Reliability of Manganese Dioxide and Conductive Polymer Tantalum Capacitors under Temperature Humidity Bias Testing

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Abstract

Despite being highly reliable under steady state operating conditions, manganese dioxide (MnO_2) tantalum capacitors are prone to catastrophic exothermic failures under surge current conditions. Such failures can be mitigated by the use of conductive polymers in place of MnO_2. However, these polymers are more susceptible to failure at elevated humidity levels. In this paper, the electrical performances of both MnO_2 and polymer tantalum capacitors are compared by subjecting them to temperature humidity bias testing at 85°C and 85% RH. The test population consists of tantalum capacitors with two voltage ratings (50V and 16V). At each of these voltage ratings, two sets of tantalum capacitors, one each with MnO_2 and conductive polymer electrodes, were tested. The voltage levels used to bias the capacitors were periodically increased in multiples of the rated voltage to accelerate degradation. The performance of the capacitors was tracked by monitoring their capacitance, dissipation factors and leakage currents, both in-situ and at room temperature. The degradation trends are discussed in light of the differences in voltage ratings and electrode types. These trends are also mapped to fundamental failure mechanisms within the capacitors.

Key words

Conductive polymer, humidity testing, manganese dioxide, step stress testing, tantalum capacitors

I. Introduction

Tantalum (Ta) capacitors offer original equipment manufacturers (OEMs) some of the highest volumetric efficiencies of any conventional capacitor technology [1]. These high efficiencies are a result of the compact construction of Ta capacitors.

Ta capacitors are formed by sintering fine Ta powders around a Ta wire to form a slug. This slug is then oxidized in a weak acid, with an applied forward bias. The resulting amorphous tantalum pentoxide layer formed around the Ta particles serves as the dielectric. The large surface area of the sintered Ta particles, in conjunction with the thin dielectric oxide layer, provides high specific capacitance. To complete the capacitor, the sintered oxidized pellet is impregnated with solid manganese dioxide (MnO_2) or a conductive polymer. The pellet is then coated with carbon and silver to complete the cathode assembly. Fig. 1 shows the construction of commercial surface mount Ta capacitors. More information on the on fabrication of Ta capacitors can be found in [2].

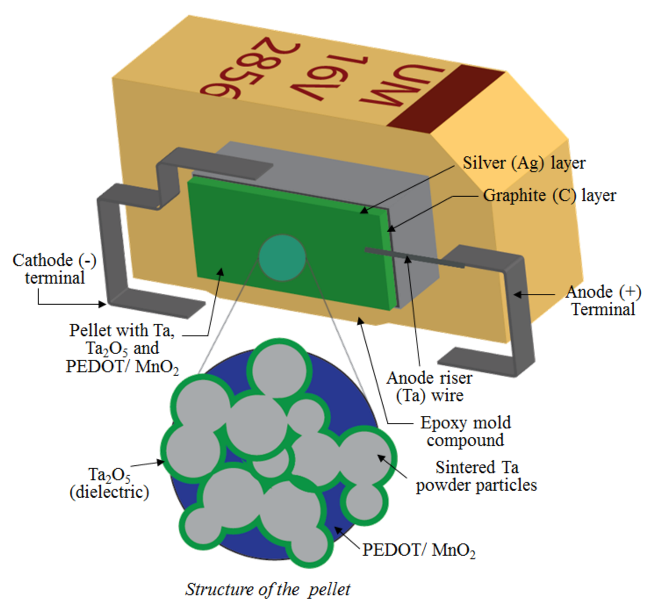

Fig. 1 Construction of a Tantalum Capacitor

Traditionally, solid Ta capacitors have used MnO_2 as the cathode. These capacitors offer higher reliability than liquid aluminum (Al) electrolytic capacitors. This is due to elimination of the risk of electrolyte evaporation and leakage. Ta capacitors also offer superior electrical performance in comparison to Al electrolytic capacitors. Ta capacitors typically have lower equivalent series resistances (ESRs) and equivalent series inductances (ESLs), and greater performance stability at high frequencies [1] [3] [4]. Ta capacitors are also preferred over MLCCs for certain applications such as analog signal processing [1] [5], since Ta capacitors do not exhibit a piezoelectric or voltage polarization effect.

Despite these advantages, MnO_2 Ta capacitors pose a serious reliability risk as they are prone to catastrophic exothermic failures under surge current conditions. Such failures can often damage other circuit components in the vicinity of the failed capacitor. These failures can be circumvented by the use of conductive polymers, which are more robust to surge currents. The tradeoff is that polymer electrodes are more susceptible to degradation at elevated temperature and humidity levels. Since moisture and humidity are already known to adversely affect the reliability of MnO_2 Ta capacitors [6-8], such conditions pose a more serious risk to polymer Ta capacitors. Even with these limitations, lower voltage (16V and lower) polymer tantalum capacitors have been shown to have comparable reliability to their MnO_2 counterparts under temperature humidity bias testing [9]. However, there has been very limited research performed comparing higher voltage polymer and MnO_2 tantalum capacitors, especially at elevated humidity levels.

In this paper we subject commercially available Ta capacitors, with both polymer and MnO_2 electrodes, to temperature humidity bias (THB) testing with voltage step stresses. Also, in order to compare the effect of different voltage ratings on the performance of Ta capacitors in THB tests, both 16V and 50V capacitors were included in the test. Capacitance (C) and DC Leakage current (DCL) were monitored over the course of the tests. The degradation trends seen in these parameters are reported in the results section. We also provide insights into the potential failure mechanisms under elevated temperature humidity conditions, and relate these mechanisms to the observed trends.

II. Test Methodology

The capacitors tested included high voltage (50V) polymer and MnO_2 Ta capacitors and low voltage (16V) polymer and MnO_2 Ta capacitors. The electrical specifications of the sample are given in Table I**.** Ten samples of each type were reflow soldered onto test boards. All test samples were manufactured by the same manufacturer. The samples were baked out at 40°C for 168 hours prior to the reflow. Electrical characterization of the samples was performed before and after the reflow soldering to verify that the samples were not affected by the soldering process.

Table I. Specifications of Ta Capacitors in THB Test

Cathode Type	**Voltage** (V)	**Capacitance** (µF)	**Rated Temp** (°C)	**DCL** (µA)	**Case Size** (EIA metric)
Polymer	50	10	85	50	7343-30
Polymer	16	47	85	75.2	7343-20
MnO_2	50	10	85	5	7343-30
MnO_2	16	47	85	7.5	7343-30

A. Test Setup

The Ta capacitors were measured using an automated test setup, diagrammatically represented in Fig. 2. An Agilent N8742A power supply was used to power the 50V Ta capacitors, whereas an Agilent N6702A was used to power the 16V capacitors. An Agilent 4263B LCR meter was used to measure capacitance, and an Agilent 4339B high resistance meter was used to measure DCL. The power sources and measurement meters were switched across the test capacitors using an Agilent 34980A multiplexer. The test boards carrying capacitors and thermocouples were placed inside an ESPEC PRA-3AP chamber.

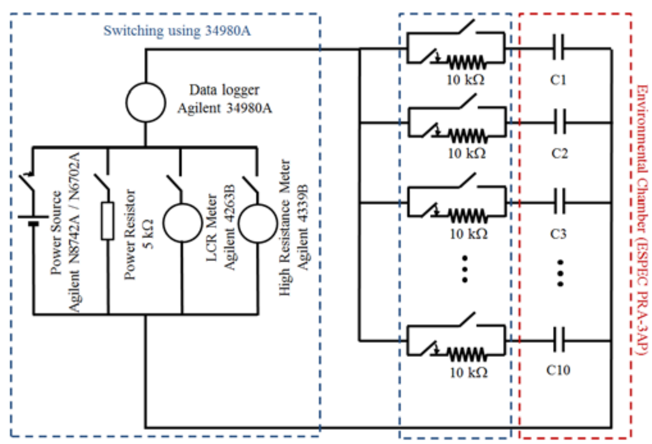

Fig. 2 Schematic Representation of the Test Setup

During the test, every test capacitor was powered in series with a 10kΩ resistor. This was done to prevent excessive current concentration along pathways with degraded, lower insulation resistance capacitors. Prior to measurement, the capacitors were first discharged across a 5kΩ power resistor. Each capacitor was then individually switched across the LCR meter without the 10kΩ series resistor connected in line.

B. Step Stress Testing

A step stress testing methodology was adopted to provide insights into the relative robustness of the various capacitor types tested in an accelerated fashion. While the environmental conditions were held constant at 85°C and 85% RH, the voltage bias used to stress the capacitors was increased every 72 hours (see Fig. 3). At the beginning of the test, the capacitors were each stressed with their rated voltages. Each step increase was $0.33 \times V_R$, where V_R represents the rated voltage of the capacitor under test. The maximum stress level applied to the capacitors was $3 \times V_R$.

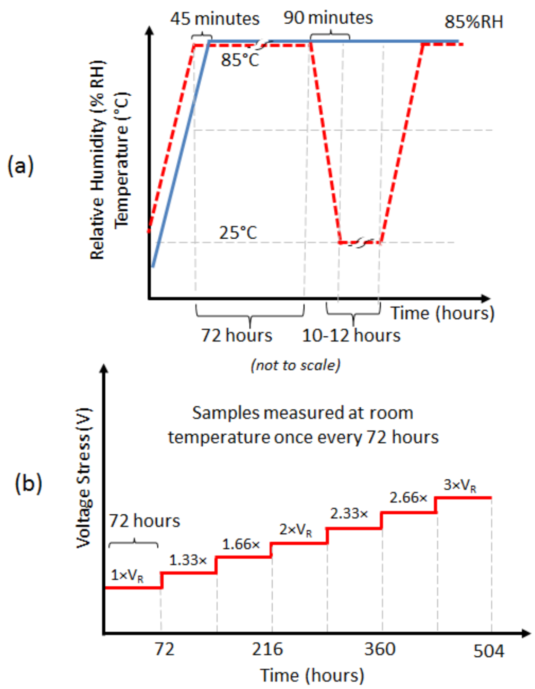

Fig. 3 (a) Temperature Humidity Profile and (b) Voltage Step Stresses Used in Ta Capacitors' test

Before increasing the voltage between successive stress levels, the chamber was ramped down to 25°C while maintaining the humidity at 85% RH. The samples were then powered down, and discharged through a 5kΩ power resistor. This was followed by electrical characterization, wherein the capacitance and DCL were measured using the test monitoring setup. The chamber was then ramped back up to 85°C and the samples were then powered up to the next voltage stress level.

III. Results

Capacitance and DCL were measured before the samples were placed in the test chamber to obtain a baseline. Once the test was started, these parameters were measured once every 72 hours at room temperature. This section reviews the data collected from the test, at the end of each stress step.

A. Variation of Capacitance

The capacitance of all test samples was measured using a 0.5V rms signal at 120 Hz. A 2V DC bias was also applied during the measurement.

In the following plots, the blue and red dotted lines represent the nominal value and tolerance limits for the tested capacitors, respectively. Each box represents the distribution of the parameter after its exposure to the stress level (multiplier) indicated on the x-axis. Baseline measurements taken prior to the test are indicated at stress level 0. Outliers are indicated in red.

Fig. 4 and Fig. 5 show the variation in capacitance for the 16V parts subjected to THB step stress tests. It is seen that the capacitance values remain relatively constant for the MnO_2 parts (Fig. 4). However, the distribution for the polymer parts (Fig. 5) drifts downwards with increase in voltage stresses, indicating a loss of capacitance. Further, the increase in spread of the distribution for the polymer Ta capacitors indicates that there is a significant amount of variation in part-to-part degradation.

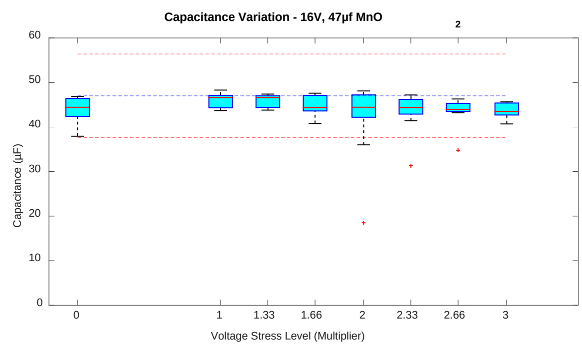

Fig. 4 Capacitance variation for 16V, 47µF MnO_2 Ta capacitors

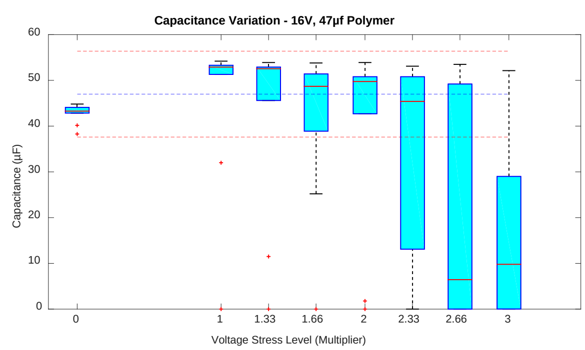

Fig. 5 Capacitance variation for 16V, 47µF polymer Ta capacitors

For the 50V components, the MnO_2 based Ta capacitors did show a noticeable downward drift in capacitance, coupled with an increase in the variance of the distribution (Fig. 6). The 50V polymer Ta capacitors (Fig. 7) showed trends similar to the 16V polymer Ta parts. The distribution drifted downwards and spread out, with increase in voltage stresses applied. The upper whisker of the box plot at the end of test shows samples with capacitance values above the upper threshold (nominal+20%). These values are anomalous, and are artifacts of the measurement process for parts with high leakage current. Since these capacitors had degraded to very high leakage states (>1mA), the instrumentation used could not accurately characterize these samples.

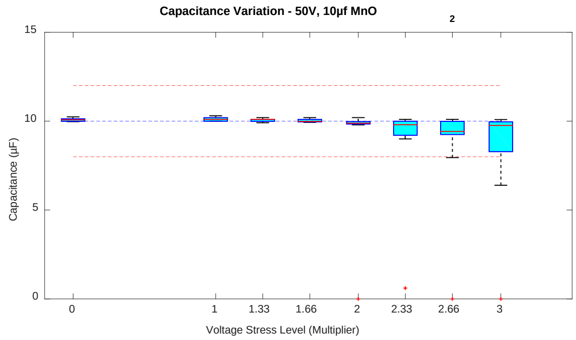

Fig. 6 Capacitance variation for 50V, 10µF MnO_2 Ta capacitors

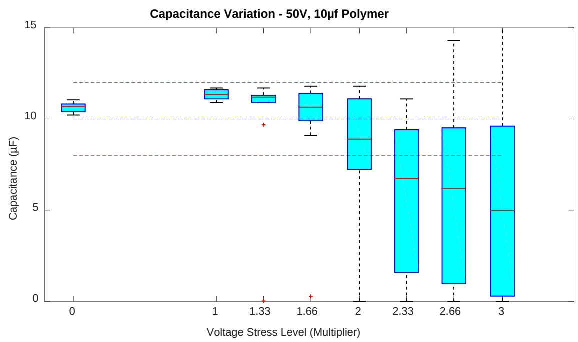

Fig. 7 Capacitance variation for 50V, 10µF polymer Ta capacitors

B. Variation of DC Leakage (DCL)

The DCL value for each sample was measured after the sample was held at its rated voltage for 5 minutes. In the following plots, the two red dotted lines indicate the maximum DCL limit (as seen in Table I) for the MnO_2 (lower line) and polymer Ta (upper line) capacitors. The red points indicate outliers. The compliance current limit for the high resistance meter used for DCL measurements was 500µA. All values higher than this limit were therefore recorded as 500µA. Consequentially, when all the test capacitors in a certain population degraded to exhibit DCL values in excess of 500µA, the distribution on the box-plots collapsed to a single line at this limit.

The DCL for the 16V MnO_2 parts (Fig. 8) progressively increased with an increase in the voltage stress applied. All samples had failed in comparison to the more conservative 7.5µA MnO_2 parametric failure threshold. However, in contrast to the MnO_2 parts, the 16V polymer Ta capacitor population only had one sample that exhibited DCL in excess of 10µA (Fig. 9) during the course of the test. 9 out of 10 samples showed DCL values that were of the order of 1µA or lower throughout the test.

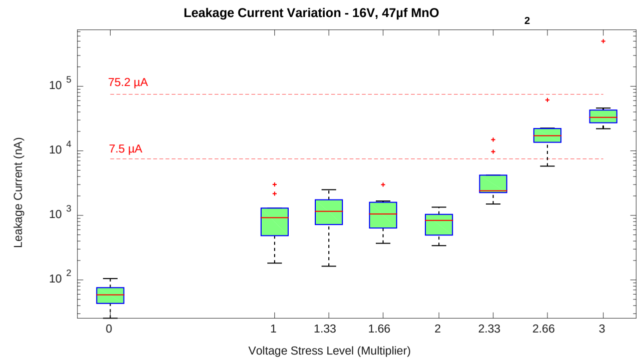

Fig. 8 DCL variation for 16V, 47µF MnO_2 Ta capacitors

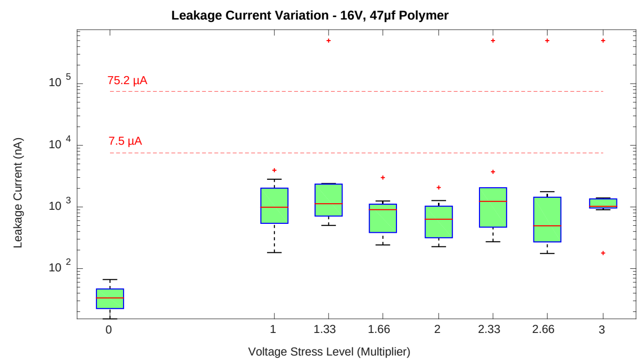

Fig. 9 DCL variation for 16V, 47µF Polymer Ta capacitors

The DCL variation for the 50V capacitors is shown in Fig. 10 and Fig.11. Unlike the 16V capacitors, both sets of 50V capacitors had failed after exposure to 2.66×V_R (133V). Significant recovery (from >500µA to ~1µA) in DCL was observed after exposure to 2.33×V_R in the 50V MnO_2 Ta caps. Such substantial recovery was not seen in any of the other test populations. However, smaller levels of DCL recovery were seen in the 16V capacitors. The 50V polymer Ta capacitors seemed to resemble the response of their MnO_2 counterparts, with the exception of the recovery in DCL.

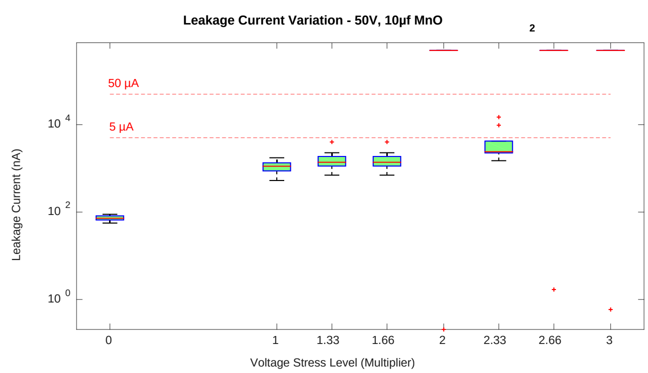

Fig. 10 DCL variation for 50V, 10µF MnO_2 Ta capacitors

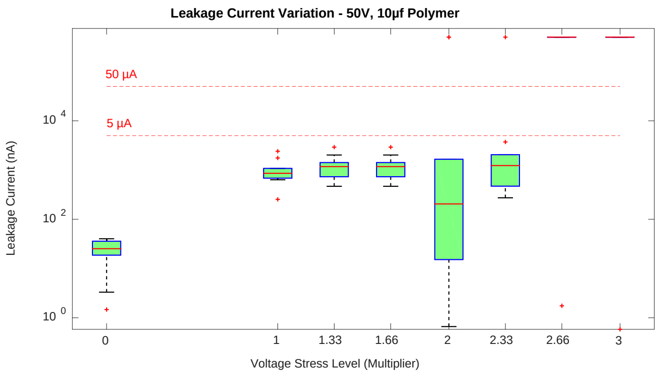

Fig.11 DCL variation for 50V, 10μF polymer Ta capacitors

IV. Discussion and Failure Mechanisms

Table II summarizes the trends seen in the measurements of capacitance and DCL. These trends help identify the underlying failure mechanisms in Ta capacitors. Additionally, the results from the tests shed light on the relative similarities and differences in the performance of the tested capacitors.

Table II Trends Observed in Capacitance and DCL

Cathode Type	Voltage	Trend in Capacitance	Trend in DC Leakage
Polymer	50V	Decreasing	Stable (after 1×V_R)
Polymer	16V	Decreasing	Sharp increase at 2.66×V_R
MnO_2	50V	Slight decrease	Sharp increase at 2×V_R
MnO_2	16V	Stable	Increase at 2.33×V_R

A. Increase in DCL – Field Crystallization

When exposed to thermal stresses (elevated temperatures) and electrical stresses (voltage / electric field), the amorphous tantalum pentoxide (Ta_2O_5) dielectric is converted to a conductive crystalline state. This phenomenon is referred to as field crystallization and is well documented in the literature [10]. Since these tests combine both thermal and electrical stresses, field crystallization would have been accelerated. The increased conductivity of the dielectric would result in an increased DCL, which was seen in all the test populations.

Field crystallization requires nucleation sites, which are found in the form of impurities in the dielectric. For MnO_2 Ta capacitors, these impurities are the residues from lubricants and other materials used in the fabrication of the capacitors. These impurities trigger field crystallization as early as the manganizing step during fabrication, carried out at temperatures above 250°C, before the capacitor is even fielded [11]. The application of the PEDOT polymer electrolyte does not require high temperatures, and hence early onset of field crystallization-based failures is not a concern for polymer Ta capacitors.

It could be this greater propensity of the dielectric in MnO_2 Ta capacitors for field crystallization that leads to earlier failures in the presence of thermal and electrical stresses in these tests. The dielectric in PEDOT-based Ta capacitors does not crystallize as readily. However the application of sufficient stress over extended durations could also cause the Ta_2O_5 in polymer Ta capacitors to crystallize. As a result, it would take greater levels of stress and longer exposure times to cause the polymer Ta capacitors to fail, as observed in these results.

B. Degradation of PEDOT in High Humidity Environments

As described earlier, PEDOT and its conductive properties in solid capacitors degrade rapidly at elevated temperatures in the presence of humidity [12]. At room temperature, elevated humidity levels do not pose a risk to the performance or reliability of the capacitor. This can be attributed to sorption of moisture by the phenolic resins in the epoxy mold compound. However, at higher temperatures (>75°C), due to greater diffusion of moisture into the mold compound, the polymer undergoes de-doping.

The de-doping causes a loss of conductivity in the cathode layer. Consequently, the anode becomes isolated from the cathode. This in turn results in a loss of capacitance and an increase of equivalent series resistance (ESR). This loss of capacitance can be seen in both 16V (Fig. 5) and 50V (Fig. 7) polymer capacitors. The isolation of the cathode from the anode could also cause a decrease in DCL, as seen with the 16V polymer Ta capacitors in Fig. 9. However, field crystallization also occurs simultaneously, causing an increase in DCL. Unless, the anode and cathode are completely isolated, increased DCL due to formation of a conductive path through the dielectric, between the two electrodes, is more likely to be observed (Fig.11).

C. Impact of Humidity on Self-Healing Ability

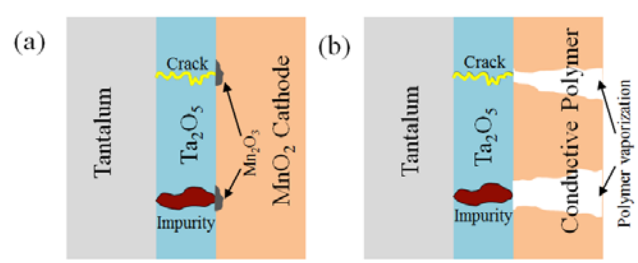

Fig. 12 Self-healing mechanism in (a) MnO_2 and (b) Polymer Ta capacitors

Self-healing refers to the ability of a Ta capacitor to recover from a degraded state (high leakage) to a healthy state, which is within manufacturer specifications. This behavior is observed for both MnO_2 and polymer Ta capacitors. In MnO_2 Ta capacitors, the MnO_2 cathode (conductive) gets converted to Mn_2O_3 (nonconductive) at elevated temperatures. Such elevated temperatures can occur locally in regions with high leakage currents. This could occur in regions where the dielectric is damaged, or when there are impurities present in the dielectric. These high leakage paths become isolated due to Mn_2O_3 formation. Similarly, in polymer Ta capacitors the conductive polymer can be vaporized in regions with elevated temperatures caused by high leakage currents. The self-healing of tantalum capacitors is depicted in Fig. 12. In the presence of humidity, it is possible for the self-healed sites in MnO_2 Ta capacitors to get reactivated [6] [13]. This would cause an increase in DCL over the course of the test in these capacitors.

Additionally, in the presence of humidity and applied bias, electro-chemical migration may also be observed [13]. The culmination of these mechanisms, combined with the increased propensity of MnO_2 Ta capacitors to undergo field crystallization, would cause the DCL to degrade more rapidly in these parts when compared to their polymer counterparts. This can be seen in Figs. 8, 9, 10 and 11.

V. Conclusions

In order to assess the effect of cathode chemistry and voltage ratings on the reliability of Ta capacitors, four sets of commercially available Ta capacitors were subjected to THB testing with voltage step stresses. The tested samples consisted of 50V and 16V parts, with conductive polymer (PEDOT) and MnO_2 cathodes.

From the results of the test, it can be seen that polymer Ta capacitors with high voltage (50V) and low voltage (16V) ratings exhibit a loss of capacitance when subjected to THB testing with voltage step stresses. At both these voltage ratings, the MnO_2 Ta capacitors had relatively stable capacitance values. However, when comparing DC leakage currents, the MnO_2 Ta capacitors clearly showed more rapid degradation and earlier failures.

The behavior of the polymer Ta capacitors can be attributed to the de-doping of the PEDOT under elevated temperature-humidity conditions. As a result, the anode and the cathode assemblies within the capacitor were isolated, leading to a drop in capacitance. While the effects of this isolation can also be seen in the slower rate of degradation of DCL at lower voltages, field crystallization tended to dominate at higher voltages ($3\times V_R$ for 50V parts).

The behavior of the MnO_2 capacitors, as seen in the results, can be attributed to the greater propensity of the dielectric in the MnO_2 Ta capacitors to undergo field crystallization. This was manifested in the form of higher DCL values at both voltages. The re-activation of self-healed sites could also contribute to the more rapid degradation of DCL. However, since the MnO_2 cathode was more robust to the environmental conditions, the drop in capacitance was relatively insignificant.

The results from the THB tests indicate that at high humidity levels, polymer Ta capacitors have a greater inclination to 'fail open', in a low leakage, low capacitance state. In contrast, MnO_2 Ta capacitors tend to fail short under such conditions. By evaluating the relative criticality of these two failure modes (open and short) in their applications, OEMs can choose the appropriate Ta capacitor technology for their products. For Ta capacitors with both types of cathodes, greater degradation in capacitance and DCL was seen in the higher rated voltage parts. This could perhaps be attributed to higher field strengths within the dielectric layers. Further material analysis is required to corroborate and confirm the hypothesized failure mechanisms.

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References

[1] G. Morita, "AN-1099: Application Note - Capacitor Selection Guidelines for Analog Devices, Inc.," Analog Devices, Norwood, MA, 2010.

[2] J. Gill, "Basic Tantalum Capacitor Technology," AVX Ltd., Tantalum Division, Paignton, England, 2002.

[3] Y. Freeman, R. Hahn, P. Lessner and J. Prymak, "Reliability and Critical Applications of Tantalum Capacitors," in *Proceedings of the Capacitor and Resistor Technology Symposium Conference*, 2007.

[4] A. Dehbi, W. Wondrak, Y. Ousten and Y. Danto, "High temperature reliability testing of aluminum and tantalum electrolytic capacitors," *Microelectronics Reliability,* vol. 42, no. 6, pp. 835-840, 2002.

[5] M. Laps, R. Grace, B. Sloka, J. Prymak, X. Xu, P. Pinceloup, A. Gaurav, M. Randall, P. Lessner and A. Tajuddin, "Capacitors for Reduced Microphonics and Sound Emission," in *International Capacitor and Resistor Technology Symposium Proceedings*, Albuquerque, NM, 2007.

[6] A. Teverovsky, "Effect of Moisture on Characteristics of Surface Mount Solid Tantalum Capacitors," in *International Capacitor and Resistor Technology Symposium*, 2003.

[7] J. Virkki, T. Seppälä, L. Frisk and P. Heino, "Accelerated Testing for Failures of Tantalum Capacitors," *Microelectronics Reliability,* vol. 50, no. 2, pp. 217-219, 2009.

[8] J. Virkki and P. Raumonen, "Testing the Effects of Seacoast Atmosphere on Tantalum Capacitors," *Active and Passive Electronic Components,* vol. 2011, 2011.

[9] E. K. Reed, "Characterization of Tantalum Polymer Capacitors," Jet Propulsion Laboratory, NASA, Pasadena, CA, 2005.

[10] T. Zednicek, J. Sikula and H. Leibovitz, "A Study of Field Crystallization in Tantalum Capacitors and its Effect on DCL and Reliability," in *CARTS USA*, 2009.

[11] Y. Pozdeev-Freeman, Y. Rosenberg, A. Gladkikh, M. Karpovski and A. Palevski, "Critical Oxygen Content in Porous Anodes of Solid Tantalum Capacitors," *Journal of Materials Science: Materials in Electronics,* vol. 9, pp. 309-311, 1998.

[12] I. Zednickova, M. Biler, J. Petrzilek and T. Zednicek, "Hermetically

Sealed SMD Tantalum Capacitors," in *Proceedings of the International Capacitor and Resistor Technology Symposium*, 2012.

[13] KEMET Electronics Corporation, "Moisture - An Old and Known Nemesis of Tantalum Caps," Greenville, SC, July 2000.