HERMETIC HYBRID CAPACITORS
(and Other Goodies)

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ABSTRACT

High-energy-density capacitors with a tantalum metal anode, Ta_2O_5 dielectric, aqueous electrolyte, and RuO_2 cathode have been described.[1] Known as Evans *Hybrid*® capacitors, these devices have the high energy density of electrochemical capacitors with the improved a.c. behavior of electrolytic capacitors. Single-cell working voltages up to 215 volts have been demonstrated.   Prior work focused on demonstrating the technology using prototype packaging. Significant effort has now been spent on designing, developing and building packaging for production capacitors. As a result, there are now two product types, a hermetic capacitor in tantalum hardware, and a polypropylene-cased tantalum Hybrid. Performance and features of both types are presented.

INTRODUCTION

The Evans Hybrid capacitor combines the best features of both electrochemical and electrolytic capacitors by using an electrochemical capacitor cathode and an electrolytic capacitor anode. Order-of-magnitude increases in volumetric energy density over aluminum electrolytic capacitors have been reported. Unlike electrochemical capacitors, Hybrid capacitors have high cell voltage capability and a.c. frequency response comparable to aluminum electrolytic capacitors.[1]

Many applications would benefit from using a capacitor with increased energy density. These include medical implants, avionics and airborne instruments, portable equipment, automotive and electric vehicle applications. Many of these uses require capacitors rated at or above 100 volts. High-voltages present serious problems for users and builders of electrochemical capacitors because the cell voltage for these devices is <3 volts, making series connections necessary. Energy density of electrochemical capacitors is proportional to the square of cell voltage. But as the number of cells in series increases, the cell voltage must be decreased to allow for imbalances arising from inevitable differences in individual cell manufacture.[2]

Energy density is therefore decreased for electrochemical capacitors with increased device working voltage.

Electrolytic capacitors are readily available with single-cell working voltages of up to 550 V. The energy density of these devices is proportional to the cell voltage. Series connection of capacitor cells is not required for applications below 550 V. Electrolytic capacitors enjoy extensive use in a.c. circuits because they exhibit acceptable performance operating at frequencies up to 100 kHz. For example, many applications operate at 120 Hz, the ripple frequency for power supplies using 60 Hz input power. Conversely, electrochemical capacitors are best suited to d.c. energy storage applications because their performance at higher frequencies is somewhat limited. Electrochemical capacitors using more highly conductive aqueous electrolytes have a higher power capability than similarly constructed non-aqueous devices, but non-aqueous devices have the advantage of higher energy density due to higher cell voltage.

The Evans Hybrid capacitor exploits the best features of both capacitor technologies. It uses the anode from an electrolytic capacitor and the cathode from an electrochemical capacitor. This combination provides a working voltage and frequency response very similar to those of an electrolytic capacitor but with greatly augmented capacitance density.[3]

DISCUSSION

Construction. The present effort is focused on developing products which employ Hybrid capacitor technologies, materials and methods generated previously. This has resulted in two products, differentiated mainly by the construction of the case in which they are housed. Both products use a porous tantalum pellet anode, RuO_2 on tantalum foil cathode and sulfuric acid electrolyte. One capacitor has a welded tantalum case and uses a glass-metal seal for the anode terminal feed through. The other has an injection molded polypropylene case which is assembled by ultrasonic welding. Each has its advantages to the particular intended application.

Considerable interest has been expressed in a hermetic capacitor for rugged, high-reliability applications. Figure 1. is a photograph of a 125 V, 3300 µF hermetic Hybrid capacitor, manufactured by Evans. This unit has five 16-gram parallel-connected anode pellets. The cathode is connected to the case. The outside dimensions are 1.4" diameter by 0.675" high. The weight is 120 grams. Figure 2. is a photograph of a 54 V, 18,000 µF polypropylene case capacitor. This capacitor has three parallel connected anode pellets. The dimensions are 1.65" X 1.61" X 0.490". The weight is 57 grams. Both capacitors are designed to operate in the temperature range of -55 to 85ºC.

Figure 3. shows the important features of the hermetic Hybrid in cross-section. The five anode pellets, each measuring 1.34" diameter by .095" thick account for over 80% of the internal volume. Six RuO_2 on 0.001" thick tantalum cathode foils are welded to the case. Non-woven glass separators, 0.005" thick are used between the anode and cathode electrodes. Teflon insulators are used between the anodes and the case. The device has a single matched coefficient of thermal expansion glass-metal seal which serves as the anode feed through. The unit is assembled dry, with electrolyte added through a small hole in the cover. A tantalum plug is then welded in the fill hole.
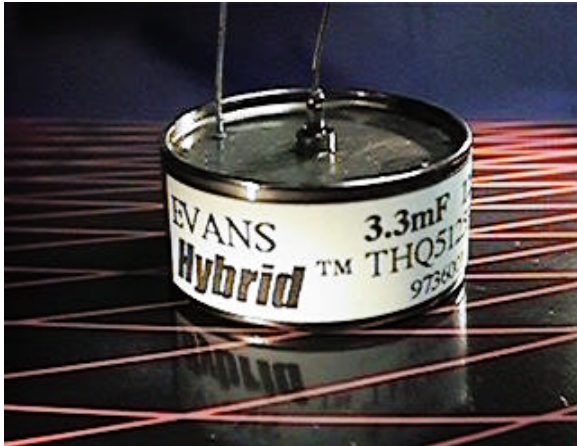
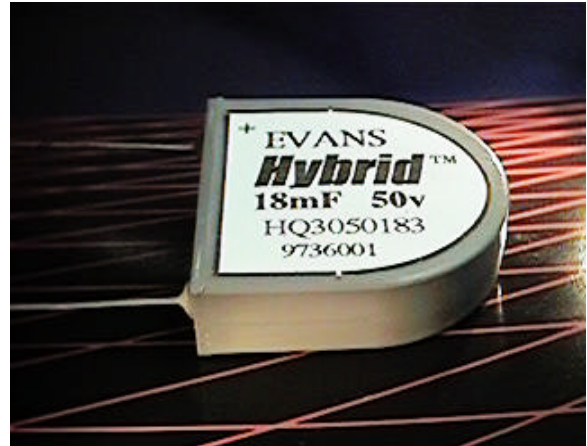Figure 1. Photograph of a 125 V, 3300mF hermetic tantalum Hybrid capacitor.

Figure 2. Photograph of a 54 V, 18,000 mF polypropylene case Hybrid capacitor.

Figure 4. Is a cross-section view of the polypropylene case Hybrid capacitor. This unit has three parallel-connected anode pellets and four cathode foils. As shown in the diagram, the arrangement of the electrodes is the same as in the hermetic version. The terminals consist of tantalum pins which are welded on one end to a nickel or copper wire. An O-ring provides a radial seal between the tantalum pin and the case. The weld is embedded in an epoxy encapsulation which anchors the terminal to the case, conducts away soldering heat, and positions the seal. The tantalum end of the terminal enters the case and is in contact with the electrolyte. A welded connection is made to each pin with the anode or cathode electrodes. Final assembly is made by ultrasonic welding.
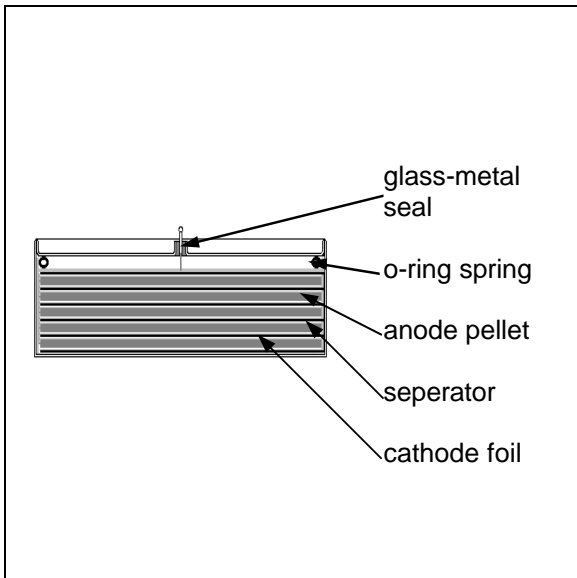

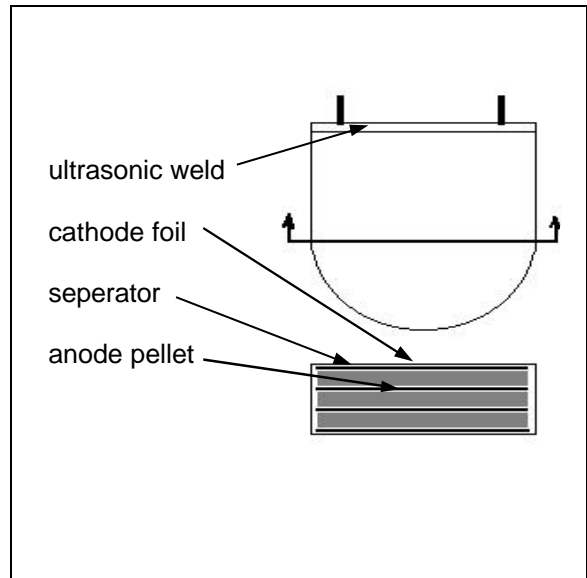Figure 3. Hermetic Hybrid capacitor cross-section view.

Figure 4. Polypropylene case Hybrid capacitor cross-section view.

Performance. Results of electrochemical impedance spectroscopy (EIS) measurements for the two devices are given in Figures 5 - 9. EIS is useful to the capacitor engineer and circuit designer for information it provides about device operation over a range of frequencies. Figure 5. is a Bode plot showing the components of the impedance vs. frequency over the range of 0.1 Hz to 100 kHz for the hermetic Hybrid. Z" is the reactance and Z' is the resistance. The self-resonant frequency is the point at which the absolute value of the reactance is a minimum, and this occurs at about 20 kHz. Figure 6. is a Nyquist plot which is another way of presenting the data of Figure 5. This shows reactance vs. resistance, with each point representing data at a specific frequency. The highest frequency data is at the lower left of the plot. The plot for an ideal capacitor is a vertical line intersecting the resistance axis at a point which is the ESR. Of course, the behavior of this unit is non-ideal, with the 45° slope at higher frequencies characteristic of capacitors with porous electrodes. Figure 7. is the Bode plot for the 54 V, 18 mF polypropylene case Hybrid. The self-resonant frequency is about 7 kHz. Figure 8. is the Nyquist plot for the unit of Figure 7. It shows nearly ideal behavior. Phase angle vs. frequency data are presented in Figure 9. The phase angle is related to the impedance by the formula

$$\theta = \tan^{-1}(Z''/Z') \ .$$

It is interesting to note that an ideal capacitor has a -90° phase angle at all frequencies. At an angle of -45°, the resistance equals the reactance. It is most electrically efficient to select capacitors with a -90° phase angle at the desired frequency of operation, but other considerations such as energy density, cost, etc. usually play a factor, so units operated in the range of -90° to -45° are often acceptable. The most efficient range for the unit shown is up to about 800Hz.

Life Performance. Because these are new products, no direct data indicating life performance are yet available. We have begun a series of aging experiments on both products to provide needed information. We are also working with a number of others interested in using these devices who are studying the issue. Information concerning life will be provided later.

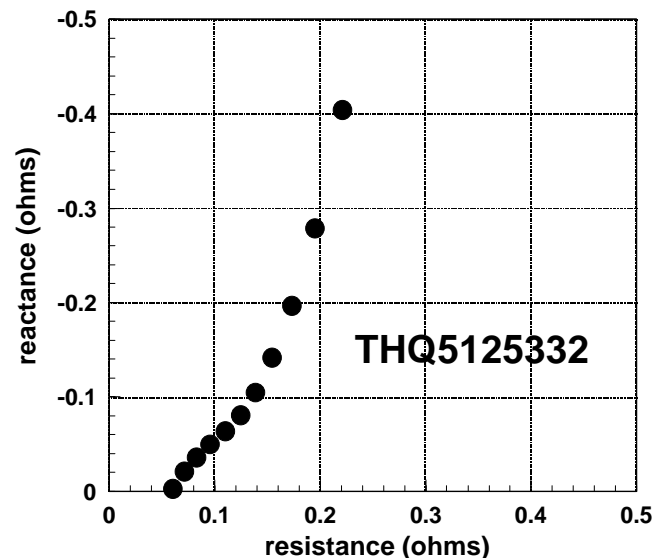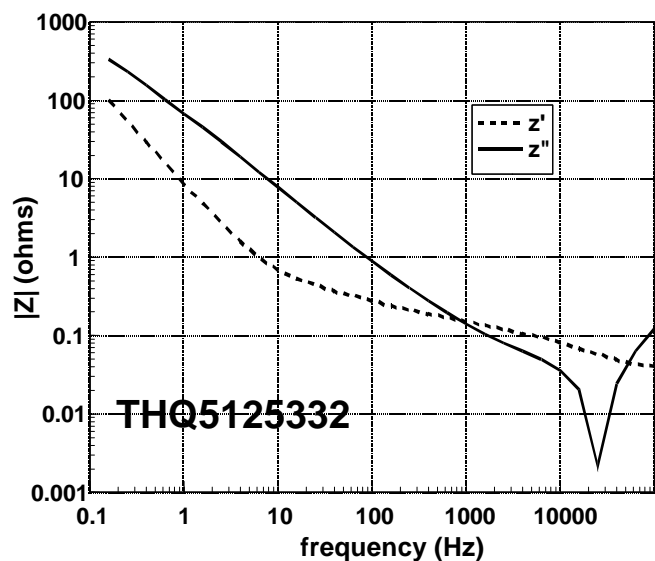*Figure 5. Bode plot for the 125 V, 3300mF hermetic Hybrid capacitor.*

Figure 6. Nyquist plot for the 125 V, 3300 mF hermetic Hybrid capacitor.
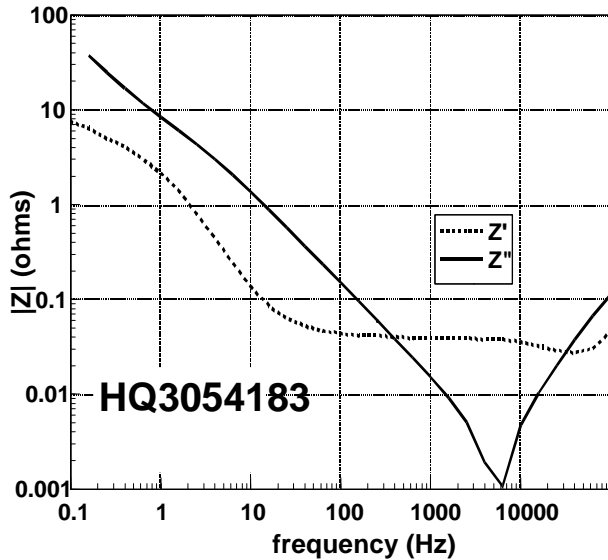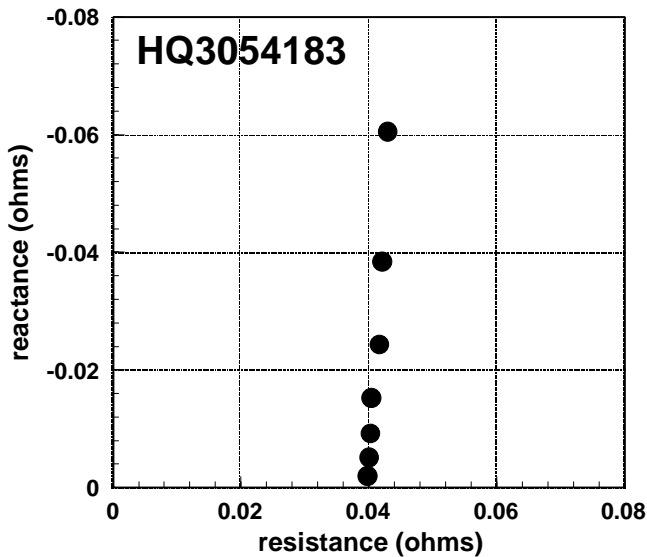
Figure 7. Bode plot for the 54 V, 18 mF polypropylene case Hybrid capacitor.

Figure 8. Nyquist plot for the 54 V, 18 mF polypropylene case Hybrid capacitor.

It may be useful to draw certain conclusions from ongoing experiments on aging of different designs using the same technology. Test results from one set of experiments have been reported for a tantalum case hermetic Hybrid.[4] The parts tested used the same anode, cathode and electrolyte technology described here. The primary difference was that instead of using the cathode foils, the devices had the cathode formed directly on the inside wall of the case. Twenty 50 V, 680 μF MIL-style capacitors were charged to the rated voltage and held at 85° C for 1000 h. All units had acceptable capacitance, ESR, and leakage current results (to the requirements of MIL-C-39006). In another experiment, a 30 V, 8 mF prototype polypropylene case Hybrid capacitor was maintained at 30 volts while held at room temperature (25° C). This temperature was chosen because the case of this unit was not designed for higher temperature operation. Figure 10. gives leakage current vs. time data for this test. The tendency of the leakage current to decrease over time can be a good predictor of long life. The leakage current appears to have stabilized at about 10 μA after 4500 h.

Energy Density. Like other Hybrid capacitor designs, these units have high energy density compared to other electrolytic capacitors. Table 1. lists performance data, ratings and energy density computed as

$$E = \tfrac{1}{2}\ C\ V^{2}.$$

CONCLUSION

Data presented for the hermetic and polypropylene case Hybrid capacitors indicate that good performance is maintained in the new capacitor designs. Electrical performance of Hybrid capacitors with high energy density is similar to other electrolytic capacitors. The new cases have features which facilitate production, helping assure a viable product. These capacitors are offered in a number of sizes and voltage ratings suited to many d.c and a.c. applications.
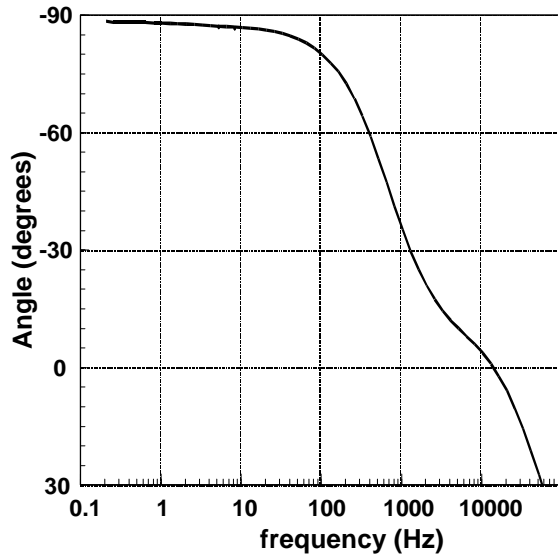
Figure 9. Phase Angle vs. Frequency for the polypropylene case Hybrid capacitor.
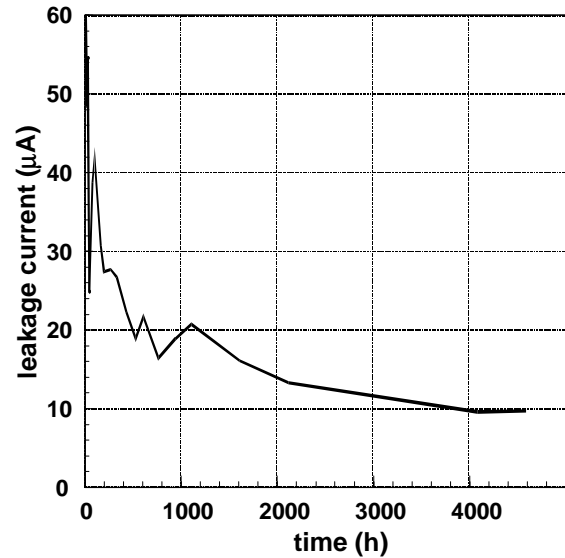

Figure 10. Leakage current vs. time for a 30 V, 8 mF polypropylene case Hybrid capacitor.

Table 1. Comparative performance data.

capacitor type	capacitance (μF, 120 Hz)	voltage (volts)	ESR (Ω, 1 kHz)	energy density J/g	energy density J/cm^3
hermetic Hybrid	3300	125	0.045	0.21	1.55
polypropylene case Hybrid	18,000	54	0.030	0.46	1.35
aluminum electrolytic[†]	18,000	50	0.008	0.16	0.164

† Nippon Chemicon series 36DA

REFERENCES

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[2]   J. R. Miller, "Electrochemical Capacitor Voltage Balance: Cell Uniformity Requirements for High-Voltage Devices", Proc. 36th International Power Sources Symposium, pp. 15-18, 6/94.
[3]   J. R. Miller and D. A. Evans, "Properties and Performance of Aluminum Electrolytic/Electrochemical Capacitors", Proc. CARTS '96: 16th Capacitor and Resistor Technology Symposium, 11-15 March 1996.
[4]   D. A. Evans and D. Stephenson, "Performance of MIL-Type Hybrid Tantalum Capacitors", Proc. CARTS '95: 15th Capacitor and Resistor Technology Symposium, 13-16 March 1995.