Electrical Properties of a Novel High CV Wet Tantalum Capacitor System

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Abstract

High CV wet tantalum capacitors, per military drawing 93026, rely on a high efficiency, high capacitance cathode system to allow the maximum volume possible of the tantalum anode. Capacitance and voltage ratings are achievable, utilizing these technologies, which are about five times higher than conventional wet tantalum capacitors (Mil-PRF-39006). There are two typical cathode systems in the field today that have been utilized since the inception of this drawing. A new high CV wet tantalum system has been developed utilizing the combination of a novel cathode system and specialized anode processing, which reaches new levels of electrical performance and higher capacitance/voltage ratings. This paper reviews some of the current technology and electrical performance versus the novel approach developed and its performance.

Introduction

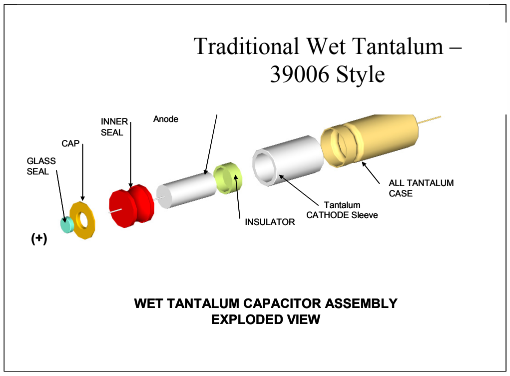
Wet electrolytic tantalum capacitors have been around for approximately 50 years. The oldest type still in wide use was developed in the late 1970s. It is still specified and purchased under the US military document Mil-PRF-39006. These devices are highly reliable and are packaged in a hermetically sealed case.

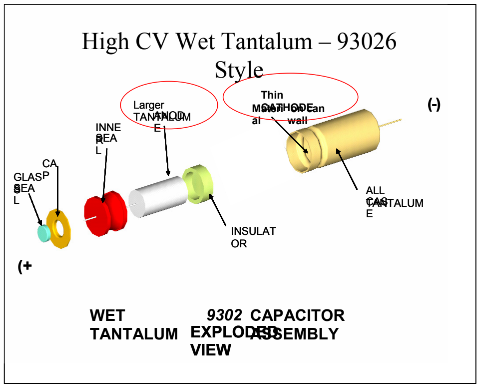
In this conventional design, the capacitance of the complete system is comprised of two series connected capacitors, one for the tantalum anode and one for the tantalum cathode.

The cathode system is comprised of a high surface area, pressed tantalum sleeve sintered to the tantalum can. Following sintering this sleeve is formed with a very thin tantalum oxide layer, to form the high capacitance cathode capacitor.

The tantalum anode is manufactured with a much thicker oxide layer. The capacitance that results from the anode represents the bulk of the capacitance for the system.

The tantalum anode should always be as large as possible to achieve maximum capacitance at a given voltage. However, with this conventional design the tantalum anode diameter is somewhat limited due to the thickness of the tantalum sleeve required. Because of this, these devices have lower energy densities than theoretically possible if the cathode sleeve thickness was minimized.





In the 1980s another type of cathode system was developed which was made from high surface area electro-deposited palladium. This system allowed for a large increase in cathode capacitance with a much thinner cathode 'sleeve'. The result was the ability to use a larger tantalum pellet anode and increase capacitance and voltage ratings, i.e. energy density.

In the 1990s, ruthenium oxide, another thin cathode material, was developed. Ruthenium oxide is a "Faradaic" cathode material, a class of materials known for its ability to actually store charge. The amount of charge the RuO_2 can absorb is roughly proportional to the voltage applied, in other words, $Q = kV$. Since the basic relationship between charge and voltage in a capacitor is $Q = CV$, the proportionality constant "acts" like a capacitor and therefore this type of electrode is commonly referred to as a "pseudocapacitor". This material has higher specific capacitance than palladium or tantalum.

Recently, AVX Corp. patented (US Patents 7,099,143 and 7,480,130) a new cathode for wet capacitors based on the concept employed in "double layer" capacitors, which is considered "non-Faradaic". This material system can also be applied very thinly, with a resulting high capacitance.

Discussion

Anode system

The anode system for all wet tantalum capacitors is made by pressing and sintering tantalum powder, to a density of about one third that of solid tantalum metal, and sintering at temperatures generally above 1400°C. Following sintering, the anode porosity that was achieved during pressing, is only slightly reduced. The combination of tantalum particle size, and volume of the anode, contributes to a very large surface area anode plate.

The dielectric material, tantalum pentoxide, is formed by immersing the tantalum anode in a weak acid bath and applying a voltage. The thickness of this insulating oxide is directly proportional to the voltage and grows at about 20 Å per volt. All formation voltages are greater than the rated voltage.

Following formation, this dielectric film is present on all the tantalum particles throughout the porous anode. The anode volume and thickness of the dielectric film determine the overall capacitance of the device.

Anode design is very critical. Powder selection, pressed density, sinter temperature and formation voltage are all factors to consider when designing an anode to meet the requirements of 93026.

Cathode system

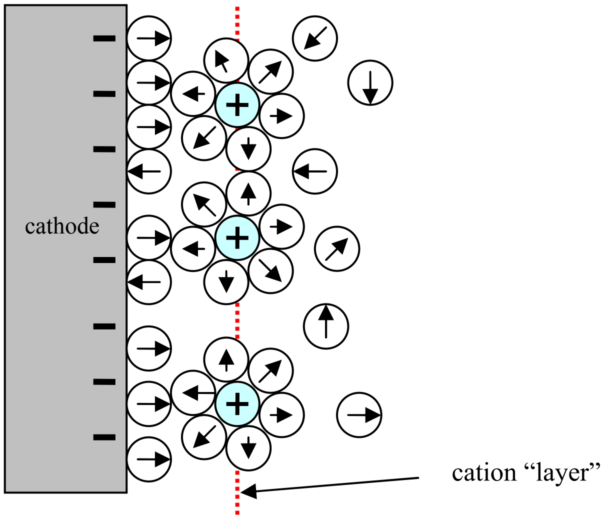
In the more classical mil style (Mil-PRF-39006) tantalum electrolytic capacitors, the cathode is made up of a sleeve of porous high CV tantalum sleeve, which is sintered to the tantalum can. Most manufacturers use the highest CV tantalum powder available for the cathode because these materials are capable of a low voltage dielectric film with the resulting highest surface area possible. The thinner dielectric and increased surface area of the cathode result in a cathode capacitance that is significantly higher than the anode. It turns out that this is what is needed for the anode capacitance to dictate the overall capacitance of the system.

$$Ct=1/(1/Cc+1/Ca)$$

Where Ct is the total device capacitance, Cc is the cathode capacitance and Ca is the anode capacitance. As long as the cathode capacitance is significantly greater than the anode capacitance than total device capacitance will be driven by the anode capacitance. If Cc=Ca, the total system capacitance would be only one half of the total of the individual capacitances. For this reason, the cathode system is made much larger than the anode capacitance. If the cathode capacitance were infinite, the capacitance of the device would equal the capacitance of the anode.

Double layer capacitors, such as that employed in this new device, are considered “non-Faradaic” because they do not involve charge transfer events across an interface at the cathode nor do they result in chemical changes to the cathode materials. For this reason they are exceptionally stable.

As the name suggests, the cathode capacitance is due to the formation of an electrical double layer at the interface between the cathode surface and the electrolyte. The double layer forms when the electric charge on the cathode causes the ions of the electrolyte to move toward the cathode, and molecules such as water, which have dipole moments, to orient themselves parallel to the electric field.

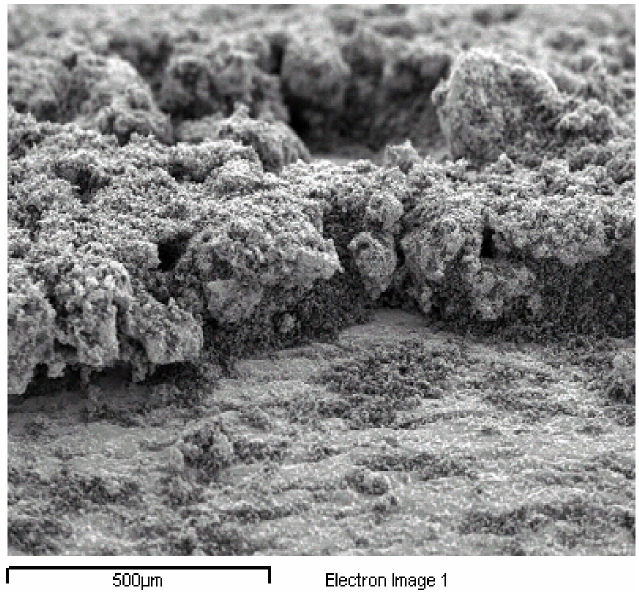


When a negative charge is placed on the cathode surface, water molecules (circles with arrows) will tend to cover the surface with their electric dipole fields largely oriented in parallel. Cations from the electrolyte (+ circles) will also be drawn to the negatively charged surface however because they are solvated (surrounded by water dipoles) they cannot quite reach the surface of the cathode. Thus there is a separation of the negative charge on the cathode and the positively charged ions of the solution - a double layer of charge. The red dotted line represents the average separation distance of the charges. This structure is essentially a parallel plate capacitor.

[1] Bockris and Reddy, Modern Electrochemistry Vol 2., p. 634.

This orientation phenomenon results in a separation of charge and therefore a capacitance. Since the charge is concentrated on only the surface of the cathode, a very large surface area is required to boost the capacitance to high levels.

In this new device, this is accomplished by coating the Ta can with a mixture of a fine powder of conducting metal oxide (NbO_2) and activated carbon. Both these materials have high specific surface areas. The carbon plays an essential role in achieving the cathode capacitance but is problematical because it is difficult to get the carbon to adhere to the Ta and the NbO_2. This problem has been solved with a unique process that "locks in" the activated carbon particles into a matrix of fine pores from which they cannot escape and where they maintain solid electrical contact to the other cathode materials. Cross-sectional view of the cathode:



Hydrogen gas generation within the system is a potential problem for all wet tantalum capacitors. The cathode design plays a critical role in minimizing the potential for hydrogen generation. From the formula $Q = CV$, the cathode must have a very high capacitance (C) so that with a given applied charge (Q), the potential (V) will not exceed the hydrogen generation potential. The electrolyte is the source of the hydrogen ions and the cathode, the negative lead, is where the hydrogen is produced. Since the cathode substrate, the can, is made of tantalum, it is vulnerable to hydrogen embrittlement. Cathode design considerations are important to keep this under control.

Electrolyte

One of the challenges in building a reliable and safe electrochemical capacitor is the proper selection of the electrolyte. The breakdown potential is usually less than 1 V for aqueous electrolytes.

A common electrolyte for wet tantalum electrolytic capacitors is sulfuric acid in water, at 36-38% by weight. This material works well up to 125 V and remains a liquid down to -62°C and has a boiling point of 127°C at 1 atmosphere, which is an operational requirement for 93026.

Performance

93026 Requirements

There are many technical requirements for product built to the 93026 drawing. Many of them are fairly straight forward with few difficulties in meeting them. Some of the more challenging specifications are listed below:

- Seal: Tracer gas test for nominal sensitivity of 10-8 atm3/s. Mil-Std-202 method 112.
- Shock: 100 g's DC rated V applied during test. Mil-Std-202 method 213. Electrical and mechanical integrity must be maintained.
- Vibration, high frequency: 20 g's for 8 hours in (2) perpendicular directions. Mil-Std-202 method 204. Electrical and mechanical integrity must be maintained.
- Surge voltage. 1000 cycles @ 85C Electrical and mechanical integrity must be maintained.
- Low temperature storage (-62C) for 72 hours. Mil-Std-810 method 502. Electrical and mechanical integrity must be maintained.
- Stability at high and low temperature. +25, -55, +25, +85, +125, +25C Cap, Df, DCL integrity.
- Life testing. The capacitors shall be capable of withstanding a 10,000 hour life test at 85°C at rated voltage, or a 2,000 hour life test at 125°C test at derated voltage. After the test, the capacitors shall meet electrical requirements.
- AC Ripple Life Test.

Sealing

To pass this hermetic seal test requirement requires good alignment between the header and the tantalum can during the laser welding operation. Once this is complete, a gross leak bubble test is performed so that any gross leaks can be repaired prior to the helium leak test. Any losses for this test are primarily a yield issue.

Shock and Vibration

This is primarily a test of the mechanical integrity of the cathode attachment to the wall of the tantalum can and good fit between the tantalum anode, insulating nests and the tantalum can. As severe as these tests appear to be, passing these requirements can be routinely successful based on a good fit of the components.

Surge Voltage

Wet tantalum capacitors, due to the inherent design, quite easily pass surge voltage testing.

Low Temperature Storage (-62°C)

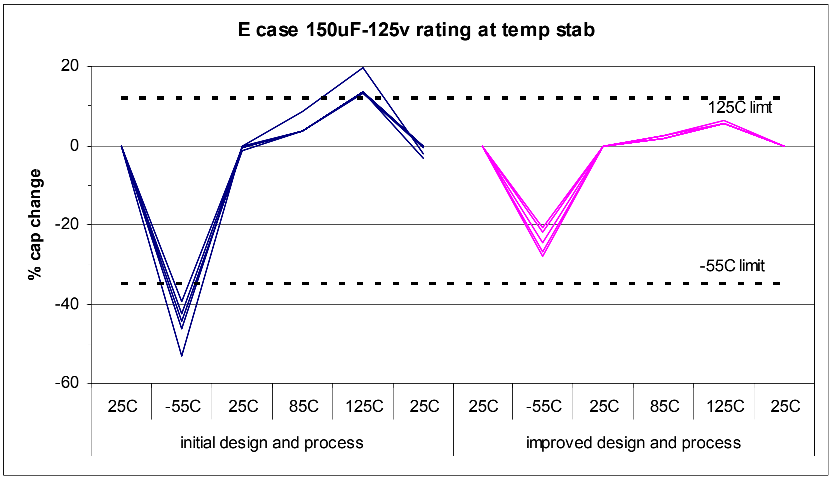
If the proper ratio of sulfuric acid in water is maintained, so that it does not freeze, this test is also one that can be passed routinely.

Stability at High and Low Temperatures

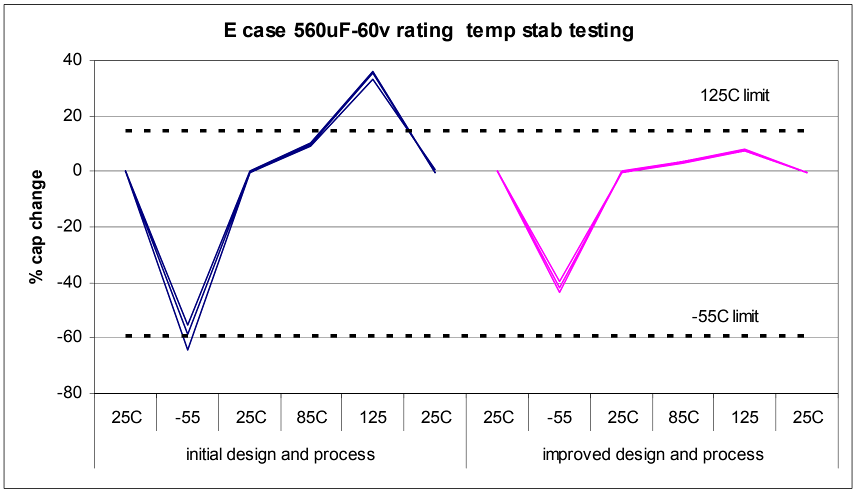
This requirement was one of the more difficult ones to meet successfully. Basically capacitance, Df (120 Hz), and DCL are measured at the various temperatures from -55°C to 125°C A number of samples of competitive product, built to 93026 requirements, were also subjected to these requirements.

The behavior of the capacitance on temperature stability testing depends on many factors, among which are: the anode dimensions, the electrolyte conductivity change with temperature, the porosity distribution of the anode, and the electrochemical interaction at the interface of the tantalum oxide dielectric and the electrolyte. A great deal of experimentation was required to make significant improvements in the temperature stability of the capacitance. Nevertheless this was achieved as illustrated in the typical representative graphs below, comparing initial designs to improved designs:

Temperature Stability - 150µF-125v

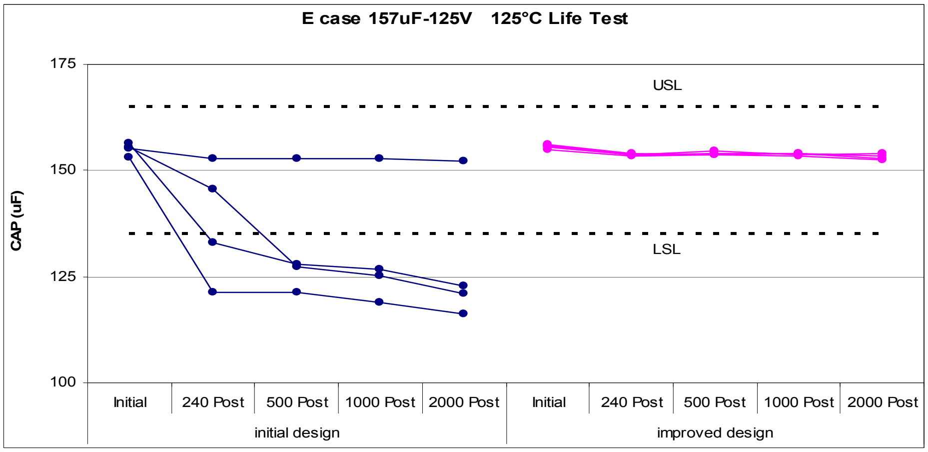


Temperature Stability - 560µF-60v

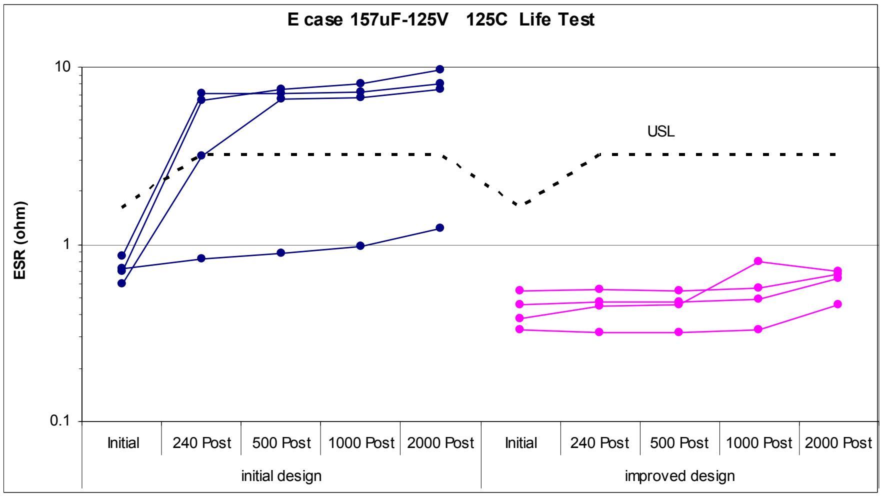


Improvement in the performance on other tests has also been achieved by design and process changes. For example see below, typical examples of initial vs. improved design results:

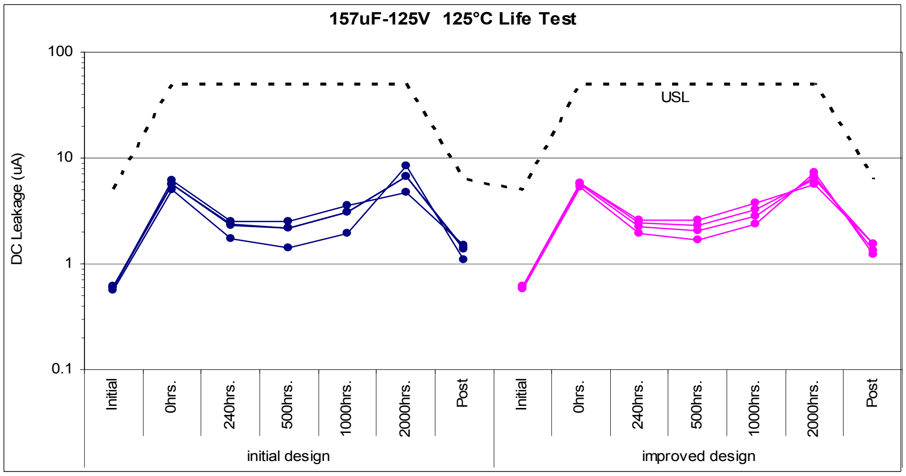
125°C Life Test Capacitance:



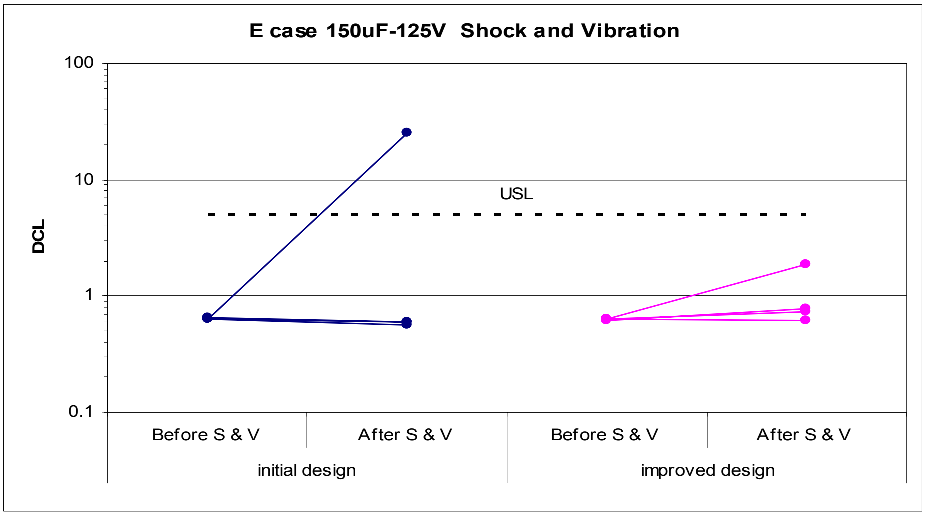
125°C Life Test ESR:



125°C Life Test DCL:



Shock and Vibration Test:



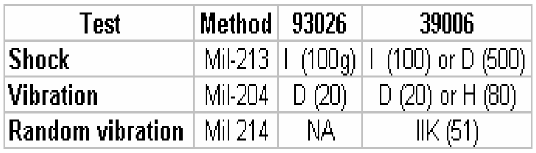
Summary and Conclusions:

A novel wet capacitor system has been developed that meets the requirements of Mil drawing 93026. The capacitance and mechanical stability of the complete system has proven to meet these difficult criteria with excellent results.

Ongoing Development:

Wet tantalum capacitor development is continuing for high temperature wet tantalum products to 200C and 50% of rated voltage and rated voltage levels beyond 125V.

Additionally, work is continuing to evaluate and improve the design to meet Mil-PRF-39006, extreme D and H level shock and vibration criteria as well as the random vibration test conditions. These criteria are 4 to 5 times more severe than what the current specification calls out.



Test	Method	93026	39006
Shock	Mil-213	I (100g)	I (100) or D (500)
Vibration	Mil-204	D (20)	D (20) or H (80)
Random vibration	Mil 214	NA	IIK (51)

Beyond the capacitance and rated voltage ratings currently listed in DSCC drawing 93026, range extensions are also being developed. A rating in development at the high voltage end is the T4 case, 200µF-125V wet capacitor. At the lower voltage end, prototype anodes have already been prepared for the T4 case, 10mF-6v and T2 case, 2.5mF-6v ratings. In theory, with higher CV/g powder materials a 20mF-6v T4 case is feasible. Sufficient cathode capacitance will be critical in these devices.

There are many other opportunities for this novel wet tantalum capacitor system that are being considered

References:

David A. Evans, “High Energy Density Electrolytic-Electrochemical Hybrid Capacitor”, Proceedings of the 14th Capacitor and Resistor Technology Symposium (CARTS 1994)

David A. Evans and Don Stephenson, “Performance of Mil-Type Hybrid Tantalum Capacitors”, Proceedings of the 15th capacitor and Resistor Technology Symposium (CARTS 1995)