrochemical capacitors because most situations will require higher voltages calling for multiple series connection of units. Since the voltage on a series of cells will not divide evenly, due to differences in cell characteristics arising during manufacture, the operating voltage must be derated, so that electrolyte breakdown does not occur in any cell. There are performance penalties, as stacking units in series not only lowers the capacitance according to the rule stated above, but also increases the ESR in direct proportion to the number of cells

Although the capacitance values of Hybrid capacitors are orders of magnitude lower compared to symmetric electrochemical capacitors of similar physical size, the Hybrid capacitor can have a similar energy density. The reason for this is the total energy stored by a capacitor is proportional to the capacitance times the square of the cell voltage. Therefore, a 100μF, 100V capacitor stores the same energy as a 1F, 1V capacitor. Because the need for series cell stacking is eliminated, Hybrid capacitors have the additional advantage of substantially lowered ESR and consequently better frequency response.

The cell potential, as stated previously, is divided unevenly in a Hybrid capacitor. Because the electrodes are in series, the charge accumulated at the negative electrode must equal the charge lost at the positive electrode, or,

$$V_a C_a = Q = V_c C_c$$

For a Hybrid capacitor  $C_c \gg C_a$ , so  $V_a \gg V_c$ . From this relationship, it also follows that,

$$V_c = V_a C_a / C_c$$

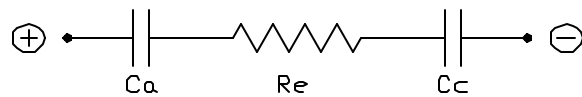


Figure 1. Electrical schematic of an electrolytic capacitor. The individual positive and negative electrode capacitances are connected in series by the electrolyte.

By design, in order to prevent the electrolyte reduction potential from being exceeded at the negative electrode, the negative electrode capacitance ( $C_c$ ) must have a minimum value. A safety margin is added to this capacitance. Typical tantalum Hybrid capacitor potential drop associated with the negative electrode is designed to be 0.3 volt maximum.

## Discussion and Results

A purpose of this work was to develop a thin, rectangular tantalum Hybrid capacitor that would be appropriate for high-volume military, avionics, and communications applications. In minimizing positive electrode thickness, not only were physical height requirements reduced, but also electrical frequency response was optimized. The case design used was simply a folded tantalum foil, coated on the inside with  $\text{RuO}_2$ , wrapped around the tantalum pellet positive electrode. Welding along the edges sealed the assembly. The electrical feed through was

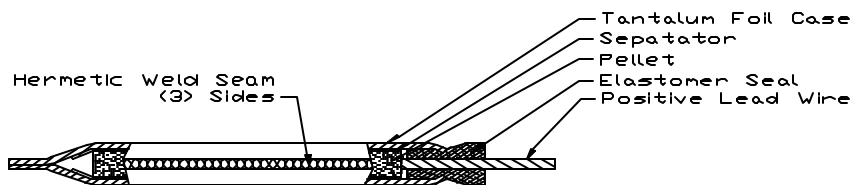


Figure 2. Drawing of the prototype capacitor showing a partial cut-away view. The overall dimensions are 19mm X 18mm X 1.4mm.

accomplished with an elastomer seal. We wanted the unit to be inexpensive and easy to assemble. This meant reducing to the minimum the number of parts required.

Another purpose was to extend Hybrid capacitor engineering principles to design the even smaller, thinner capacitors needed for surface-mount applications, and to predict their performance. For this it was useful to compare the electrical effects of using a thin tantalum pellet and a gelled electrolyte with the characteristics of a Hybrid capacitor using standard components.

Figure 2 is a drawing showing the parts of the prototype capacitor. The case was made from 0.12mm thick tantalum foil. The foil case had two preformed cavities, which when folded along a line that separated them, became a hollow that held the positive electrode, separator, and electrolyte. On the inner surface of the cavities was bonded a film of  $\text{RuO}_2$ , which was the negative electrode. It had a capacitance density of  $0.05\text{F}/\text{cm}^2$ . A 0.08mm thick non-woven glass-polyolefin separator was used. The electrolyte was 38wt.% sulfuric acid, gelled with a 5% addition of fumed silica. The positive electrode was pressed from 1 gram of FTW700 tantalum powder and sintered 30 minutes at  $1360^\circ\text{C}$ . The dimensions were 14.7mm X 12.2mm X 0.9mm. An electrochemical oxide was formed in a 0.1wt.%,  $85^\circ\text{C}$  phosphoric acid solution to 6.75 volts. A Viton® elastomer feed-through provided an insulating seal for the positive electrode wire. Figure 3 is a photograph of a disassembled unit, and Figure 4 is a photograph of a complete capacitor. As shown in Figure 3, the complete assembly has only four parts.

Electrical impedance spectroscopy (EIS) was used to measure capacitor electrical char-

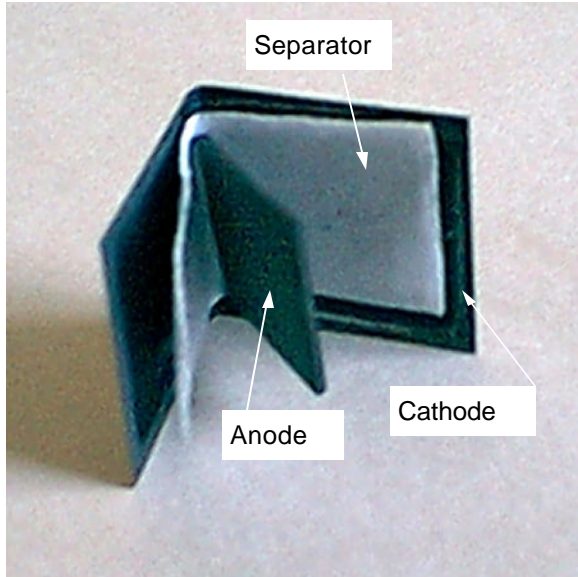


Figure 3. Photograph of a disassembled prototype tantalum Hybrid capacitor showing the cathode coating, anode pellet, and separator. The case is partially unfolded to show interior.

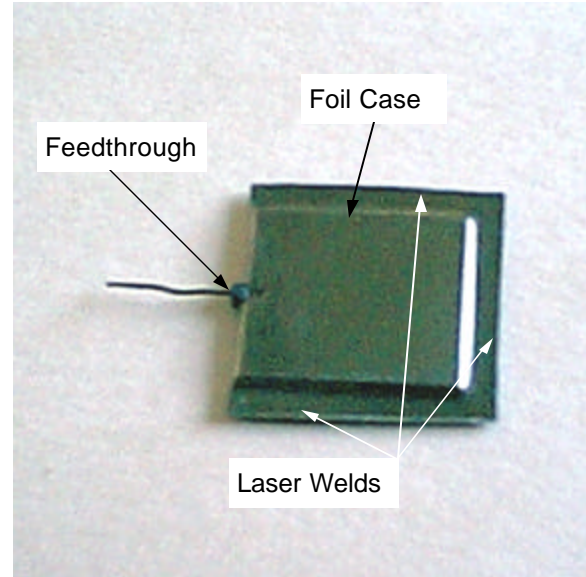


Figure 4. Photograph of the prototype tantalum Hybrid capacitor. This particular unit has a capacitance of 8mF at a rating of 5.5 volts. The case is only 1.4 mm thick.

acteristics. These measurements were made with a Gamry Instruments CMS-100 system. Figure 5 is a plot of impedance vs. frequency. From the figure, the ESR is 0.029 ohms at a frequency of 10kHz. Figure 6 is a plot of capacitance vs. frequency. The capacitance equals 7.1mF at 100Hz. Between 10kHz and 100kHz, the plot gives a false indication of capacitance, due to the fact that the capacitor is being evaluated at its self-resonant frequency. Figure 7 is a plot of phase angle vs. frequency. An ideal capacitor has a phase angle equal to  $-90^\circ$ . The plot shows nearly ideal behavior for frequencies below about 100Hz. The device still functions as a capacitor at a frequency of 10kHz, although a lossy one, because the phase angle has increased to  $-15^\circ$  at that frequency. At 630Hz, the reactive impedance equals the resistive impedance, and the capacitor has a phase angle of  $-45^\circ$ . This characteristic frequency of the prototype capacitor is at least two orders of magnitude higher than for electrochemical capacitors with symmetric electrodes. Table 1 summarizes the important performance data for the prototype capacitor.

The results show little of the “transmission line” behavior attributed to the porous electrodes of electrochemical capacitors, and are more comparable to those of electrolytic capacitors. Table 2 compares its electrical properties with those of an extended range tantalum electrolytic capacitor (MIL-C-39006/25).

Table 1. Prototype tantalum Hybrid capacitor properties.

Capacitance	Voltage	ESR	Leakage Current	Weight	Dimensions
7.1 mF	5.5 volts	0.029 ohms	25 mA	2.7 grams	19mm X 18mm X 1.4mm

Table 2.

	Prototype Tantalum Hybrid	MIL-C-39006 /25
capacitance	7.1 mF	2.2 mF
voltage	5.5	6.0
energy density (J/cc)	0.224	0.021
energy density (J/g)	0.040	0.0025
ESR	0.029	0.10

**Conclusion**

A new tantalum Hybrid capacitor was designed and prototype units were fabricated and evaluated using EIS. The new capacitor incorporates a relatively thin positive electrode that yields a low ESR. The capacitor electrical performance is similar to that of tantalum electrolytic capacitors, but the energy density for the Hybrid is at least a factor of ten higher. This suits the unit for electrolytic capacitor applications that benefit from higher energy density such as military, avionics, and wireless communications. Work will continue more fully characterizing the performance of these capacitors under a range of conditions.

**Reference**

1. B. E. Conway, "Electrochemical Supercapacitors", p. 466, Kluwer Academic / Plenum Publishers (1999).

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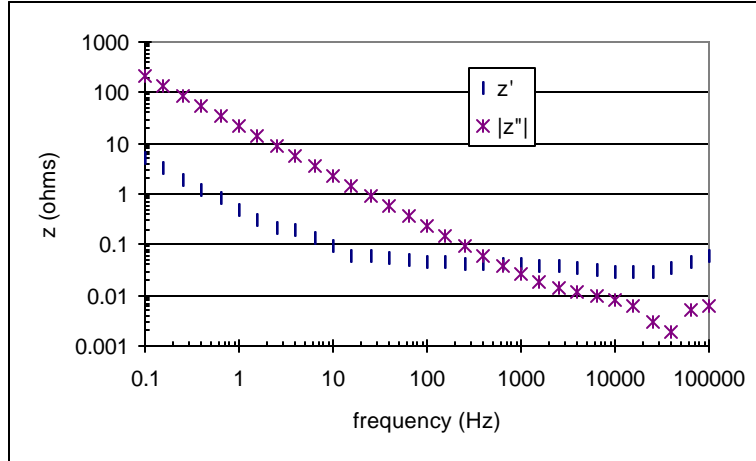


Figure 5. Resistance and reactance vs. frequency in the range of 0.01Hz to 50kHz.

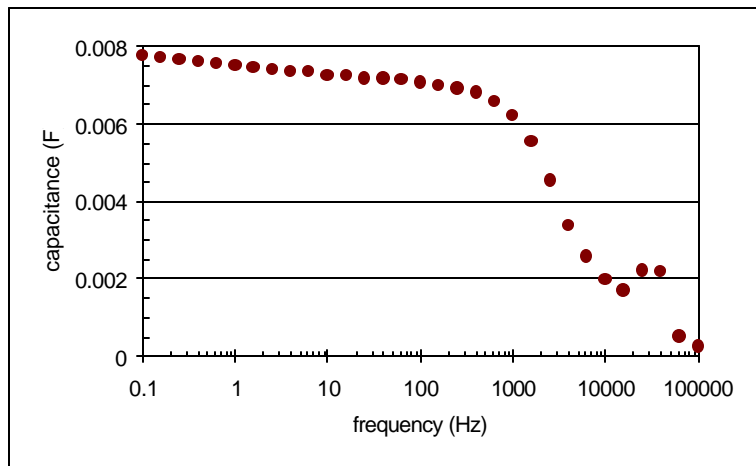


Figure 6. Capacitance vs. frequency.

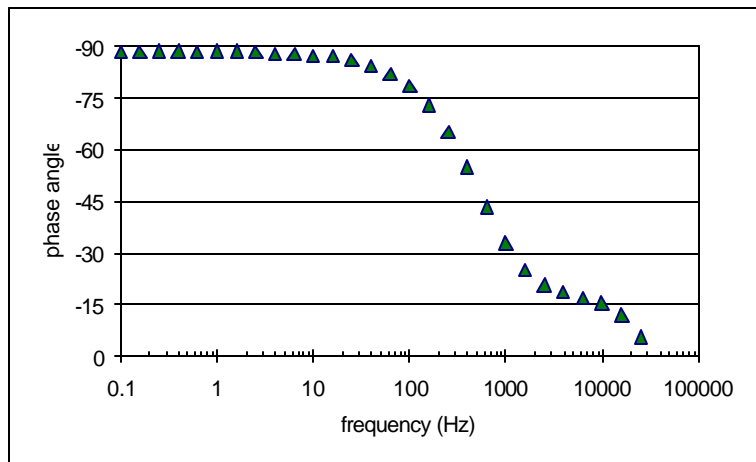


Figure 7. Phase angle vs. frequency.