

Hermetically Sealed Conductive Polymer Tantalum Capacitors for High Power/High Reliability Applications

M. Weaver, J. Petrzilek, M. Biler

AVX Corporation, One AVX Blvd, Fountain Inn, SC 29644

Tel.: (864)-228-4595, e-mail: mitch.weaver@avx.com

Abstract

This article outlines recent developments for expanding the application range of surface mount (SMT) Tantalum capacitors using solid conductive polymer electrolytes, which offer intrinsic low ESR and high voltage behavior. It will also review studies of established best-in-class technologies and material sets that can permit stable operation as high reliability designs, offering thousands of hours of operation at temperatures of 125°C and voltages beyond the norm of traditional molded designs.

The key development task required use of an optimized anode for minimal DC leakage current (DCL), pre-polymerized PEDT-PSS material with distinctive additives as the cathode, a unique hermetically sealed SMT package, and special ageing and screening considerations. The unique hermetic design offers significant advantages over traditional conductive polymer surface mount capacitors (molded package) in terms of lifetime and reliability, while promoting higher voltages and lower ESR over traditional MnO₂ designs.

The anode optimization also permits a new class of conductive polymer capacitors, exhibiting extremely low DCL specifications. However, a significant challenge encountered was the resolution of the relatively slow decrease in DCL upon voltage application. This phenomenon can be explained by the necessity for water content in the PEDT-PSS material, which helps to establish an additional barrier on the interface between the dielectric and conductive polymer. An explanation is likely to be based on the interaction of water with sulphonic groups of PSS material, but water can be replaced with other compounds that lead to faster DCL decrease and even lower DCL. The culmination of these advancements enables components that are ideal for high reliability applications in aerospace, automotive, and industrial sectors.

Introduction

Tantalum surface mount capacitors with a solid electrolyte have been the favorite capacitor technology choice in many electronic devices for more than five decades, thanks to their stability, high reliability, and superior volumetric efficiency. The traditional manganese dioxide (MnO₂) cathode material provides good mechanical robustness and relatively stable performance with temperature and humidity, which is desirable for many applications. Tantalum capacitors with MnO₂ cathodes can even be utilized at temperatures as high as 230°C under specific limitations [1, 2]. However, there are two major disadvantages of MnO₂-based tantalum capacitors: their relatively high ESR, which is unrealistic for many power applications, and their propensity for thermal runaway failure mode under excessive application beyond manufacturer's recommendations. These issues can be overcome with the use of conductive polymer as a cathode material; and, in addition, newly developed technologies using dispersed PEDOT are

pushing the maximum levels of rated voltages for solid electrolytic tantalum capacitors up to, and even beyond, 125V [3, 4].

Although better than MnO₂ cathodes in some respects, conductive polymer electrodes are not entirely without fault. For example, they can exhibit sensitivity to external conditions, such as high humidity and mechanical stresses. These organic compounds can also exhibit degradation at elevated temperatures, especially in the presence of oxygen or humidity [5, 6]. Such changes can include oxidation and morphology alterations, in addition to other degradations, all of which can lead to a reduction in the cathode's conductivity and result in an increase of ESR and/or a drop in capacitance. The logical solution for overcoming such limitations and ensuring the high stability and reliability of polymer tantalum capacitors is to use hermetically sealed packaging, which can nullify external environmental influences, and to subject the parts to special ageing and screening processes [3, 7]. Such procedures improve BDV distribution, decrease DCL, and remove maverick capacitors with potentially latent unstable behavior. As such, when properly sealed and subjected to appropriate testing, hermetically sealed high voltage polymer tantalum capacitors prove fully capable of satisfying the demands of high reliability power applications.

Experimental Details

To create the hermetically sealed polymer tantalum capacitors to be tested for use in high power, high reliability applications, porous tantalum pellets were pressed with an embedded tantalum wire, sintered, and then anodized to form an appropriate dielectric layer. Special processes were also applied in order to achieve the best quality amorphous dielectric with minimal defects. Then, a conductive polymer cathode was created on the dielectric with PEDT-PSS dispersion materials using a dipping and drying process. The external cathode layer was then coated with graphite and silver, also via a dipping process. Prepared capacitors were assembled into a special ceramic package [2], dried extensively, and immediately hermetically sealed under an inert atmosphere. Additionally, special ageing and screening mechanisms were applied before long-term performance testing.

Results and Discussion

Hermetically sealed polymer tantalum capacitors rated at 100 μ F/35V were tested at 125°C and 35V for 10,000 hours. Capacitance and ESR was measured over time, and the results are plotted in Figures 1 and 2. Only minimal capacitance loss and a slight increase in ESR were observed. Steady-state DCL at rated voltage (35V) and 125°C measured <250nA, which is much lower than the standard 10% of capacitor CV limit applied to traditional, non-hermetic conductive polymer capacitors. So, in this instance, the limit should be 10% of 100*35 = 350 μ A. In fact, the hot steady-state DCL measured in our experiments was still three orders of magnitude below the standard limit of tantalum polymer capacitors using the traditional molded package. So, based on these results, we can conclude that this combination of technologies leads to an extremely stable, low ESR, low leakage capacitor that is ideal for use in high reliability power applications.

To further evaluate DCL after life test, DCL measurements at rated voltage and temperatures of 25°C, 85°C, and 125°C were recorded with time (Figure 3). It is clear that DCL decreases significantly with time and that reaching a steady state depends upon temperature. Room

temperature DCL declines slowly, and the reading at 60 minutes is 40x lower than readings recorded at five minutes. Such behavior patterns can complicate DCL evaluation, since standard tantalum capacitors stabilize DCL much faster; therefore, typical DCL specifications for such devices are recorded and presented at just five minutes at room temperature.

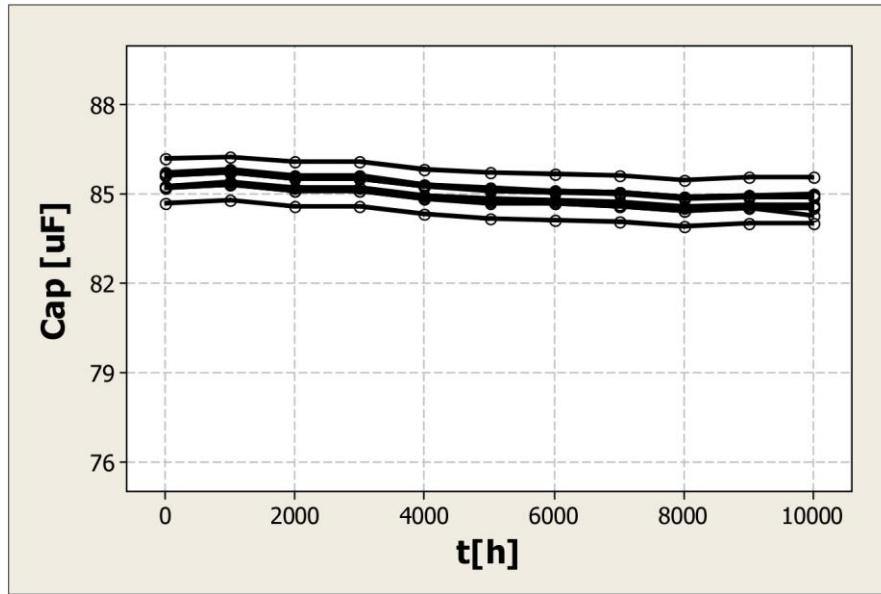


Figure 1: Capacitance stability of a hermetically sealed, 100 μ F/35V conductive tantalum polymer capacitor at 125°C and rated voltage over 10,000 hours

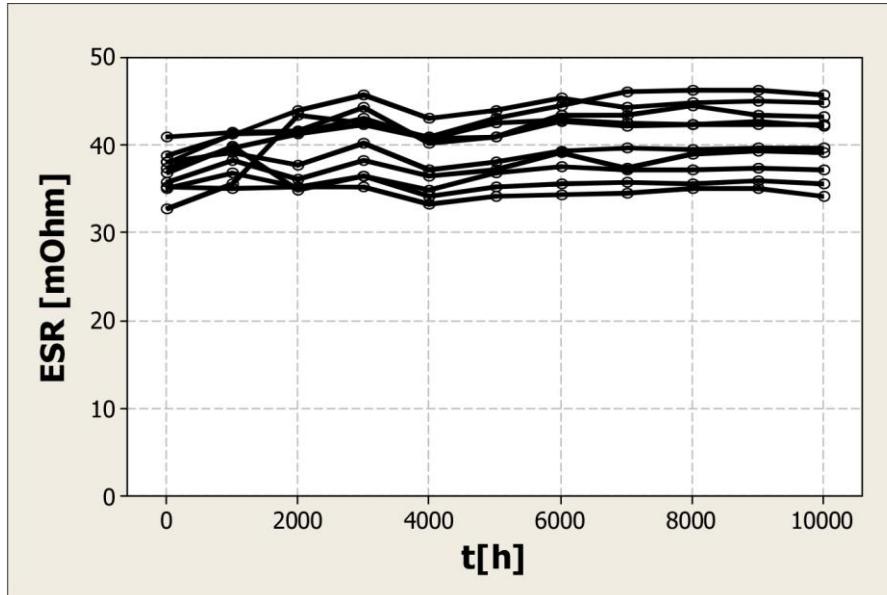


Figure 2: 100kHz ESR stability of a hermetically sealed, 100 μ F/35V conductive tantalum polymer capacitor at 125°C and rated voltage over 10,000 hours

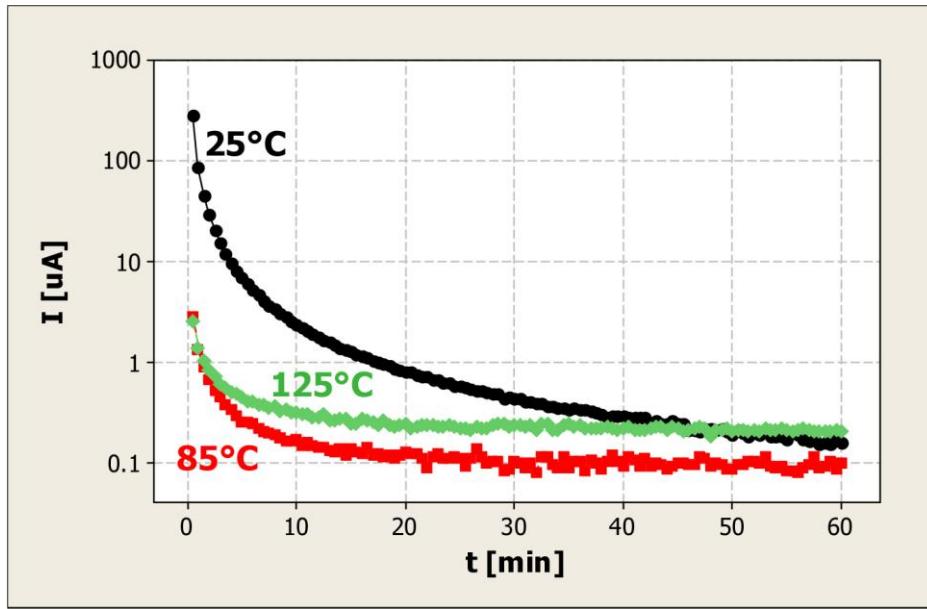


Figure 3: DCL at 35V of a hermetically sealed, 100 μ F/35V conductive tantalum polymer capacitor after 10,000 hours at 125°C and rated voltage

The phenomenon of slowly decreasing DCL over time is common when using PEDT polymeric dispersion technologies. Parameters that influence the rate of DCL decrease with time include temperature and, even more importantly, humidity level. DCL measurements on excessively dried parts split into two groups — hermetically sealed and unsealed — and stored at standard relative humidity (RH), 50%, were taken at 25°C, 85°C, and 125°C (Figure 4). The unsealed humidified capacitors stabilized much sooner than the sealed capacitors after connection to voltage, and temperature did not play a significant role in the stabilization rate. Alternately, the stabilization of the dried and sealed parts took more than an hour at room temperature, but sped up substantially with elevated temperatures. A similar effect was demonstrated on a standard 330 μ F/6.3V molded polymer capacitor. In this case, the same part was measured after humidification (30°C and 70% RH for 12 hours) and drying (125°C for 4 hours, and 25°C and 1% RH for 12 hours). So, again, DCL for the humidified part stabilized much faster than the dried part (Figure 5).

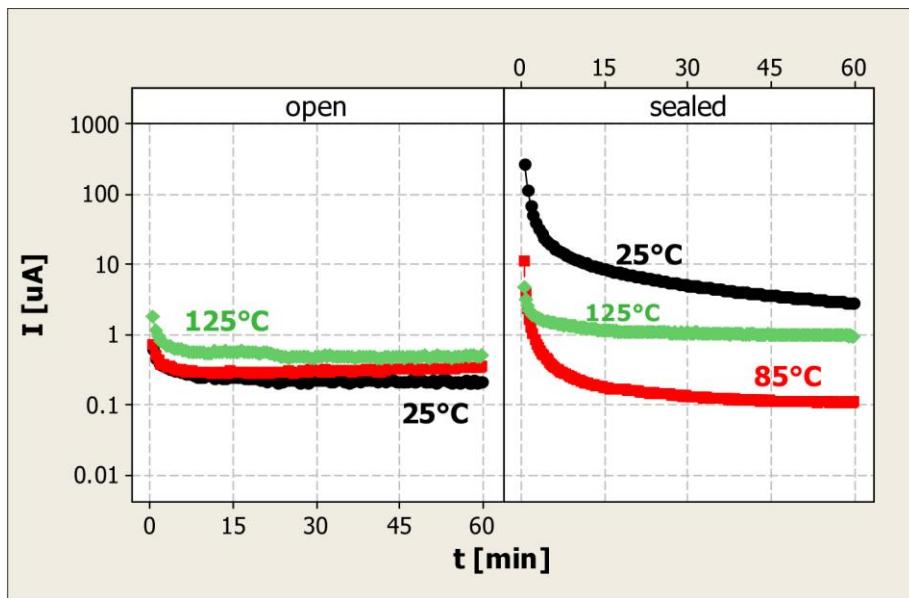


Figure 4: DCL measurements for hermetically sealed and unsealed $33\mu\text{F}/25\text{V}$ tantalum polymer capacitors at rated voltage

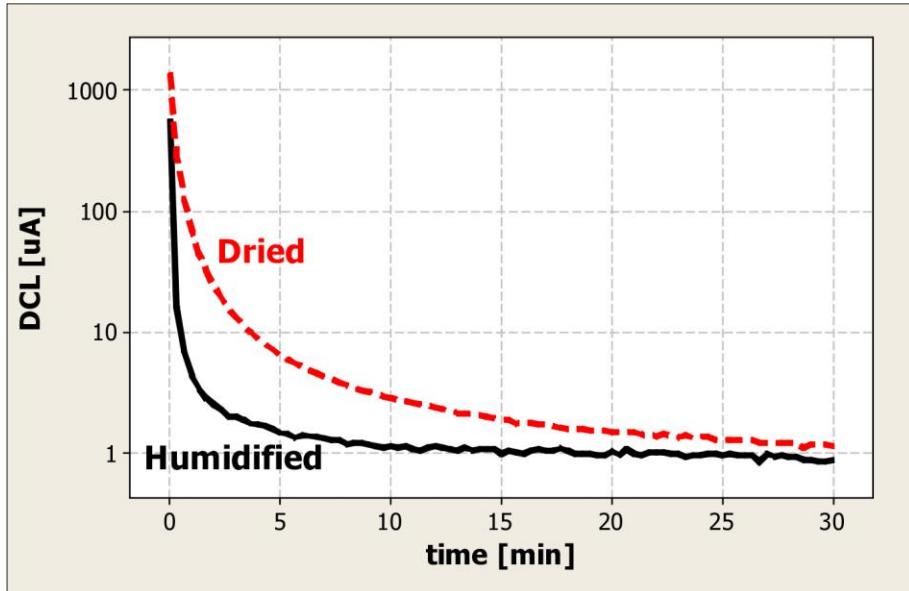


Figure 5: DCL measurements for dried and humidified $330\mu\text{F}/6.3\text{V}$ standard molded tantalum conductive polymer capacitors, at rated voltage

Based on the aforementioned results, we can conclude that using pre-polymerized PEDT-PSS dispersions leads to extremely low DCL; although, the DCL decrease with time after applied voltage is significantly dependent on the level of humidification of the capacitor. Higher humidity parts exhibited fast DCL decay, but excessively dried parts exhibited a significant dependency on temperature. The slowest DCL decreasing rate was demonstrated by the dried capacitors at low temperature.

Such behavior suggests that, after a voltage is applied, a certain barrier is created on the surface of the cathode at the boundary with the dielectric. This is linked with ion mobility, as higher temperatures increase ion mobility, and therefore lead to faster DCL decrease. PEDT-PSS is based on two different polymers: a positively charged PEDT cation, which assures the intrinsic conductivity via its highly conjugated electronic structure, and a negatively charged polystyrene sulphonate, which works as counter ion to PEDT. Each aromatic ring of the polystyrene contains a sulphonic group, SO_3H , but only a certain percentage of them are dissociated to SO_3 and a compensating PEDT positive charge. There are many sulphonic groups that can be dissociated in the presence of water; consequently, the result is a structure in which relatively large polymeric molecules of polystyrene sulphonic acid will be dissociated and, thus, negatively charged. After voltage is applied, we can assume that the orientation of such negatively charged groups is toward the dielectric, and therefore blocking DCL, and that the kinetics of such structures will be faster at higher temperatures.

Water is volatile, so its content in PEDT-PSS can change significantly, which can lead to changes in capacitor parameters. As such, other, more stable volatile compounds that could potentially replace water for the solvation of hydrogen in the sulphonic groups were researched. For example, hydroxy functional non-ionic polymers, like polyethylene glycol (PEG), were successfully tested in sealed and unsealed tantalum polymer capacitors. The DCL measurements that resulted from testing the hermetically sealed parts are presented in Figure 6. The addition of PEG not only significantly sped up the rate of DCL decrease, but also lowered the final DCL. Additionally, at room temperature, the DCL of parts with PEG was two orders of magnitude lower when compared to parts without the additive.

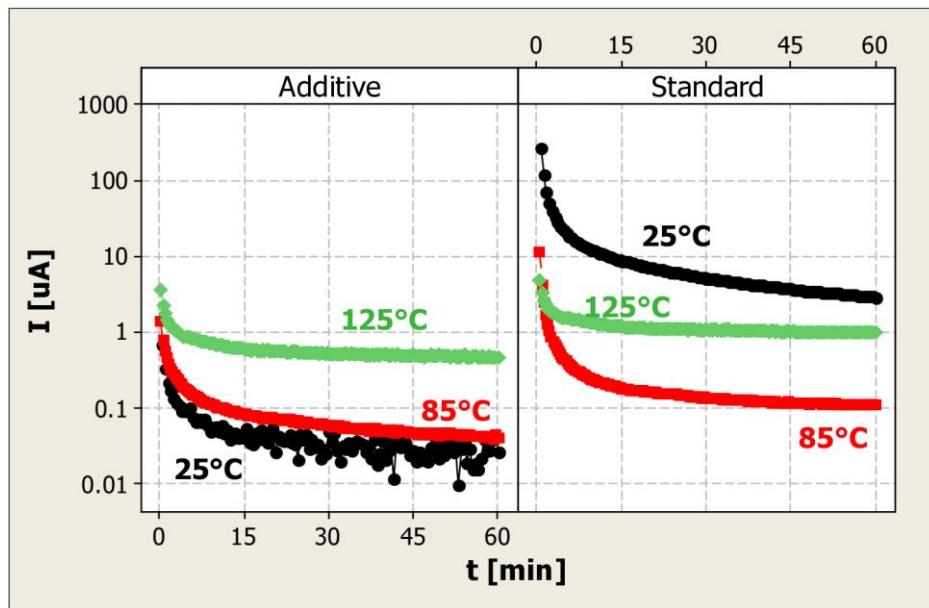


Figure 6: DCL measurement of hermetically sealed $33\mu\text{F}/25\text{V}$ conductive polymer capacitors with and without PEG additives at rated voltage

The comprehension gained from these efforts can benefit even traditional molded conductive polymer series, including extensions of existing series, including AVX's low profile, facedown TCN Series tantalum solid electrolytic chip capacitors.

Conclusions

Hermetically sealed tantalum polymer capacitors have been proven to provide stable performance and high reliability during long-term life testing exceeding 10,000 hours, even in elevated temperature and humidity environments. The combination of the best available technologies and materials is enabling long-term stability on high voltage tantalum polymer capacitors that also exhibit extremely low DCL and low ESR performance. The key elements of the new technology are: an optimized anode, pre-polymerized PEDT-PSS cathode material and additives, a hermetically sealed package, and the use of special ageing and screening processes.

Extremely low DCL levels measured at steady state are enabling a new class of conductive polymer capacitor. The phenomenon of slow DCL decrease can be explained by the need for water content in the PEDT-PSS material, which helps to establish an additional barrier at the interface between the dielectric and conductive polymer. This barrier is likely caused by an interaction between water and the sulphonic groups of PSS, and initial results show that alternative compounds (such as PEG) can lead to even faster DCL decrease and even lower DCL specification in next-generation capacitor technology. In fact, many of the attributes yielded by these studies are currently available in AVX's TCH Series hermetically sealed tantalum polymer chip capacitors, which are ideal for aerospace, avionics, and defense applications, as well as for automotive applications, in which ever-higher reliability and safety specifications are paramount. Consequently, surface mount hermetically sealed tantalum polymer capacitors are expected to lead the way in extreme long lifetime, low ESR applications, especially as lifetime and voltage ratings continue to increase.



Figure 7: AVX's TCH Series hermetically sealed tantalum polymer chip capacitors are ideal for aerospace, avionics, and defense applications, and are now rated for extended lifetimes of up to 10,000 hours

References

- [1] I. Zednickova, M. Biler, J. Petrzilek, T. Zednicek: Hermetically Sealed SMD Tantalum Capacitors, CARTS USA (2012).
- [2] T. Zednicek, M. Biler, J. Petrzilek, I. Pinwill: Hermetically Sealed 230°C MnO₂ Tantalum Capacitors, CARTS USA (2013).
- [3] J. Petrzilek, T. Zedníček, M. Uher, I. Horáček, J. Tomáško, L. Djebara: Next Generation of High Voltage, Low ESR Tantalum Conductive Polymer Capacitors, CARTS USA (2011)
- [4] http://www.avx.com/wsnew_PressReleaseDetail.asp?id=577&s=0
- [5] H.S.Nalwa: Handbook of Organic Conductive Molecules and Polymers, Willey&Sons (1997).
- [6] A. Skotheim, J.R.Reynolds: Conjugated Polymers, CRC Press (2007).
- [7] J. Bates, M. Beaulieu, M. Miller, J. Paulus: Reaching the Highest Reliability for Tantalum Capacitors, CARTS USA (2013).