# Tantalum Hybrid Button Cell Capacitor

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**Abstract**

A tantalum Hybrid capacitor with a thin circular case has been developed. The new button cell, rated 1800uF at 50V has a diameter of 23mm, a thickness of 2.5mm, and a weight of 8g. The device will fit standard 2325 size coin cell battery holders. The tantalum case features nickel plated exterior faces which serve as low resistance terminals.

The tantalum Hybrid capacitor is combination of a high voltage sintered tantalum pellet positive electrode, bearing a $Ta_2O_5$ dielectric film, coupled with a low voltage high-capacitance density electrochemical redox pseudocapacitance negative electrode based on $RuO_2$. Unlike symmetric electrochemical capacitors which have no dielectric and are limited by electrolyte breakdown voltage, the Hybrid capacitor permits high voltage single cell operation. This eliminates the need for series connections. The device has over 10X the specific energy of aluminum electrolytic capacitors with similar electrical properties. Although the specific energy can be lower than that of electrochemical capacitors, the Hybrid resistance is about three orders of magnitude lower, and consequently, the specific power is much higher.

Electrical characteristics, including electrical impedance spectroscopy are presented.

## Introduction

The tantalum Hybrid capacitor is a series combination of a dielectric oxide film capacitance, $Ta_2O_5$, and a high electrochemical capacitance, a film of the conductive metal oxide, $RuO_2$. The result is a polar capacitor; with the $Ta_2O_5$ film, the positive and the $RuO_2$ film the negative electrodes. A high potential can be maintained across the thin electrochemically formed $Ta_2O_5$ film, while the $RuO_2$ 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, $1/C = 1/C_a + 1/C_c$,

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where $C_a$ and $C_c$ respectively are the positive and negative electrode capacitances.

In the Hybrid capacitor, since $C_c >> C_a$, the overall capacitance is determined by $C_a$. Because the $RuO_2$ 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 $Ta_2O_5$ 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 170 volts for devices produced by Evans Capacitor. The voltage rating of the capacitor is less than the $Ta_2O_5$ formation voltage, and for Hybrid capacitors, the ratio of formation voltage to rated voltage is at least 1.3. This voltage margin is critically important because the leakage current rises sharply as the cell voltage approaches the formation voltage, and life is proportional to the time integral of the leakage current.

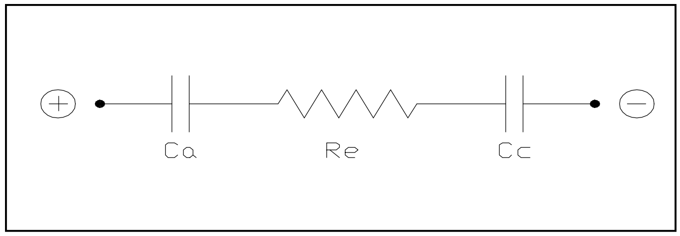



Figure 1. Electrical schematic of an electrolytic capacitor. The individual positive and negative electrode capacitances are connected in series by the electrolyte.

The negative electrode is a high capacitance density film of $RuO_2$ bonded to a thin tantalum foil. The bulk capacitance of the $RuO_2$ electrode material is approximately 50F/g. The capacitance density of the $RuO_2$ film is approximately $100mF/cm^2$. Therefore, only a small amount of $RuO_2$ is required.

Symmetric electrochemical capacitors have a cell voltage, limited to the electrolyte breakdown potential (ca. 1.2 volts, aqueous, 3.5 volts, nonaqueous). This is a consideration of practical importance in applying this type of device because most situations will require higher voltages calling for multiple series connection of cells. Since the voltage on a series of capacitors will not divide evenly, due to differences in cell characteristics arising during manufacture or use, the operating voltage must be reduced, 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. Hybrid capacitors use aqueous sulfuric acid electrolyte, yet they are capable of high working voltages without resorting to series connected cells. In the Hybrid capacitor the voltage drop is across the dielectric so the electrolyte operates well within its stable potential window.

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 100uF, 100V capacitor stores the same energy as a 1F, 1V capacitor. Because the need for series cell stacking is eliminated, Hybrid capacitors have the advantage of substantially lowered ESR and consequently better frequency response. As an additional economic advantage, much less $RuO_2$ is required per joule of energy stored in the Hybrid capacitor compared to a symmetric $RuO_2$ device.

The cell potential, as stated previously, is divided unevenly in a Hybrid capacitor. Because the electrodes are in series, the charge (Q) accumulated at the negative electrode must equal the charge lost at the positive electrode. Since Q=C • V, the following relationship exists

$$Va \cdot Ca = Q = Vc \cdot Cc$$

Rearranging these terms it follows that,

$$Vc = Va \cdot Ca/Cc$$

For a Hybrid capacitor Cc >> Ca, so Va >> Vc. By design, in order to prevent the electrolyte reduction potential from being exceeded at the negative electrode, the negative electrode capacitance (Cc) must be greater than 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.

The preceding charge-voltage analysis applies for DC, where the capacitor is charged or discharged only very slowly, but for high currents commonly encountered, the effects of resistance related voltage jump must also be considered. It has been determined that the cathode voltage jump is proportional to the ratio of the internal resistance of the cathode electrode to the total resistance of the capacitor.[2] The effect of the voltage jump on capacitor life has not yet been established.

**Capacitor Construction**

Figure 3 shows a cross-section view of the button cell. Central to the capacitor cell is the positive, or anode electrode. It is comprised of high surface area tantalum powder, pressed and

Figure 2. Photographs of the tantalum Hybrid button cell. The top photo is of the compete unit. The bottom photo shows the components of a dismantled unit. This cell has only four parts, making for easy reliable assembly.

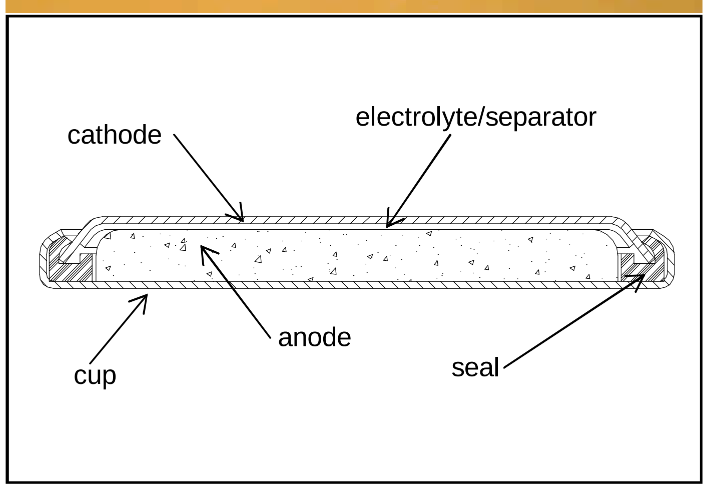




Figure 3. Cross section view of button cell showing major components. The case top and bottom are made from tantalum. The capacitor is assembled dry, and electrolyte is admitted by vacuum impregnation process. Final seal is secured by crimping the exterior perimeter of the anode cup.

sintered, forming a porous pellet. The anode pellet is attached to the inside of a tantalum cup which forms half of the case and is the positive terminal for the cell. Sintering the cup and pellet together forms an intimate electrical connection between the two. The dimensions of the anode pellet are 18.8mm diameter and 1.8mm thick. The pellet has a density of 5-8g/cm$^3$, which is 1/3 to 1/2 the specific gravity of tantalum metal, making the pellet at least 50% open volume. The capacitor dielectric, $Ta_2O_5$, covers all exposed anode surfaces, including both the pellet and the cup. The dielectric is electrochemically formed in an aqueous phosphoric acid solution. The negative electrode or cathode is constructed of tantalum sheet covered on one side with a thin coating of $RuO_2$ active material. The cathode is formed into a cap which serves as the top half of the case and as the negative terminal of the cell. Between the cathode and the anode is a non-woven polymer-based separator which absorbs the electrolyte and prevents electronic contact. The edge of the cathode cap is surrounded by a resilient elastomer seal which positions the cap in the center of the case and prevents electrical contact between the cap and anode-cup. After about 350mg of 38% sulfuric acid electrolyte is admitted by vacuum impregnation, the anode cup is crimped at the periphery, engaging the seal and forming a leak-proof joint. Finally, the outer surfaces of the assembled capacitors are covered with nickel electro-

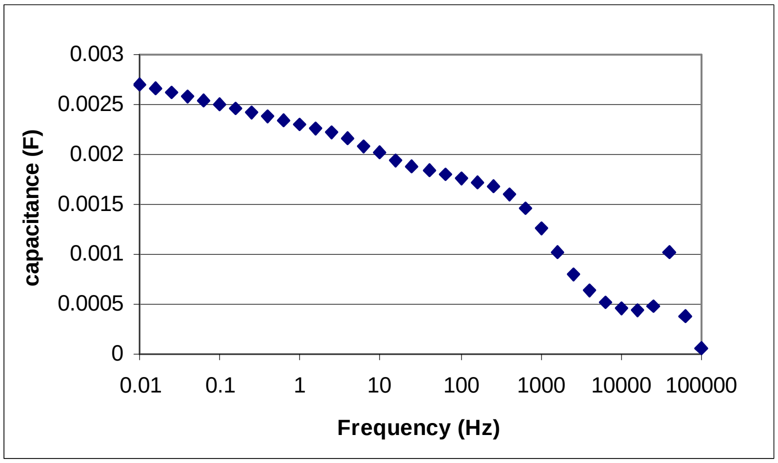



Figure 4. Capacitance vs. frequency for 50 volt button cell. The capacitance is 1750uF at 120Hz.

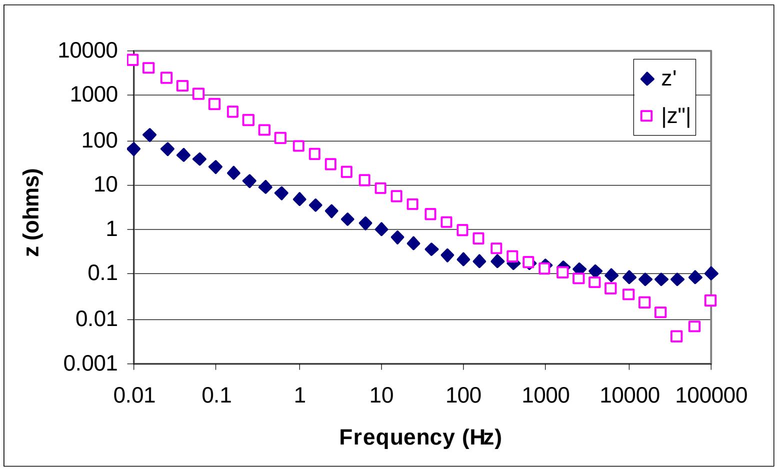



Figure 5. Impedance vs. frequency for 50 volt button cell. The ESR is 161mohm at 1kHz.

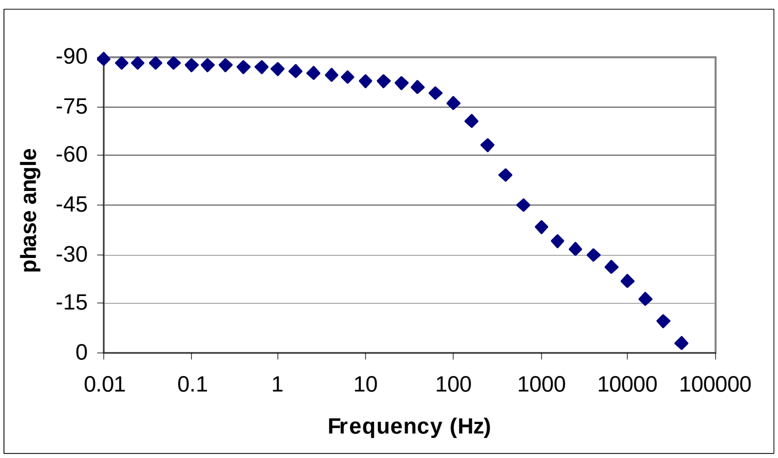



Figure 6. Phase angle vs. frequency for 50 volt button cell. The capacitor has a phase angle of –45° at a frequency of 630Hz. At lower frequencies, the phase angle rapidly approaches –90°.

plating.   Figure 2 are photographs of the finished capacitor and a dismantled unit.

**Results and Discussion**

A set of button cell capacitors was fabricated.  The anodes had a formation voltage of 65 volts, corresponding to a 50 volt rating.   Electrical impedance spectroscopy was performed using a Gamry Instruments CMS-100 system.  Measurements were made at room temperature with a 2V DC bias and 10mV rms signal.

Figure 4. is a plot of capacitance vs. frequency.  Capacitance was calculated from the raw impedance data using the relationship:

$$C = 1/(6.283fz'')$$

The capacitance at 120Hz was calculated to be 1750uF.  The capacitance increased with decreasing frequency to about 2700uF at 0.01Hz.  Characteristic of all tantalum Hybrid capacitors, this unit had a DC capacitance of about twice the 120Hz value.  The total stored energy based on the 120Hz result of 1750uF at 50 volts is 2.2 joules.  Since the volume of the capacitor is $1.0cm^3$, the energy density is 2.2 joules/$cm^3$ at 120Hz.

Figure 5 is a plot of the impedance vs. frequency where z' is the resistance and z" is the reactance.  The resistance reached its minimum value of 0.076 ohms at 25kHz and had a value of 0.161 ohms at 1kHz.  Figure 6 is a plot of phase angle vs. frequency.  An ideal capacitor has a phase angle of –90°.  The self resonant frequency is the point at which the phase angle is zero degrees, which for the 50V button cell corresponded to 40kHz.  At a phase angle of –45°, the reactance equals the resistance.  For this capacitor, the frequency of –45° phase angle was about 630Hz.  At 630Hz, the resistance was 0.172 ohms and the capacitance was 0.0015F.  The RC product, a measure of the capacitor time constant, was therefore 0.25msec.  This is comparable to other tantalum Hybrid capacitors and is at least three orders of magnitude smaller than for other high energy density capacitors including carbon electrochemical capacitors.  For that reason, Hybrid capacitors are able to be used in many applications that, because they require very high currents or high repetition rates, are out of the range of conventional electrochemical capacitors.  These applications include filtering, laser and radar pulse power supply, radio communications, timing, and other circuits where electrolytic capacitors are in common use.

Figure 7 is a Ragone plot giving discharge energy vs. power for the range of 10 to 175W.  These measurements were made using a Kikusui PLZ153W electronic load and a LeCroy Wavepro 7100 digital storage oscilloscope (DSO).  Two channels of the DSO were used to monitor capacitor voltage and current, and these were multiplied together to give power.  The integral of power over time is equal to the energy.  The maximum power tested, 175W, was the maximum power that could be handled by the electronic load.  The peak power of the capacitor as calculated from the relationship $P = V^2 /4R$ is >3.5kW, was much higher.

Figure 8 is a plot of voltage vs. time for various constant current loads.  From the relationship, $C\,V = I\,t$, the capacitance can be calculated by dividing the current by the slope of the discharge curve.  The result of the calculation was a capacitance value of between 1700uF at 0.1A to 2080uF at 2A.  This is in fairly good agreement with EIS and bridge measurements, although the lower capacitance at low current is somewhat unexpected, and may reflect the effect of incomplete charging of the capacitor during re-charge between measurements or of a high leakage current.

Table 1 is a listing of various voltage and capacitance ratings which could be made in the 2325 button cell case size.  The values are the result of engineering estimation based on the present 50V prototype and our experience with larger tantalum Hybrid capacitors.

Table 1. These are estimated values of capacitance for the 2325 button cell tantalum Hybrid capacitor based on characteristics of the prototype 50 volt cells.

| **Voltage (WVDC)** | 6.3 | 8 | 10 | 16 | 25 | 35 | 50 | 63 | 80 | 100 | 110 | 125 | 170 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Capacitance (uF)** | 17000 | 13500 | 12000 | 8100 | 5200 | 2700 | 1800 | 900 | 630 | 470 | 330 | 240 | 100 |

## Conclusion

Tantalum Hybrid button cell capacitors with a rating of 50V were constructed and several simple measurements of electrical characteristics and performance were made. The capacitor had a capacitance of 1750uF at 120Hz and an ESR of 0.161 ohms at 1kHz. EIS data showed its frequency response to be typical of cells having porous electrodes. The capacitor had an energy density of 2.2J/cm$^3$, which is at least an order of magnitude higher than that of conventional electrolytic capacitors of similar electrical performance. A family of similar capacitors with different voltage ratings was designed.

Work in ongoing to determine life at various temperatures and voltages and to make further preparations for volume production.

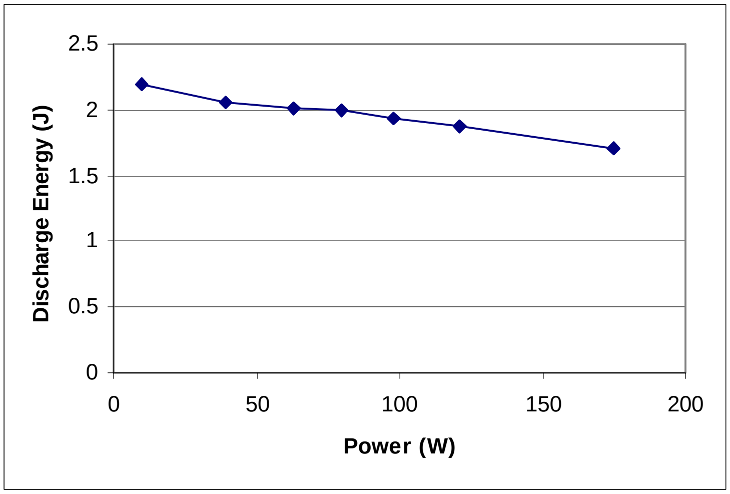
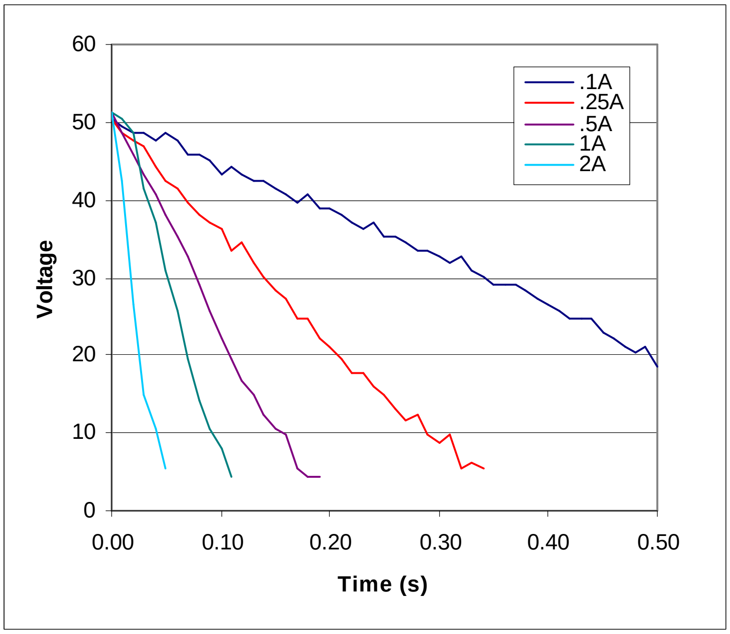



Figure 7. Ragone plot for the 50V 2325 button cell prototype. The maximum load power of 175W represents the limit of the electronic load used to make the measurements. The peak power capability of the capacitor is much higher.

Figure 8. Plot of voltage vs. time for various constant current discharges of the 50V button cell. Capacitance equals the slope of the curve divided




## References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2. T. Y. Chang et al, “Electrochemical-Electrolytic Hybrid Capacitors”, p. 72-75, in Proceedings of the 40th Power Sources Conference (2002).



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