TECHNICAL PAPER

Hermetically Sealed Conductive Polymer Tantalum Capacitors

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Abstract:

The aim of the paper is to review what combination of known, available, best-in-class technologies and possible materials can be utilized to prepare tantalum capacitors with high rated voltage, low ESR, super low DCL and stable electrical parametric behaviour over 1000 hours of operation, even at 125degC with rated voltage applied. The key development task consists of using an optimised anode, pre-polymerized PEDT-PSS material for the cathode, a hermetically-sealed case and special ageing and screening processes. The extremely low DCL levels measured at steady state allow a new class of polymers, with a low DCL specification, to be offered. The only challenge that needs to be resolved is the slow DCL decrease phenomenon seen after voltage application. This can be explained by the necessity for water content in the PEDT-PSS material that 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. Water can be replaced with other compounds that lead to faster DCL decrease and even lower DCL.

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INTRODUCTION

Tantalum surface mount capacitors with a solid electrolyte have been the favourite capacitor technology choice in many electronic devices for more than five decades, thanks to its high stability, reliability and volumetric efficiency. The traditional cathode material - manganese dioxide - provides good mechanical robustness, as well as relatively stable performance with temperature and humidity that suits many applications. Such cathodes can even, with some limitations, be used at temperatures as high as 230degC [1, 2]. The two major disadvantages of MnO_2 tantalum capacitors are the thermal runaway failure mode and relatively high ESR.

Both of these issues have been overcome by using conductive polymers as a cathode material. In addition, newly developed technologies using dispersed PEDOT are pushing the maximum levels of rated voltages of solid electrolyte tantalum capacitors up to 125V and even higher [3, 4].

On the other hand, conductive polymer capacitors show some significant sensitivity to external conditions such as humidity, mechanical stresses and high temperature. 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, morphology alterations or other mechanisms of degradation which all lead to a reduction of the cathode’s conductivity and result in an increase of ESR or a drop in capacitance. To overcome such limitations, the next logical step to ensure high stability and reliability is the use of hermetically sealed packaging which significantly nullifies external environmental influences. The final step to ensure stability and reliability is to use special ageing and screening processes [3, 7]. Such procedures improve BDV distribution, decrease DCL and remove maverick capacitors with potentially latent unstable behaviour.

This article discusses the potential of hermetically sealed high voltage polymer tantalum capacitors.

EXPERIMENTAL DETAILS

Porous tantalum pellets have been pressed with an embedded tantalum wire, then sintered followed by anodization to form an appropriate dielectric layer. Special processes have been applied in order to achieve the best quality amorphous dielectric with minimal defects. Then a conductive polymer cathode was created on the dielectric using PEDT-PSS dispersion materials using a dipping and drying process. The external cathode layer was then coated by dipping into graphite and silver. Prepared capacitors were assembled into a ceramic package [2], extensively dried and immediately hermetically sealed under an inert atmosphere. Special ageing and screening mechanisms have been applied before long term performance testing.

RESULT AND DISCUSSION

Hermetically sealed polymer capacitors rated at 100µF/35V were tested at 125degC and 35V for 10,000 hours. Capacitance and ESR was measured over time; the results are plotted in Figures 1-2. Very little decrease in capacitance and just a slight increase in ESR were observed. Steady state DCL at rated voltage (35V) at 125degC measured over time was lower than 250nA. Based on these results, we can conclude that this applied combination of technologies leads to an extremely stable, low ESR, low leakage capacitor. Measured DCL is much lower than standard limits applied to conductive polymer capacitors (10% of capacitor CV, in our case 10% of 100*35 = 350µA). In fact, the hot steady state DCL measured in our experiments is three orders of magnitude below the standard limit for tantalum polymer capacitors. To further evaluate DCL after the life test, DCL measurements at rated voltage and temperatures of 25, 85 and 125degC were recorded with time (Figure 3). It is clear that DCL decreases significantly with time and reaching a steady state depends upon temperature. Room temperature DCL declines slowly and the reading at 60 minutes is 40 times lower than readings recorded at 5 minutes. Such behaviour patterns can complicate DCL evaluation, since standard tantalum capacitors stabilize DCL much faster, so commonly, DCL specifications for such devices are recorded and presented at just 5 minutes at room temperature.

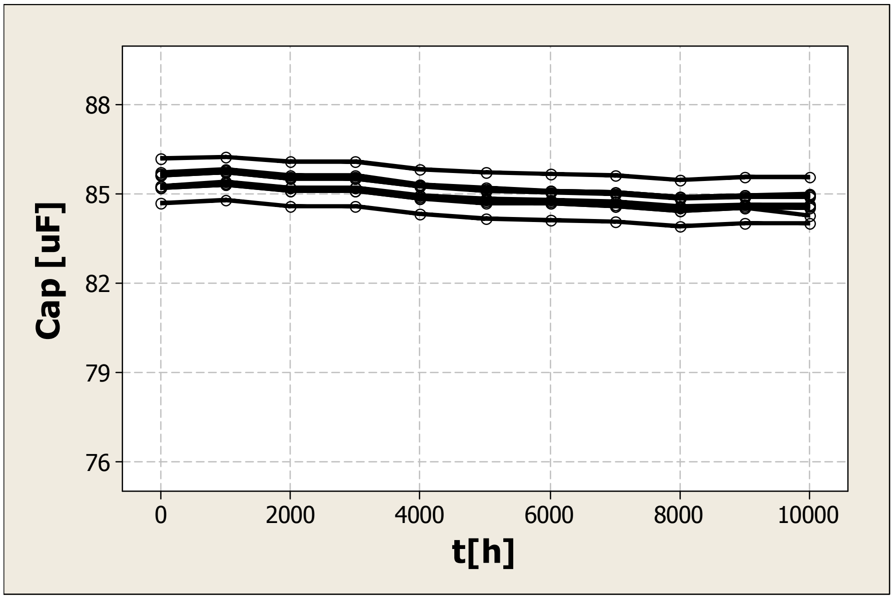

Figure 1. Hermetically sealed polymer capacitor at 100μF at 35V at 125degC and rated voltage

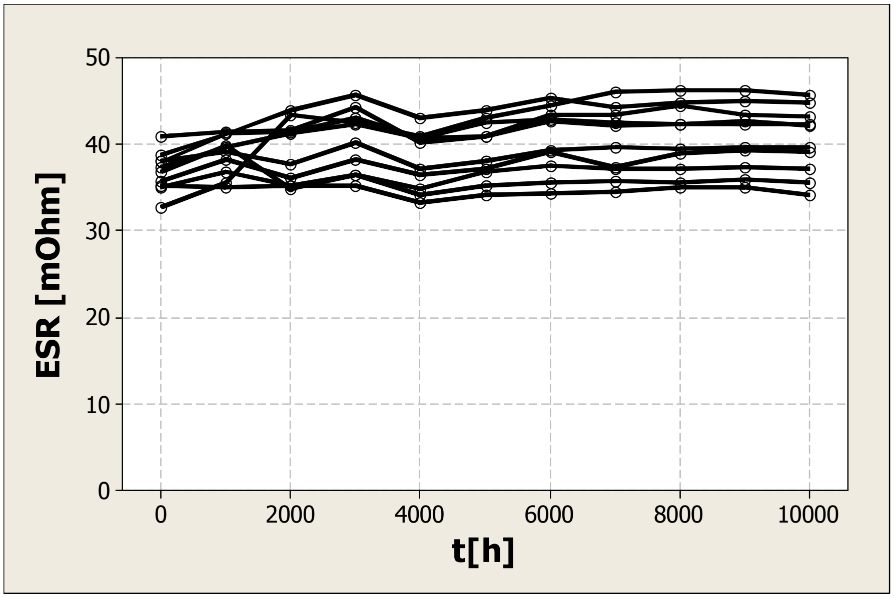

Figure 2. Hermetically sealed polymer capacitor at 100μF at 35V at 125degC and rated voltage

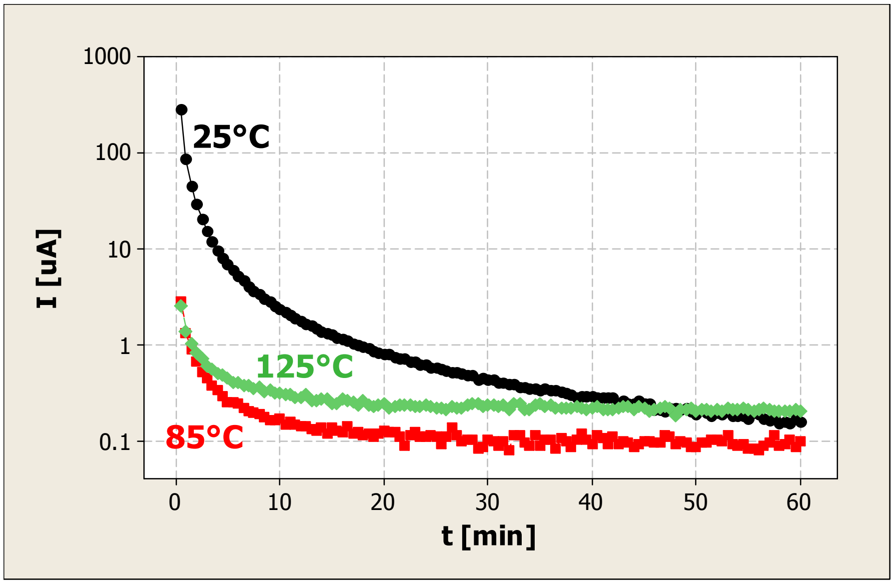

Figure 3. Hermetically sealed polymer capacitor at 100µF at 35V after 10000h at 125°C and 35V, DCL measurement

The phenomenon of slowly decreasing DCL over time is common when using PEDT polymeric dispersion technologies. Parameters which influence rate of DCL decrease with time not only include temperature, but also – and very importantly - the level of humidification of the part. DCL measurements at 25, 85 and 125degC of excessively dried, then hermetically sealed parts and the same type of capacitor, not sealed (and kept at normal room RH 50%), are plotted at Figure 4. Humidified capacitors stabilize DCL very soon after connection to voltage. Temperature does not play a significant role in this case. On the other hand, the stabilization of the dried and sealed parts takes hours at room temperature and elevated temperature speeds up the stabilization process substantially. A similar effect is demonstrated on a standard moulded polymer capacitor rated 330µF at 6.3V, where the same part was measured after humidification (30degC/70% RH, 12 hours) and drying (125degC 4 hours, 25degC/1% RH 12 hours). Again, DCL for the humidified part stabilizes much faster than the dried part (Figure 5).

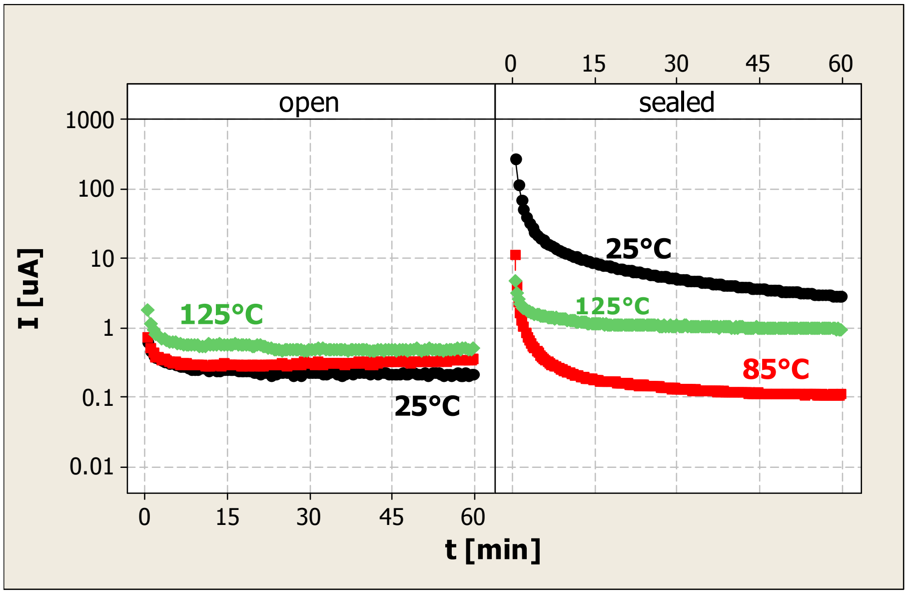

Figure 4. Hermetically sealed and unsealed polymer capacitor 33µF at 25V, DCL measurement at rated voltage

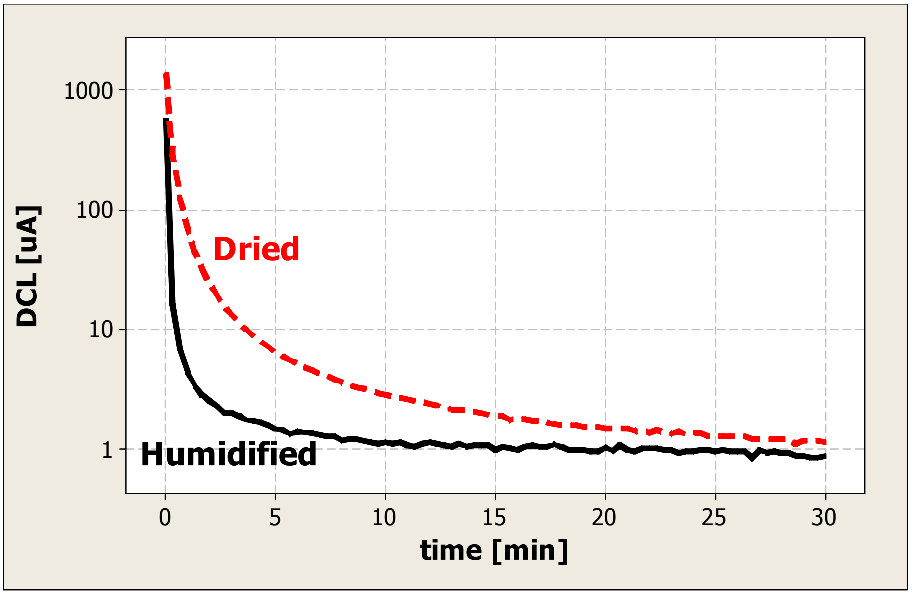

Figure 5. Standard moulded tantalum polymer capacitor 330µF at 6.3V, DCL measurement at 6.3V

Based on the above given results, we can conclude that using pre-polymerized PEDT-PSS dispersions leads to very low DCL, but the DCL decrease with time after applied voltage is significantly dependent on the level of humidification of the capacitor. Parts with water show fast DCL decay, but excessively dried part exhibits significant dependency on temperature. The slowest DCL decreasing rate is exhibited by the dried capacitor at low temperature.

Such behaviour 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 (a higher temperature increases ion mobility and would therefore lead to faster DCL decrease). PEDT- PSS is based on two different polymers, a positively charged PEDT cation (assuring 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; thus the result is a structure where 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 towards the dielectric therefore blocking DCL. The kinetics of orientation of such structures will be faster at higher temperature.

Water is volatile and thus its content in PEDT-PSS can change significantly. Such changes will lead to changes of capacitor parameters. Therefore, other, more stable volatile-compounds were researched that could replace water for the solvation of hydrogen in sulphonic groups. Hydroxy functional non-ionic polymers like polyethylene glycol (PEG) were tested successfully in sealed or unsealed tantalum polymer capacitors. The results of DCL measurements on the hermetically sealed parts are presented at Figure 6. The addition of PEG not only significantly speeded up the rate of DCL decrease but also lowered the final DCL. At room temperature, the DCL of parts with PEG was two orders of magnitude lower in comparison to parts without the additive.

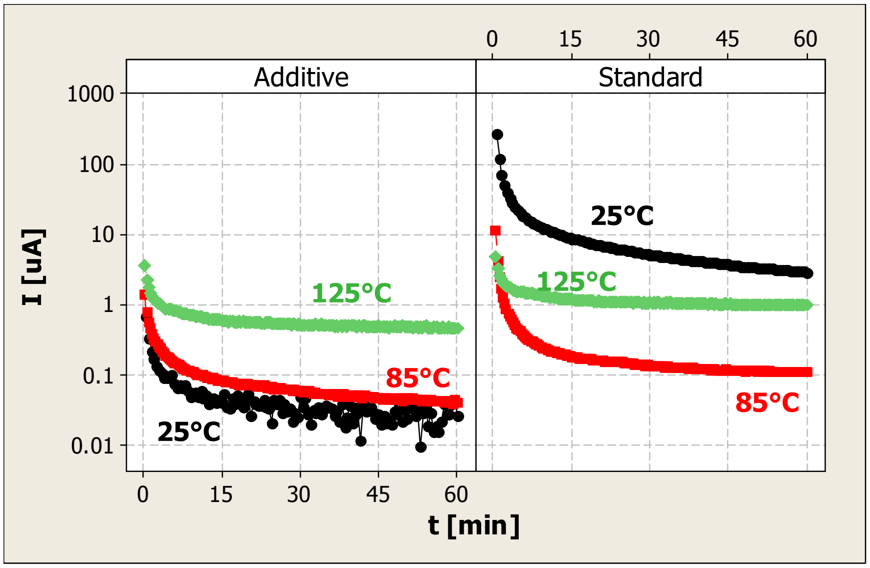

Figure 6. DCL measurement at rated voltage of hermetically sealed sealed polymer capacitor rated at 33µF at 25V with and without additives.

CONCLUSIONS

Hermetically sealed polymer capacitors have been proven to provide stable performance and reliability during long life testing exceeding 10 000 hours, even at elevated temperature and humidity conditions. The combination of the best available technologies and materials is enabling long-term stability on high voltage tantalum polymer capacitors, exhibiting super-low DCL and low ESR performance – better than has ever been possible before. The key elements of the new technology are: an optimized anode; pre-polymerized PEDT-PSS cathode material; a hermetically sealed case; and the use of special ageing and screening processes.

Extremely low DCL levels measured at steady state can make possible a new class of polymer capacitors with low DCL specifications. The phenomenon that needs to be better specified is the slow DCL decrease after a voltage is applied. 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. The likely cause can be associated with an interaction between water and the sulphonic groups of PSS. During further development work, water may be replaced by other compounds leading to a faster DCL decrease and even lower DCL specification on future generations of tantalum polymer capacitors.

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