Effect of High Temperature Storage on AC Characteristics of Polymer Tantalum Capacitors

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Abstract

Replacement of MnO2 with conductive polymers as cathode materials in chip tantalum capacitors allows for a substantial reduction of the equivalent series resistance (ESR), improvement of frequency characteristics, and elimination of the possibility of ignition during failures. One of the drawbacks of chip polymer tantalum capacitors (CPTCs) is a relatively poor long-term stability at high temperatures. In this work, variations of capacitance, dissipation factor, and ESR in different types of capacitors including automotive grade parts from three manufacturers have been monitored during storage at temperatures from 100 ºC to 175 ºC for up to 18,000 hours. Results show that ESR is the most and capacitance the least sensitive to degradation parameter. Times to parametric failures have been simulated using a Weibull-Arrhenius model that allowed for assessments of activation energies of the degradation and prediction of times to failure at the use temperature. Degradation of CPTCs was explained by thermo-oxidative processes in conductive polymers that result in exponential increasing of the resistivity with time of ageing. This process starts after a certain incubation period that depends on packaging materials and design and corresponds to the time that is necessary to form delamination between the encapsulating molding compound and lead frame. The effectiveness of the existing qualification procedures to assure stable operation of CPTCs is discussed.

Key words

Aging, Capacitor, failure, reliability, tantalum, testing.

I. Introduction

One of the major drawbacks of the new technology of manufacturing tantalum capacitors using polymer cathodes is that AC characteristics of the parts that include capacitance, dissipation factor (DF), and ESR might degrade substantially under environmental stresses. The conductivity of PEDOT-PSS polymers that are used for cathode materials decays with time under high relative humidity or high-temperature storage in dry conditions [1, 2]. As a result, characteristics of polymer capacitors degrade under combined stresses of temperature and humidity [3, 4]. Until recently, operating temperature of chip polymer tantalum capacitors (CPTCs) was limited to 85 °C or 105 °C. However, in 2014 KEMET and AVX introduced automotive grade capacitors that can pass biased testing at 85 °C and 85% RH for 1000 hours and unbiased storage at 125 °C for 1000 hours. In 2019, KEMET introduced their new automotive grade T599 series that can endure 1000 hr of storage at 150 °C [5].

A certain level of ESR degradation and failures caused by environmental stresses occur also in MnO2 tantalum capacitors [6]. However, environments do not degrade manganese dioxide with time any significantly, and parametric ESR failures of MnO2 capacitors are typically caused by delamination and increased resistances at the interfaces between cathode layers (MnO2/carbon or carbon/silver epoxy).

Because of the sensitivity of CPTCs to environmental stresses, qualification procedures for automotive grade parts, contrary to military grade MnO2 capacitors, include high temperature storage (HTS) life testing. This testing is typically carried out at 125 ºC for 1000 hours (Automotive Electronics Council, AEC-Q200 requirements). Some general purpose CPTCs do not have HTS requirements, but high-quality parts are tested typically for 2000 hours at 105 ºC or 1000 hours at 125 ºC. According to manufacturers' specifications, post-HTS values of ESR are relaxed substantially compared to the initial limits, from 2 to 5 times. This easing of the requirements reflects intrinsic degradation processes in polymer cathode materials. For the same reason, degradation at operating temperatures but for substantially longer periods of time (years of operation) is also possible and there is no warranty that degradation during applications will not exceed the relaxed requirements of standard HTS

testing. There is a need for a model that can predict degradation of the parts at operating conditions to assess the end-of-life characteristics of CPTCs.

In this work, different types of polymer tantalum capacitors from three manufacturers have been stored at temperatures from 100 ºC for periods up to 18,000 hours to 175 ºC for up to 1,500 hours to reveal common features in their behavior and develop a model for reliability predictions. AC characteristics of capacitors have been measured periodically during the ageing and distributions of times to parametric failures were approximated using a Weibull-Arrhenius model. Possible mechanisms of degradation and the effect of packaging are discussed.

II. Experiment

Ten types of Mfr.A, four types of Mfr.B, and eight types of Mfr.C capacitors have been used in this study. Specified characteristics of the parts, including capacitance, C, voltage rating, VR, maximum ESR, DF, maximum operating temperature (T_{max}), the case size and quality level are shown in Table 1. In all cases, the tolerance for capacitance values was ±20%. Five types of the parts were general purpose, ten types were manufactured for the automotive industry per AEC-Q200 requirements, and seven types were hi-rel or COTS+ capacitors.

Different groups of capacitors, from 5 to 20 samples in each (typically 10 samples), have been stored at 100 ºC, 125 ºC, 150 ºC, and 175 ºC, and their AC characteristics measured periodically; C and DF at 120 Hz and ESR at 100 kHz.

Times to failure, TTF, were determined separately for each parameter based on variations of characteristics with time of storage. The failure criteria were decreasing of capacitance to below 20% of the initial value, increasing DF above the specified maximum, and increasing ESR above 3 times the initial limit. Distributions of TTFs have been approximated with a Weibull-Arrhenius model that allows calculation of the probability of failure after time t during operation at a temperature T:

$$P(t) = 1 - \exp\left[-\left(\frac{t}{\eta}\right)^{\beta}\right], \quad \eta = C_0 \times \exp\left(E_a / kT\right), \qquad (1)$$

where the slopes of the distributions β, scale parameters η, constants C_0 and activation energies E_a were determined using the maximum likelihood estimation (MLE) method and ALTA-7 software available from ReliaSoft.

III. Test results

Examples of variations of AC characteristics with time of HTS for two general application capacitors are shown in Fig.1. In spite of some data spreading, there is a clear trend of increasing degradation rate with temperature. Degradation resulted in capacitance dropping eventually to below 10% of the initial value, DF increasing to more than 100%, but the most significant increase, ~1000 times, occurred with ESR that in many cases was increasing exponentially with time of storage.

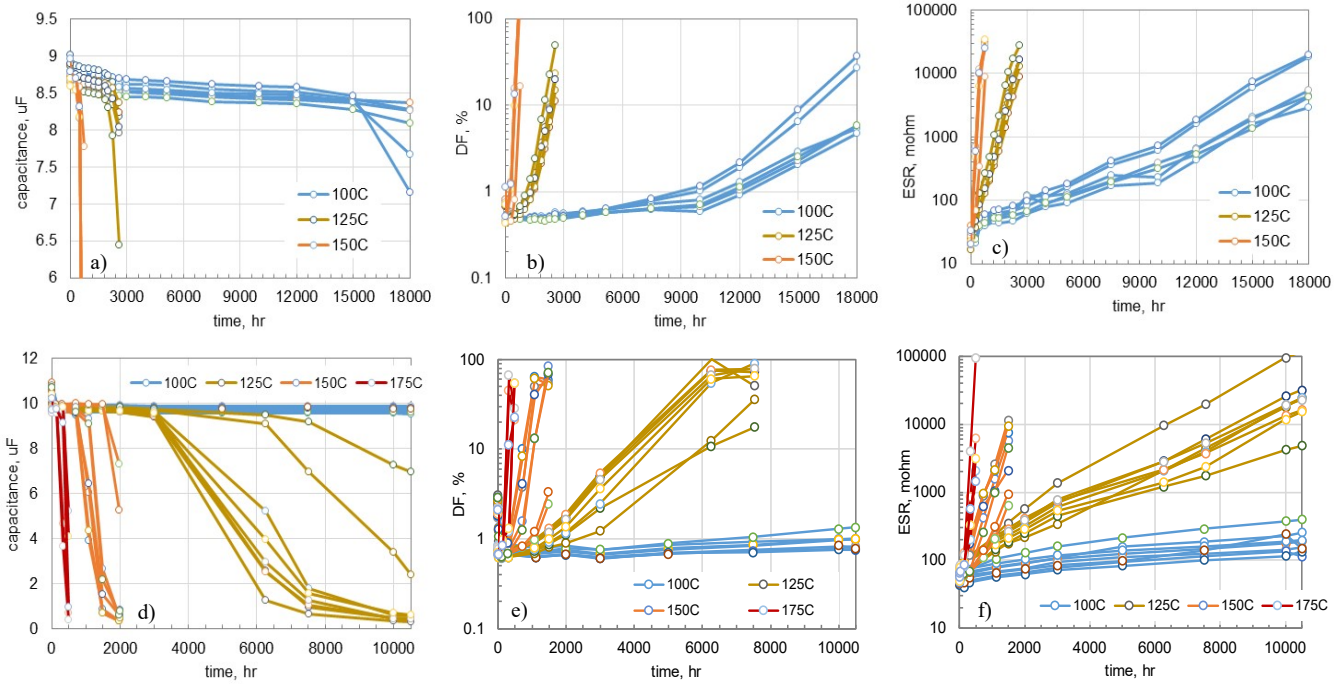


Fig. 1. Capacitance (a, d), dissipation factor (b, e), and equivalent series resistance (c, f) degradation during high-temperature storage for the general purpose A7 (a, b, c) and B1 (d, e, f) capacitors.

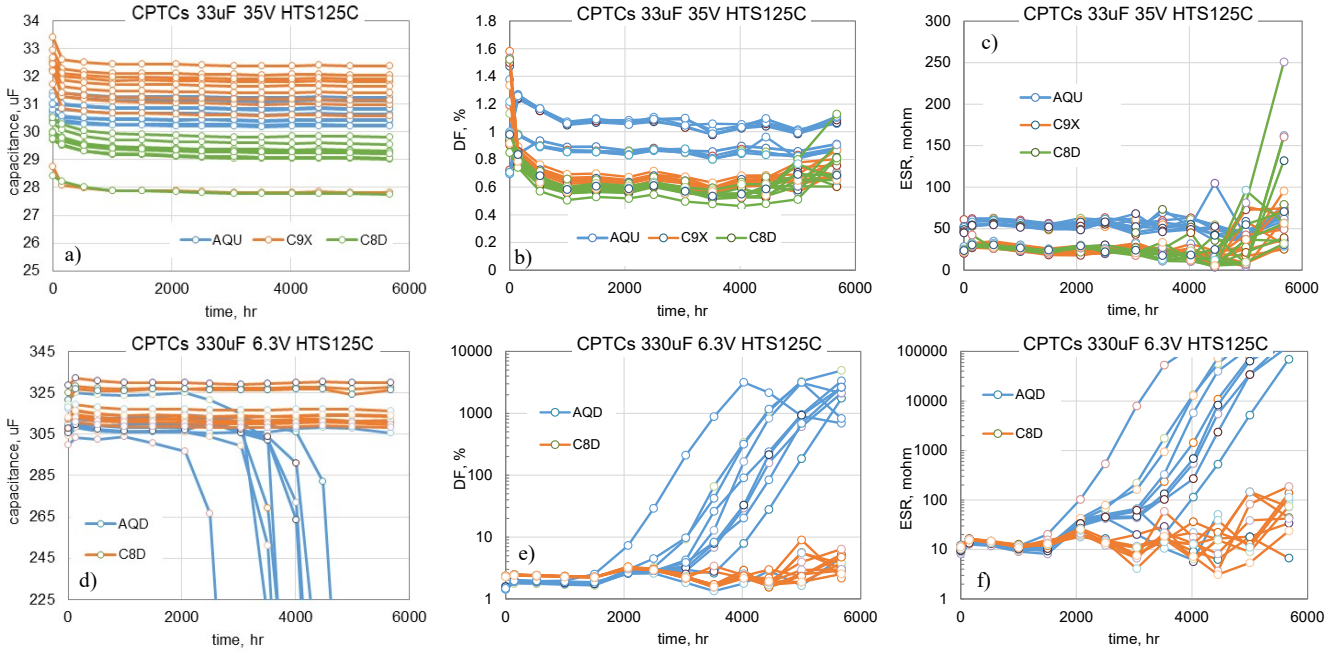
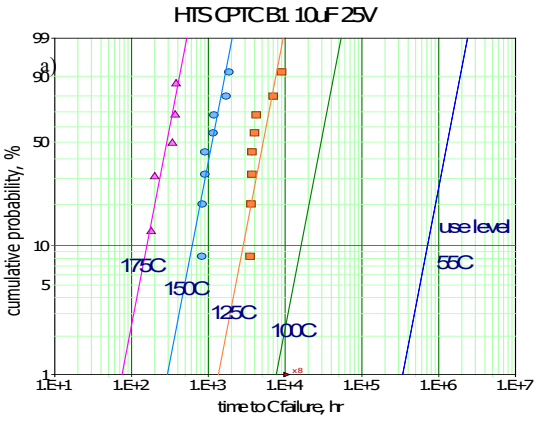


Fig. 2. Results of HTS at 125 C for 33 µF 35 V (a, b, c) and 330 µF 6.3 V (d, e, f) automotive grade capacitors

Based on analysis of variations of AC characteristics similar to those shown in Figure 1 and 2, TTF values have been determined for C, DF, and ESR for all parts at different test conditions, and the relevant TTF distributions were approximated with Weibull-Arrhenius models according to Eq.(1). An example of such approximations for capacitance and ESR failures is shown in Figure 3. The charts show also distributions of TTF calculated at the use temperature that was assumed 55 ºC. Times to ESR failures were smaller compared to capacitance failures. For the case shown in Fig.3, the median TTF at 150 ºC was ~550 hr for ESR and ~1100 hr for capacitance.



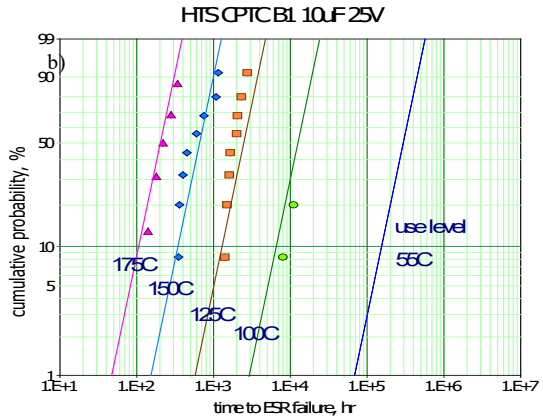


Fig. 3. Distributions of times to failure for capacitance (a) and *ESR* (b) for B1 capacitors. Here and below marks indicate experimental data, solid lines are model's approximations, and dashed lines give prognosis for the use condition (55 ºC). Red marks on (a) indicate suspended points and correspond to the maximum time of testing with no failures.

Fig. 4 shows TTF distributions at the use temperature calculated for C, DF, and ESR for B1 type capacitors. The times for capacitance failures (TTF_C) are ~4.5 and for DF failures (TTF_{DF}) ~2 times less than for ESR (TTF_{ESR}). Note that the slopes of the distributions are similar thus indicating that the same mechanisms are responsible for degradation of all AC characteristics.

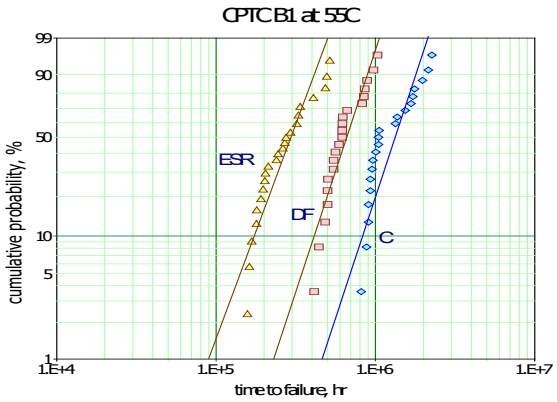


Fig. 4. Comparison of distributions of times to failure for C, DF, and ESR predicted for use temperature for B1 capacitors.

For most tested capacitors, TTF_C and TTF_{DF} values were substantially greater than TTF_{ESR}. Table 1 displays ratios of medians of the relevant TTF values at the use condition for seven part types ($R_C = TTF_C/TTF_{ESR}$ and $R_{DF} = TTF_{DF}/TTF_{ESR}$.). On average, TTF_{ESR} was 2 times smaller than TTF_{DF} and 3.5 times smaller than TTF_C. Obviously, *ESR* is the most and capacitance is the least sensitive parameter to HTS degradation.

TABLE 1. RATIOS OF MEDIAN TIMES TO CAPACITANCE (R_C) AND *DF* (R_{DF}) FAILURES AND MEDIAN TIMES TO *ESR* FAILURES.

Part	*A2*	*A3*	*A6*	*C2*	*B1*	*B2*	*B4*
R_C	1.49	2.92	2.1	5.86	4.37	3.60	3.9
R_{DF}	1.41	3.4	1.7	1.58	2.19	2.56	1.16

Parameters of the distributions, β and E_a, for different groups of capacitors are displayed in Table 2. The slopes of distributions (β) for all part types exceeded 1 averaging at 3.5 at a standard deviation of 2. This indicates that HTS failures in CPTCs are due to intrinsic wear out mechanisms. Activation energies are varying in a relatively wide range, from 0.38 eV to 0.93 eV. The average value of E_a is 0.62 eV and standard deviation 0.17 eV.

Table 3 has also results of predictions of the median (TTF_{50}) and the first percentile (TTF_1) times to failure at the use temperature, median times to failure at 125 ºC, TTF_{125}, and the probabilities of failure, P_{125}, during a standard life or endurance testing that is typically carried out at 125 ºC for 1000 hours. Reliability characteristics for several part types that did not have sufficient number of failures were estimated using average values of β and E_a.

Different part types have substantially different susceptibility to parametric failures during long-term storage. The median time to *ESR* failures at operating conditions varies from a few to 471 years. However, the times to the failure inception that can be defined as a time to the first percentile of TTF distributions are much shorter, from one to 88 years.

TABLE 2. RESULTS OF MODELING OF ESR FAILURES.

Part type	Qual. level	β	E_A, *eV*	TTF_{50}, *yr.*	TTF_1, *yr.*	TTF_{125}, *khr*	P_{125}, %
A1 10-35	COTS+	2.09	0.48	7.6	1.0	3.4	5.3
A2 10-35	COTS+	3.47	0.46	6.2	1.8	3.1	1.3
A3 15-25	COTS+	2.49	0.45	5.4	1.0	2.9	4.5
A4 15-25	COTS+	4.43	0.38	3.9	1.5	3.1	0.4
A5 100-10	auto	10.2	0.43	4.8	3.2	2.8	0.002
A6 10-35	auto	3.31	0.53	33.2	2.9	3.4	1.2
A7 10-100	general	2.69	0.93	29.0	6.0	0.5	76.2
A8 47-16	general	2.15	0.64	32.3	4.5	>2	2
A9 33-35	auto	-	-	>66*	>21*	>13*	<0.005
A10 330-6	auto	6.6	0.61	16	10.2	3.2	0.01
B1 10-25	general	2.9	0.77	33.8	7.9	1.5	4.86
B2 220-10	general	6.8	0.71	33.3	17.9	3.5	0.01
B3 22-25	general	4	0.52	55.0	19.1	14	0.01
B4 220-16	COTS+	3.39	0.52	19.2	5.5	6.5	0.11
C1 33-35	COTS+	2.51	0.89	471.0	88.0	6.7	0.07
C2 33-35	auto	3.11	0.75	76.4	19.5	6.1	0.22
C3 330-6	auto	1.15	0.76	71.9	1.8	4.9	9.0
C4 330-6	COTS+	1.65	0.77	73.7	5.7	5.9	4.5
C5 33-25	auto	2.58	0.57	12.6	2.4	>2	0.03
C6 33-35	auto	-	-	>66*	>21*	>13*	<0.005
C7 33-35	auto	-	-	>66*	>21*	>13*	<0.005
C8 330-6	auto	-	-	>66*	>21*	>13*	<0.005

* Calculated at $\beta = 3.5$ and $E_a = 0.62$ eV.

Although some automotive industry CTPCs (A9, C2, C3, C6-C8) showed exceptional results during HTS testing (see Fig. 2), on average, behavior of these parts does not change substantially from the general purpose parts. One of the reasons for that might be insufficient requirements of AEC-Q200 for the hight temperature exposure testing that is specified for 1000 hours only. Passing the specified test, in general, does not guarantee stability during long term storage or operation at high temperatures.

The median time to ESR failure at 125 ºC, TTF_{125C}, is in the range from 500 to 6,700 hours, and the calculated probability of ESR failures during qualification testing at 125 ºC for 1000 hours, P_{125}, varies from 0.002% to 76%. Results in Table 2 show that parts with $P_{125} < 0.1\%$ might have median life at the use temperature as low as 3.5 years. This means that no failures during standard HTS testing does not guarantee long-term stability of the parts during operation. On the other hand, parts that have a relatively large probability of failure during qualification testing might remain stable at the use temperature for more than 10 years. Apparently, the standard HTS tests currently are not sufficient to assure long-term stability of AC characteristics at high temperatures. Although no correlation was found between the probability of failure during qualification testing and at operation conditions, there is a trend of increasing TTF at 55 ° C for lots with higher activation energy. For lots having large enough values of E_a, acceptable results of HTS qualification testing can provide more confidence that no failures will occur during use conditions. For example, HTS testing at 125 ºC for 1000 hours is equivalent to 1.4 years of

storage or operation at 55 ºC if E_a = 0.4 eV, and to more than 17 years if E_a = 0.8 eV.

IV. Discussion

Degradation of capacitance and dissipation factor during HTS is due to a substantial increase of *ESR*. Analysis of variations of *C* and *ESR* with frequency for CPTCs in the process of aging at 150 ºC showed that the roll-off frequency decreased from more than 100 kHz initially to less than 10 Hz after 1000 hours of testing, and capacitance at 120 Hz decreased eventually to less than 40% of the initial value, whereas *ESR* increased by two orders of magnitude. These effects are attributable to a reduction of the AC signal reaching internal parts of the tantalum slug as a result of increasing resistance of the cathode layers and can be simulated by presenting the equivalent circuit of a tantalum capacitor as an *R*-*C* ladder [7].

Degradation of *ESR* in CPTCs at high temperatures is due to thermo-oxidative processes in conductive polymers. Testing of PEDOT:PSS organic solar cells showed that their stability was much better when the cells were kept in vacuum or dry nitrogen compared to air storage [8]. Thermal and thermo-oxidative degradation kinetics of poly(3-hexyl thiophene) (P3HT) conducting polymers in nitrogen and air medium was investigated in [9]. The activation energy of degradation of P3HT was ~ 2 eV in nitrogen, while in air E_a varied with the extent of the thermo-oxidative conversion from ~0.5 eV to 1.5 eV. Direct measurements of the sheet resistance for in-situ polymerization PEDOT films in [10] showed that the resistance increased from 64 ohm to more than 10^6 ohm after 16 hours of storage in air at 175 °C, while in dry nitrogen the increase was from 44 ohm to 100 ohm only. Because activation energy of thermal degradation in oxygen-free environments is increasing, stability of CPTCs operating in vacuum, as in case of space applications, or in small hermetically sealed packages might improve substantially.

Degradation of *ESR* in CPTCs in most cases occurred after a certain incubation period. This behavior can be explained considering that packaging limits oxygen access to the slug and delays degradation process. When sealing is compromised, intrinsic thermo-oxidative degradation of conductive polymers results in exponential growth of *ESR* with time of storage.

Knowing the activation energy of the degradation process, we can estimate the period of time this testing would be equivalent to at lower temperatures. Fig. 14 shows results of these estimations. A 1000 hours of storage at 125 ºC without failures (ESR remains below $3\times ESR_{limit}$) would be equivalent to more than one year of storage or operation at 55 ºC if E_a = 0.4 eV, and to more than 20 years at E_a = 0.8 eV.

For CPTCs used in space, thermo-oxidative degradation occurs mostly during the ground phase testing and integration periods. In general, activation energies of thermal degradation of polymers in vacuum are substantially greater than in the presence of oxygen [11]. Studies of thermal degradation of polystyrene (PS), polyethylene (PE), and polypropylene, (PP) in both inert nitrogen and air atmospheres showed that average activation energy of degradation reduced from ~2.3 eV in N2 to 0.7 eV in air for PE, from ~2.0 eV in N2 to 0.87 eV in air for PP, and from ~2.1 eV in N2 to 1.1 eV in air for PS [12].

Similar effects were observed for the conductive conjugated polymers. Testing of PEDOT:PSS organic solar cells showed that their stability was much better when the cells were kept in vacuum or dry nitrogen compared to air storage [8]. Thermal and thermo-oxidative degradation kinetics of P3HT conducting polymers in nitrogen and air medium was investigated in [9]. The activation energy of degradation of P3HT was ~ 2 eV in nitrogen, while in air E_a varied with the extent of the thermo-oxidative conversion from ~0.5 eV to 1.5 eV. Our previous testing [4] showed that 2000 hours storage at 100 ºC in 3 μtorr vacuum does not cause degradation in CPTCs, whereas in air a noticeable increase of ESR was observed. Direct measurements of the sheet resistance using in-situ polymerization PEDOT films in [10] showed that the resistance increased from 64 ohm to >1 Mohm after 16 hours of storage in air at 175 °C, while in dry nitrogen the increase was from 44 ohm to 100 ohm only.

Based on a substantial increase of activation energy of thermal degradation in oxygen-free environments, it is reasonable to assume that stability of CPTCs operating in space, or in small hermetically sealed packages will be improved substantially. An increase in E_a from 0.6 eV that is typical for air conditions even to 1 eV in vacuum for capacitors that can demonstrate stable behavior at 125 °C for 1000 hours would increase their operational life in vacuum at 65 °C from 2 years to more than 20 years, which is sufficient for most applications.

V. Conclusion

1. Measurements of AC characteristics of 22 types of polymer tantalum capacitors in the process of extended storage (thousands of hours) at temperatures from 100 ºC to 175 ºC showed that *ESR* is the most sensitive to degradation parameter that can increase dozens and thousands times compared to the initial value. Times to *C* and *DF* failures are on average 3.5 and 2 times greater than for *ESR*. A decrease of capacitance and increase of *DF* are results of *ESR* degradation.

2. Degradation of AC characteristics with time has been described using Weibull-Arrhenius models. In all cases, the slopes of distributions exceeded one thus indicating wear-out mechanisms of failure. Activation energies of the degradation process depend on the part type and vary in a wide range, from 0.38 to 0.93 eV. On average, E_a = 0.62 ± 0.17 eV.

3. Successful results of qualification testing at 125 ºC for 1000 hours can guarantee stability of parts at operating conditions only for lots with a relatively high activation energy of degradation. Considering that the E_a increases substantially in vacuum, successful results of 1000 hr testing at 125 ºC can assure reliable operation of CPTCs for most space missions.

4. On average, stability of AC characteristics during HTS testing is greater for automotive grade capacitors than for general purpose parts. All tested automotive grade CPTCs can withstand more than 2000 hours at 125 ºC and 4 types remained stable for 4000 hours at 150 ºC. The automotive grade polymer capacitors should be the prime source for selecting components for space applications.

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