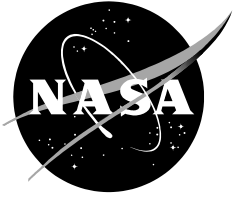


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# Effect of High Temperature Storage on AC Characteristics of Polymer Tantalum Capacitors

*Alexander A. Teverovsky*

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May 2021

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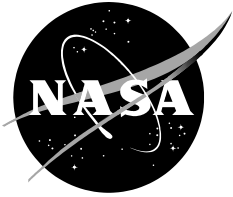
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# Effect of High Temperature Storage on AC Characteristics of Polymer Tantalum Capacitors

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## Abstract

Replacement of MnO<sub>2</sub> 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 °C to 175 °C 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.

## Introduction

Evolution of tantalum capacitors goes in the direction of further improving volumetric efficiency, reducing equivalent series resistance (ESR), and increasing operating voltages. ESR is one of the most important characteristics of tantalum capacitors that determines the rate of energy delivery in the pulse-power systems and the level of ripple currents and voltages when capacitors are used for filtering in power lines. A substantial reduction of ESR was achieved with introduction of conductive polymers based on poly(3,4-ethylenedioxythiophene), PEDOT [1], as a replacement of MnO<sub>2</sub> cathode materials in traditional tantalum capacitors. Manganese oxide has resistivity ~1 ohm<sub>cm</sub>, while the resistivity of PEDOT based compositions is approximately 10 times less. Production of chip polymer tantalum capacitors (CPTCs) that started in late 1990s with manufacturing of low-voltage capacitors has grown substantially, and now most new types of capacitors are manufactured using polymer cathode technology. In addition to low ESR, benefits of CPTCs compared to traditional MnO<sub>2</sub> parts include a safe failure mode (no ignition) and less severe voltage derating requirements [2, 3]. A breakthrough technology in CPTCs was achieved by introducing a water-soluble poly-styrene sulfonate (PSS) in the polymer composition and formation of pre-polymerized PEDOT:PSS systems. This new technology and materials that have been available since 2009 allows for production of capacitors with high voltage ratings, up to 125 V, that could not be realized by the old technology [4]. A better performance and improved quality and reliability of CPTCs that had been achieved over the last years made these parts not only preferred components for many commercial applications, but their employment has begun in reliability-demanding automotive, medical, military and space systems [5, 6].

One of the major drawbacks of the new technology is that AC characteristics of CPTCs that include capacitance, dissipation factor (DF), and ESR might degrade substantially under environmental stresses. The conductivity of PEDOT-PSS polymers decays with time under high relative humidity or high-temperature storage in dry conditions [7, 8]. As a result, characteristics of polymer capacitors degrade under combined stresses of temperature and humidity [4, 9]. Until recently, operating temperature of 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 pass 1000 hr storage testing at 150 °C [10].

A certain level of ESR degradation and failures caused by environmental stresses occur also in MnO<sub>2</sub> tantalum capacitors [11]. However, environments do not degrade manganese dioxide significantly over time, and parametric ESR failures of MnO<sub>2</sub> capacitors are typically caused by delamination and increased resistances at the interfaces between cathode layers (MnO<sub>2</sub>/carbon or carbon/silver epoxy). Similar failures are often due to insufficient margin between the specified maximum and actual values of ESR. In this situation, even relatively minor changes in the compressive stresses caused by moisture-related swelling or baking-related shrinking of molding compound (MC) might change the level of delamination or cracking between the cathode layers thus resulting in ESR variations. These variations occur mostly during relatively short periods of moisture sorption/desorption processes in MC and typically do not result in long-term degradation of capacitors.

Because of the sensitivity of CPTCs to environmental stresses, qualification procedures for automotive grade parts, contrary to military grade MnO<sub>2</sub> capacitors, include high temperature storage (HTS) life testing. This testing is typically carried out at 125 °C 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 °C or 1000 hours at 125 °C. 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 °C for periods up to 18,000 hours to 175 °C 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.

## 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  $\pm 20\%$ . 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.

Table 1. Characteristics of capacitors.

PART	C, $\mu\text{F}$	VR, V	ESR, mohm	DF, %	$T_{\text{MAX}}$ , $^{\circ}\text{C}$	Case size	Quality/application	Time of HTS, khr			
								100 $^{\circ}\text{C}$	125 $^{\circ}\text{C}$	150 $^{\circ}\text{C}$	175 $^{\circ}\text{C}$
A1	10	35	70	8	125	D	upscr. COTS+	6.2	6.8	2.5	1
A2	10	35	70	8	125	D	upscr. COTS+	6.2	6.8	2.5	1
A3	15	25	70	8	125	D	upscr. COTS+	6.2	6.8	2.5	1
A4	15	25	70	8	125	D	upscr. COTS+	6.2	6.8	2.5	1
A5	100	10	40	6	125	D	auto	6.2	6.8	2.5	1
A6	10	35	70	6	125	D	auto	6.2	6.8	2.5	1
A7	10	100	50	8	105	V	gen. purpose	18	3	0.8	-
A8	47	16	70	6	125	D	gen. purpose	15	2	2	-
A9	33	35	70	12	125	U	auto	-	5.7	4.2	-
A10	330	6.3	25	6	125	D	auto	-	5.7	4.2	-
B1	10	25	100	8	105	B	gen. purpose	11	11	2	0.6
B2	220	10	18	10	105	D	gen. purpose	11	11	2	0.6
B3	22	25	100	14	105	BB	gen. purpose	18	16	4	1
B4	220	16	25	10	125	EE	hi-rel COTS	10	10	3	2
C1	33	35	60	10	125	X	hi-rel COTS	8	8	5	1.5
C2	33	35	65	10	125	X	auto	8	8	5	1.5
C3	330	6.3	25	10	125	D	auto	8	8	5	1.5
C4	330	6.3	40	10	125	D	hi-rel COTS	8	8	5	1.5
C5	33	25	60	10	125	D	auto	10	2.2	1.5	1.5
C6	33	35	65	10	150	X	auto	-	5.7	4.2	-
C7	33	35	65	10	125	D	auto	-	5.7	4.2	-
C8	330	6.3	25	10	125	D	auto	-	5.7	4.2	-

Different groups of capacitors, from 5 to 20 samples in each (typically 10 samples), have been stored at 100  $^{\circ}\text{C}$ , 125  $^{\circ}\text{C}$ , 150  $^{\circ}\text{C}$ , and 175  $^{\circ}\text{C}$ , and their AC characteristics measured periodically; C and DF at 120 Hz and ESR at 100 kHz. Duration of testing at each temperature is indicated in the last four columns of Table 1.

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  $T$ :

$$P(t) = 1 - \exp\left[-\left(\frac{t}{\eta}\right)^{\beta}\right],$$

$$\eta = C_0 \times \exp\left(\frac{E_a}{kT}\right), \quad (1)$$

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

## Test results

Figure 1 shows examples of variations of AC characteristics with time of HTS for two part types. 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.

Additional measurements have shown that the steady-state leakage currents remained low even after a significant degradation of AC characteristics. This means that degradation of the polymer does not cause degradation of the dielectric (Ta<sub>2</sub>O<sub>5</sub>) that controls DC characteristics of tantalum capacitors. A similar degradation of C, DF, and ESR occurs during biased operation and unbiased storage of the parts. Apparently, degradation of AC and DC characteristics are related to different mechanisms, hence require different approaches for quality assurance.

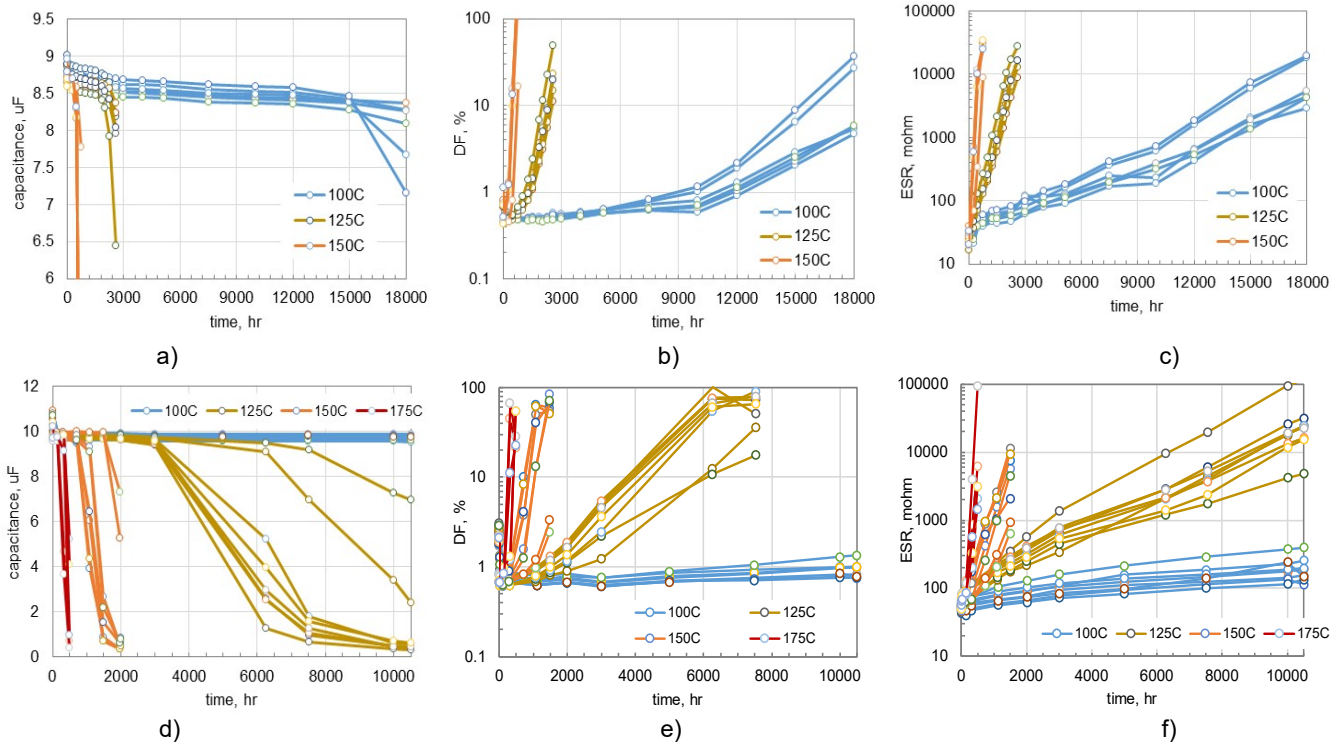


Figure 1. Capacitance (a, d), dissipation factor (b, e), and equivalent series resistance (c, f) degradation during high-temperature storage for the general purpose A7 (a, b, c) and B1 (d, e, f) capacitors.

Results in Figure 1 show that in the general-purpose capacitors a significant degradation occurs already after 1000 hr of storage at 125 °C. Variations of AC characteristics for three types of 33 μF 35 V and two types of 330 μF 6.3 V automotive grade capacitors are shown in Figure 2. According to these data, 4 out of 5 automotive grade capacitors can withstand 5200 hours at 125 °C. One part type, A10, degraded catastrophically by the end of testing; however, it withstood the required 1000 hours without significant degradation of characteristics. The four part types that were stable at 125 °C withstood also storage at 150 °C for 4000 hours.

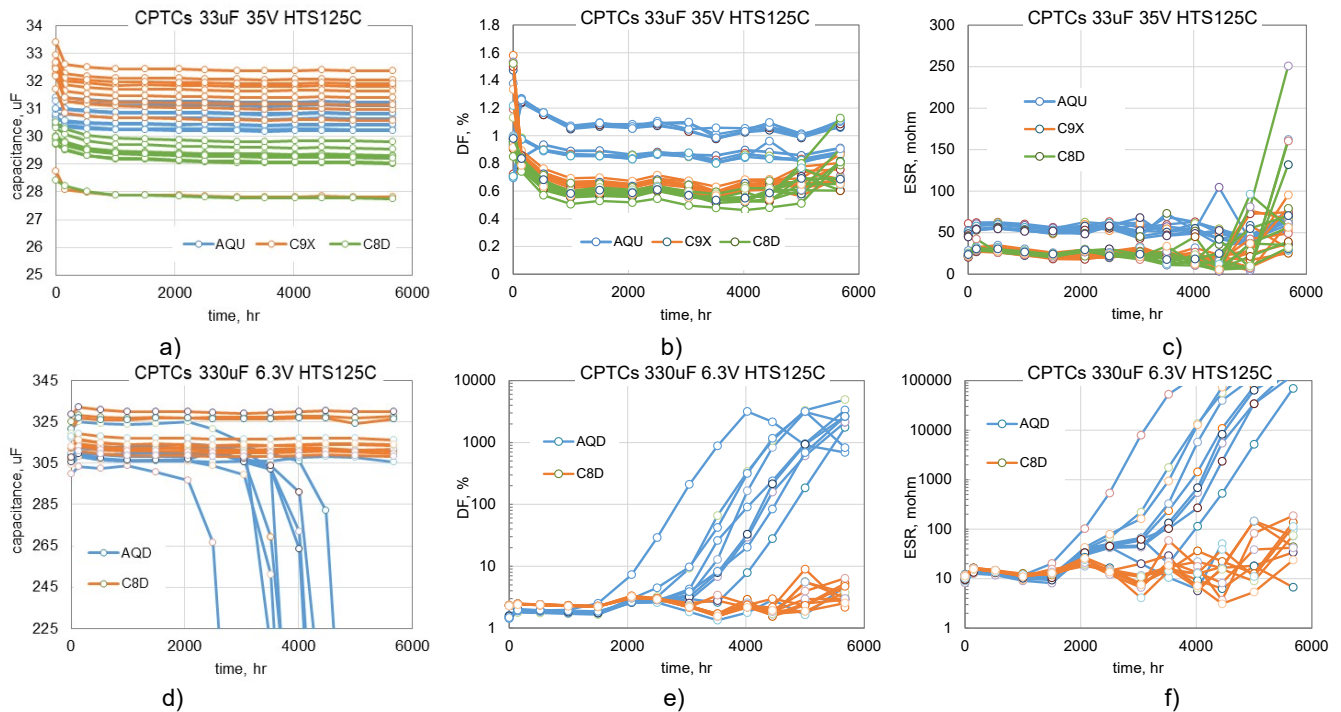


Figure 2. Results of HTS at 125 C for 33  $\mu\text{F}$  35 V (a, b, c) and 330  $\mu\text{F}$  6.3 V (d, e, f) automotive grade capacitors.

In all cases there was a capacitance drop by 2% to 10% during the initial periods of HTS that depending on temperature occurred after a few (at 150 and 175 °C) to ~100 hours (at 100 and 125 °C). This drop is related to moisture out diffusion and different levels of the decrease are due to different levels of the initial moisture content in the parts [12].

Based on analysis of variations of AC characteristics similar to those shown in Figure 1, 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 °C. Times to ESR failures were smaller compared to capacitance failures. For the case shown in Fig.3, the median TTF at 150 °C was ~550 hr for ESR and ~1100 hr for capacitance.

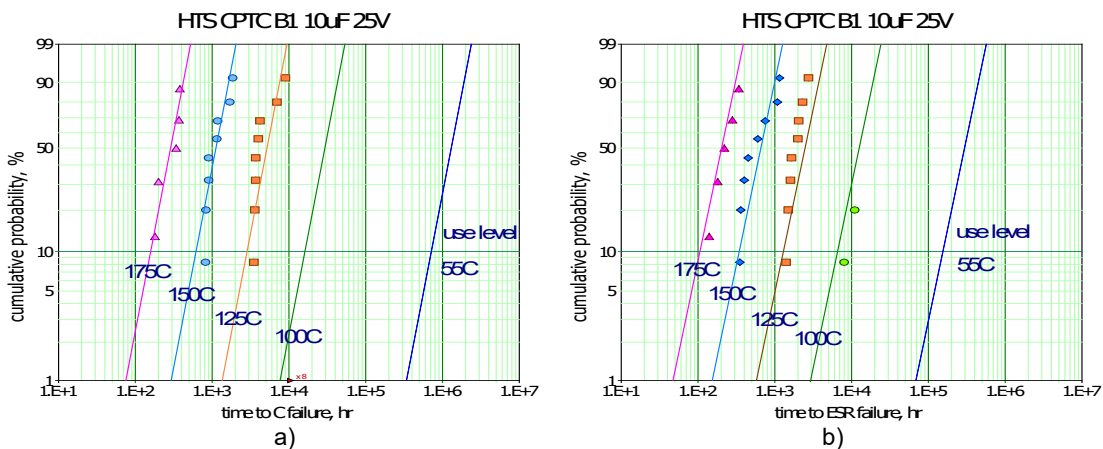


Figure 3. Distributions of times to failure for capacitance (a) and ESR (b) for B1 capacitors. Here and below marks indicate experimental data, solid lines are model's approximations, and dashed lines give prognosis for the use condition (55 °C). Red marks on the time axis indicate suspended points and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

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

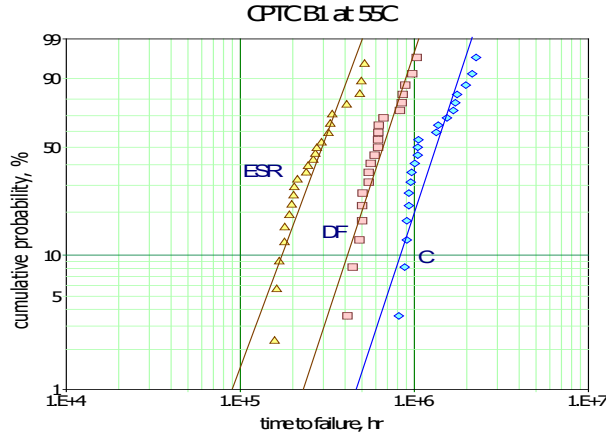


Figure. 4. Comparison of distributions of times to failure for C, DF, and ESR predicted for use temperature for B1 capacitors.

For most tested capacitors, TTF<sub>C</sub> and TTF<sub>DF</sub> values were substantially greater than TTF<sub>ESR</sub>. Table 2 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<sub>ESR</sub> was 2 times smaller than TTF<sub>DF</sub> and 3.5 times smaller than TTF<sub>C</sub>. Obviously, ESR is the most and capacitance is the least sensitive parameter to HTS degradation.

Table 2. Ratios of the median times of capacitance ( $R_C$ ) and DF ( $R_{DF}$ ) failures to the median time of 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

Analysis of ESR variations with time of storage shows that there is a certain delay time or incubation period,  $t_i$ , before the inception of ESR growth, and this time is decreasing with temperature. As an example, Figure 5 shows results of HTS testing at different temperatures for B2 type capacitors. The delay time decreases from ~8000 hours at 100 °C to ~2500, ~900, and ~100 hours at 125 °C, 150 °C, and 175 °C respectively. After  $t_i$ , ESR increases with time exponentially.

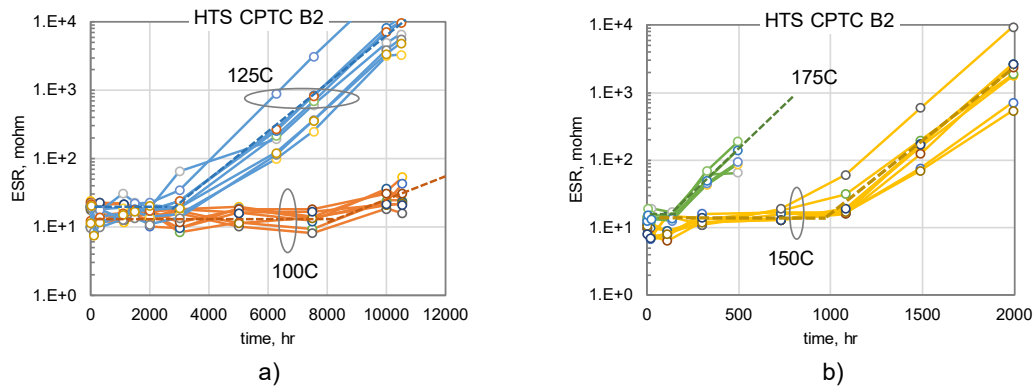


Figure 5. Results of HTS for B2 capacitors at 100 °C and 125 °C (a) and at 150 °C and 175 °C (b).

A larger proportion of ESR failures compared to failures of capacitance and DF allows for obtaining more data and more accurate approximations of  $TTF_{ESR}$  using the Weibull-Arrhenius model. Respectively, a more reliable prediction of parametric failures at operating conditions can be obtained. Examples of  $TTF_{ESR}$  distributions at different temperatures for two part types are shown in Figure 6.

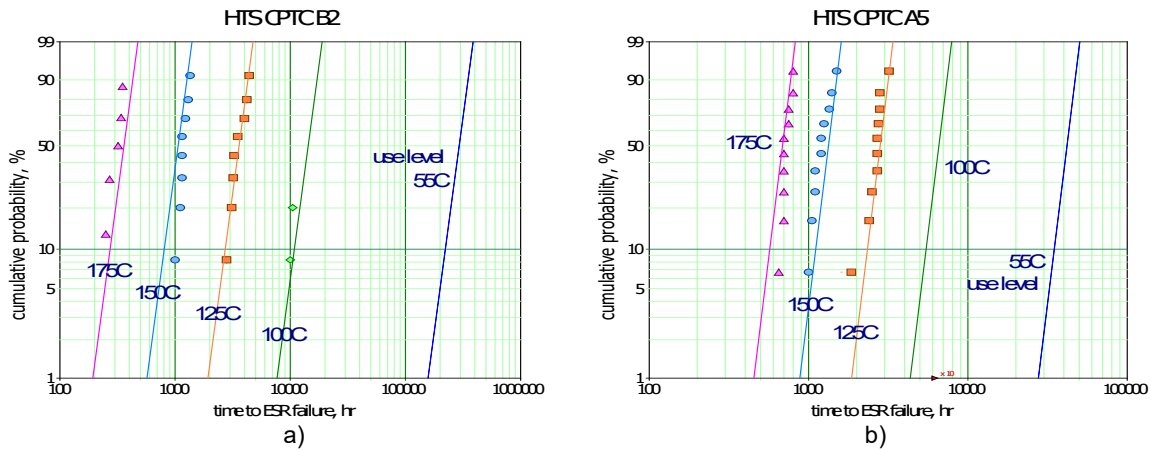


Figure 6. Distributions of times to ESR failure at different temperatures of storage for B2 (a) and A5 (b) capacitors.

Parameters of the distributions,  $\beta$  and  $E_a$ , for different groups of capacitors are displayed in Table 3. The slopes of distributions ( $\beta$ ) 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 °C,  $TTF_{125}$ , and the probabilities of failure,  $P_{125}$ , during a standard life or endurance testing that is typically carried out at 125 °C for 1000 hours. Reliability characteristics for several part types that did not have sufficient number of failures were estimated using average values of  $\beta$  and  $E_a$ .

Table 3. Results of modeling of ESR failures.

Part type	$\beta$	$E_A$ , eV	TTF <sub>50</sub> , yr.	TTF <sub>1</sub> , yr.	TTF <sub>125</sub> , khr	P <sub>125</sub> , %
A1	2.09	0.48	7.6	1.0	3.4	5.3
A2	3.47	0.46	6.2	1.8	3.1	1.3
A3	2.49	0.45	5.4	1.0	2.9	4.5
A4	4.43	0.38	3.9	1.5	3.1	0.4
A5	10.2	0.43	4.8	3.2	2.8	0.002
A6	3.31	0.53	33.2	2.9	3.4	1.2
A7	2.69	0.93	29.0	6.0	0.5	76.2
A8	2.15	0.64	32.3	4.5	>2	2
A9	-	-	>66*	>21*	>13*	<0.005
A10	6.6	0.61	16	10.2	3.2	0.01
B1	2.9	0.77	33.8	7.9	1.5	4.86
B2	6.8	0.71	33.3	17.9	3.5	0.01
B3	4	0.52	55.0	19.1	14	0.01
B4	3.39	0.52	19.2	5.5	6.5	0.11
C1	2.51	0.89	471.0	88.0	6.7	0.07
C2	3.11	0.75	76.4	19.5	6.1	0.22
C3	1.15	0.76	71.9	1.8	4.9	9.0
C4	1.65	0.77	73.7	5.7	5.9	4.5
C5	2.58	0.57	12.6	2.4	>2	0.03
C6	-	-	>66*	>21*	>13*	<0.005
C7	-	-	>66*	>21*	>13*	<0.005
C8	-	-	>66*	>21*	>13*	<0.005

\* Calculated at  $\beta = 3.7$  and  $E_a = 0.61$  eV. (avg 3.5, 0.62)

Different part types have substantially different susceptibility to parametric failures during long-term operation or 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.

On average, TTF<sub>50</sub> is 20.4, 35.3, and 112.9 years for manufacturers A, B, and C respectively. However, coefficients of variations are rather large, from 42% to 130%, and considering that even similar part types from the same vendor might be manufactured at different facilities using different materials and processes, the effects of vendor and part type require additional analysis.

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 high 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.

There is no correlation between TTF<sub>50</sub> at the use temperature and specified maximum operating temperature. The latter, is typically set at 105 °C for general-purpose and 125 °C for auto and COTS+ capacitors. However, there is no standard procedure for determining maximum operating temperatures of the parts, and in most cases, T<sub>max</sub> is selected based on successful results of life testing that is typically carried out for 1000 hours. The standard HTS tests currently are not sufficient to assure long-term stability of AC characteristics at high temperatures.

The median time to ESR failure at 125 °C,  $TTF_{125C}$ , is in the range from 500 to 6,700 hours, and the calculated probability of ESR failures during qualification testing at 125 °C for 1000 hours,  $P_{125}$ , varies from 0.002% to 76%. Considering a typical sample size for qualification testing of 22 samples and assuming the probability of failure is less than 0.1%, the probability that 1000 hours testing at 125 °C will have zero failures is greater than 97.8%. However, results in Table 3 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. 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 °C for 1000 hours is equivalent to 1.4 years of storage or operation at 55 °C if  $E_a = 0.4$  eV, and to more than 17 years if  $E_a = 0.8$  eV.

## Failure analysis

Cross-sectioning of several samples after 1000 hours of storage at 150 °C (see Figure 7) clearly shows discolorations in the molding compound (MC) that were caused by thermo-oxidative degradation of epoxy. Thin layers of brownish color along the surface of the case and the lead frame (LF) interface with MC indicate a diffusion-limited oxidation of MC. A sample shown in Fig. 7a did not fail, whereas samples in Fig. 7b failed marginally at 200 mohm and another sample (Fig. 7c) failed catastrophically at 2 ohm. No discoloration around the pellet is observed in Fig.7a, but it can be seen around the whole surface of the slug in Fig. 7c, whereas only a part of the surface close to the cathode portion of the lead frame had some discoloration in Fig. 7b. A similar difference between the level of discoloration around the slug that correlated with the level of ESR degradation was observed in other part types. In all cases a less severe degradation after HTS corresponded to the absence of discoloration in molding compound at the internal areas around the slug. Obviously, these areas of discoloration in MC indicate the path for oxygen diffusion towards the conductive polymer on the surface and inside tantalum slugs.

Several samples that had the worst degradation in the group were found to have cracks in the package (see Fig.7 e-f). A sample that had 440 mohm after 2000 hours of testing had a crack on a side of the package as shown in Fig. 7e. Another sample (Fig. 7g) that failed catastrophically, at 2.67 ohm after 1000 hr had a crack under the anode terminal. Similarly, a sample from Gr. A7 that had a crack at the bottom of the package failed after 300 hr and had 2.4 ohm after 1000 hr of HTS at 150 °C (Fig. 7f).

Discoloration is obvious for CPTCs with light yellow MCs, and are much less obvious for parts encapsulated with black MCs. However, color analysis software allows for mapping of discolored areas in these parts as well (see Fig. 7d). Results indicate similar discoloration and degradation processes in all types of MCs used for CPTCs.

Discoloration of MC along the cracks shows that cracks provide a direct path for oxygen penetration and accelerate degradation processes substantially. Contrary to MnO<sub>2</sub> capacitors, where cracks can facilitate some delamination, but generally can be considered as cosmetic defects, cracking of the cases in polymer capacitors poses a serious reliability risk. Improvements in quality of packaging and a thorough control over the encapsulation process have been used by manufacturers to assure stability of automotive grade capacitors under environmental stresses [1].

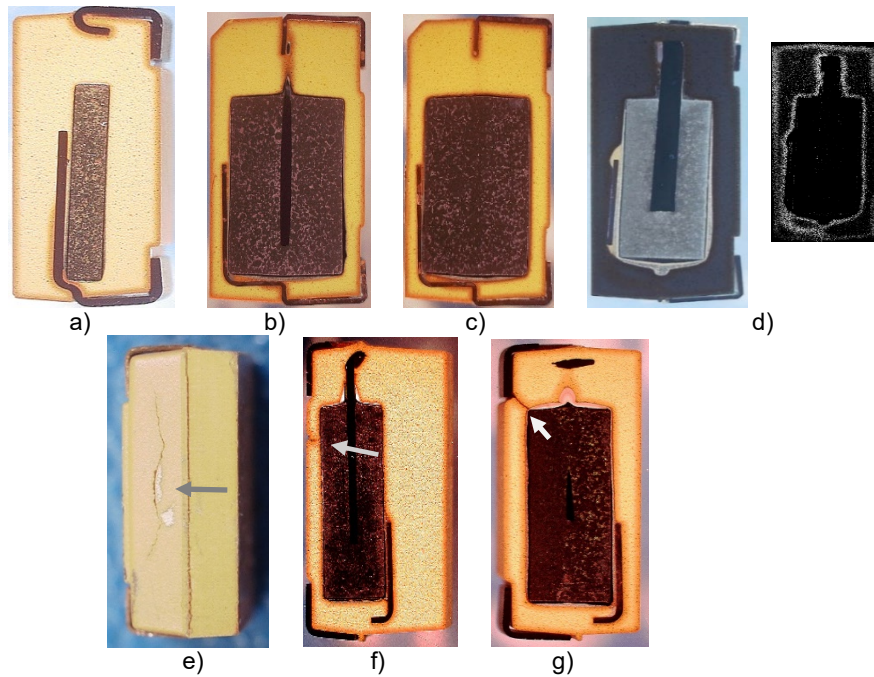


Figure 7. Cross-sections of capacitors after 1000 hours at 150 °C showing discoloration of molding compound. Examples of discoloration at the surface and along LF/MC interfaces in CPTCs with yellow (a - c) and black (d) molding compounds after HTS. An insert in (d) shows mapping of the discolored areas. Figures e-f show examples of parts with cracks in the package.

It is known that copper has a catalytic effect on degradation of polymer materials in general, and on epoxy resins in particular [13]. In the presence of a copper substrate, the rate of degradation and the relevant activation energy for epoxy adhesives decreases substantially. It is possible that the presence of copper LF facilitates thermo-oxidative decomposition of epoxy MCs and delamination thus enhancing penetration of oxygen to the slug. Using LF based on copper alloys or materials having no copper, e.g. alloy 42, might improve stability of ESR for high-temperature applications.

Degradation of ESR during HTS can be explained by two processes [9]: increasing of delamination between different cathode layers and rising of the intrinsic resistivity of polymer cathode materials. Delamination between different layers of conductive polymers, and especially between carbon layer and polymer are often observed even in virgin CPTCs, whereas vertical cracks are typical for parts after HTS (see Figure 8).

Both types of cracks are unlikely to cause complete separation between the layers and increase ESR substantially. Due to a high conductivity of PEDOT:PSS polymers, even a relatively small contact area should be sufficient to assure low resistance of the interconnects [11]. The major mechanism of ESR degradation is thermo-oxidative processes in PEDOT:PSS compositions.

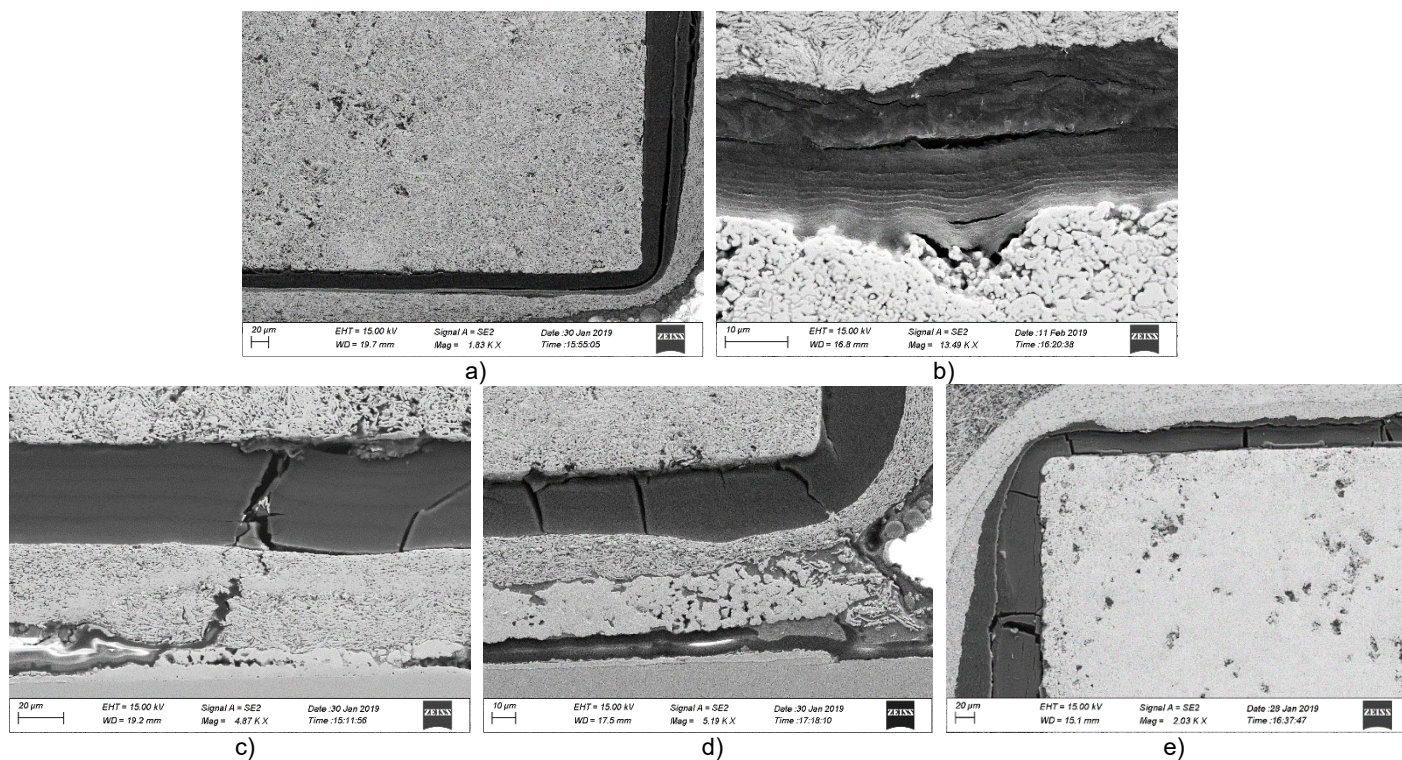


Figure 8. SEM views of cross-sectioned virgin (a, b) and post-HTS (c-e) samples. Note the presence of vertical cracks in samples after HTS.

Examinations of pores in the pellet revealed extremely thin (dozens of nanometers) cathode layers (see Figure 9). A certain proportion of the surface inside the pores appears not covered by PEDOT:PSS. It is possible that these areas are responsible for a significant variation of capacitance with moisture level. Some cracking and grainy structure of the in-pores coating was observed before and after HTS. Apparently, large vertical cracks occur mostly in the cathode shell layers.

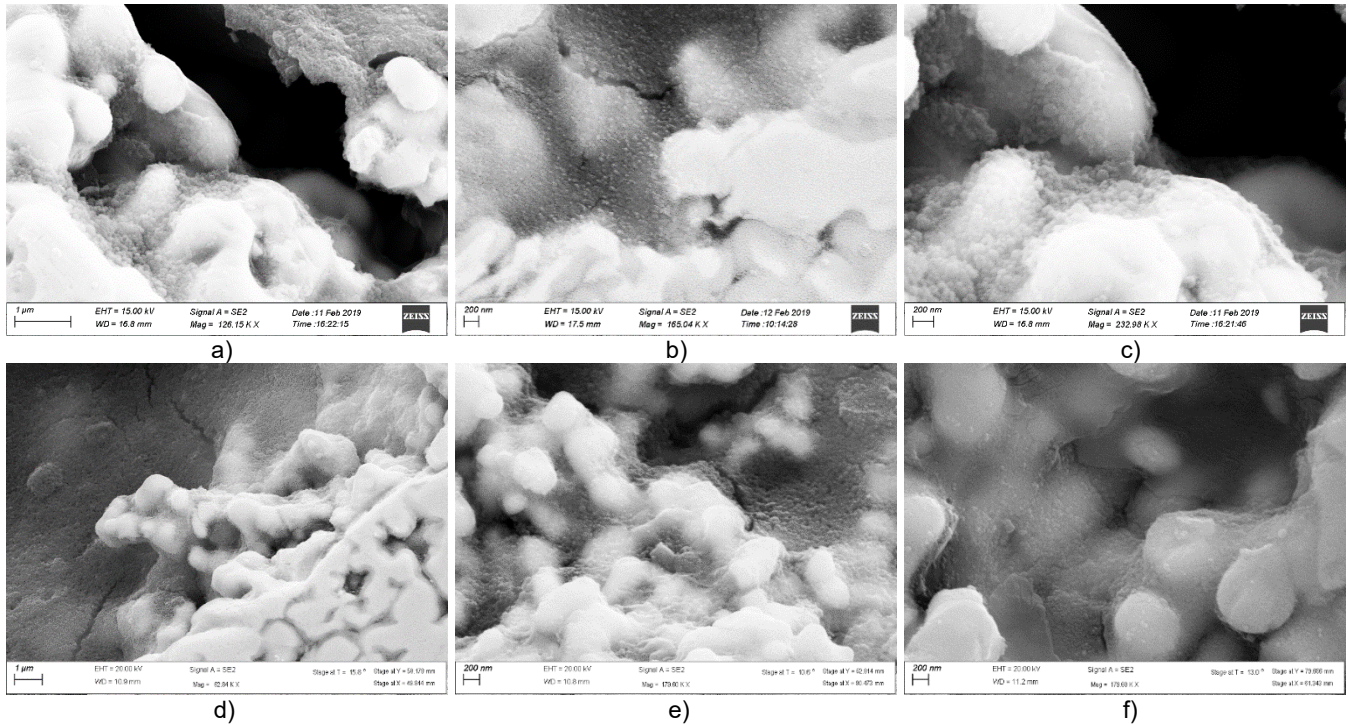


Figure 9. Morphology of PEDOT:PSS cathodes in pores of tantalum pellets for various virgin (a-c) and post-HTS (d-f) capacitors.

The presence of liquid polymer oozed from the shell cathode coating was observed in various types of CPTCs after cross-sectioning (see Figure 10). In some cases, this polymer dried out forming a thin and fragile layer on the surface of the shell. These liquids are likely not due to HTS testing because they were also observed in virgin samples. The significance of the presence of small amounts of liquid polymers in the cathode layers of CPTCs is not clear, and its effect on reliability of the parts requires additional analysis.

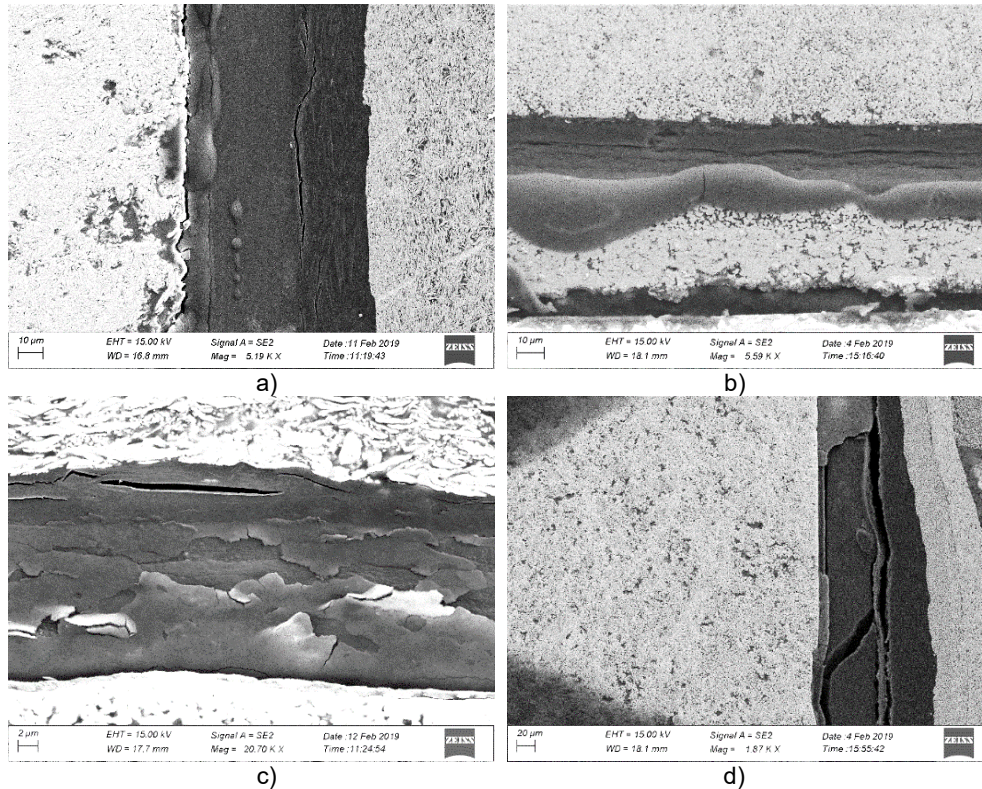


Figure 10. Examples of liquid polymer oozed from the shell cathode areas after cross-sectioning for virgin C1 (a) and B2 (b) post-HTS150 (c, d) capacitors.

Several anomalies were observed during SEM examinations of cross-sectioned samples. These include formation of silver (Figure 11), Sulphur (Figure 12), and calcium (Figure 13) containing crystals that apparently were formed by reactions with water during cross-sectioning and the following exposure to room humidity. Similar formations might happen in non-cross-sectioned parts containing cracks. Moisture accumulated in the parts stored for a long time in environments containing moisture might facilitate formation of silver-containing compositions and cause increased leakage currents and local scintillation breakdowns. However, due to a small size, these crystals most likely will burn-out after voltage applications and are unlikely to cause catastrophic failures.

The Sulfur containing crystals were formed on 6.3V capacitors that employ typically in-situ polymerization cathode layers (see Figure 12). This type of crystals might be specific for the in-situ polymerized PEDOT compositions. Calcium in compositions shown in Figure 13 most likely originates from the fabrication process of PEDOT:PSS, and Sulphur is a part of the polymer composition. Calcium sulfate ( $\text{CaSO}_4$ ) crystals are likely formed in the presence of moisture and might be specific to a certain type of capacitors.

The significance of various types of crystals on the surface of PEDOT:PSS and their effect on performance of the parts needs more analysis. Apparently, their existence indicates that conductive polymers used in CPTCs are chemically active and can form different types of compositions in the presence of moisture.

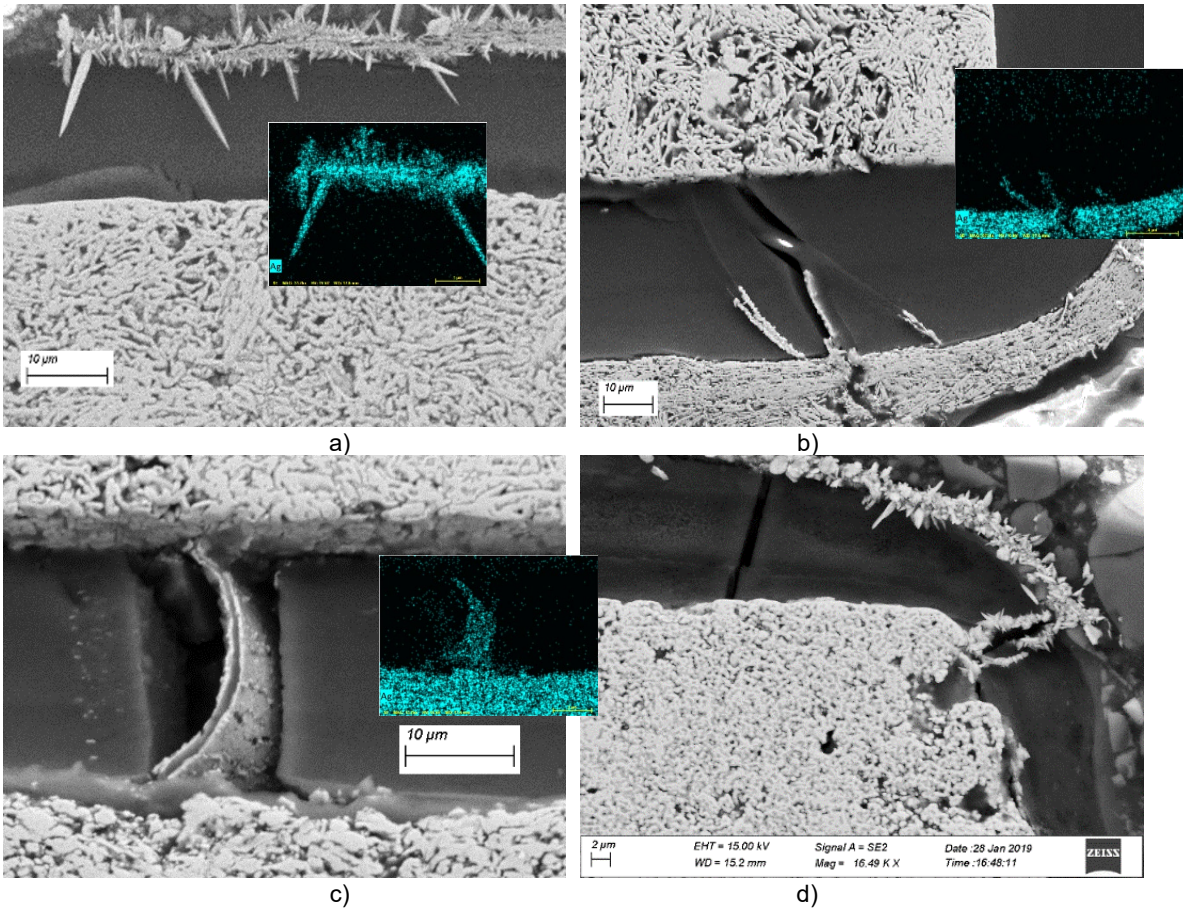


Figure 11. Examples of Ag-containing crystals on silver epoxy in virgin (a) and post-HTS (b, c) C5 capacitors. Figure (d) shows similar formations on post-HTS B1 capacitors.

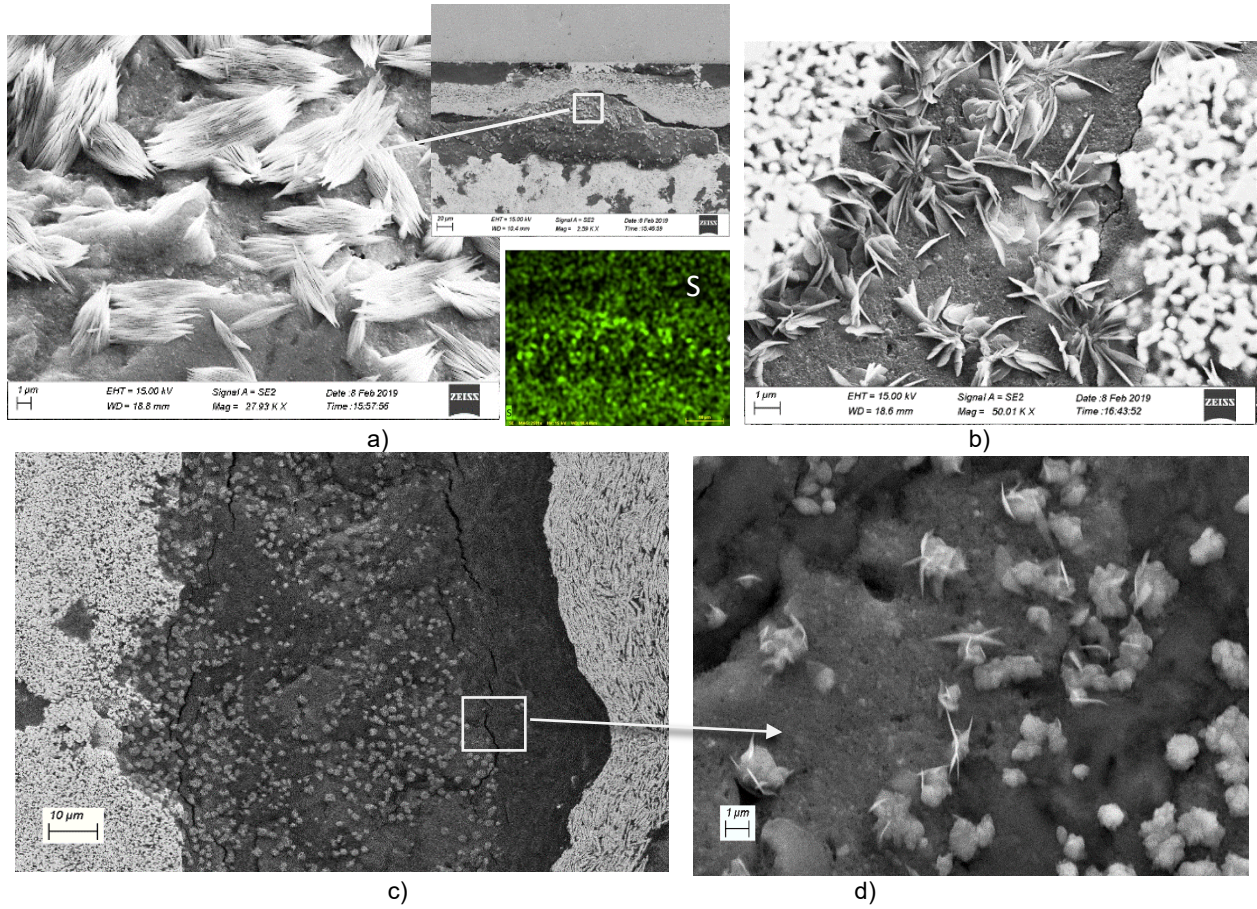


Figure 12. Examples of Sulfur containing compositions on the surface of conductive cathodes in C4 (a, b) capacitors after HTS150 and in virgin C8 (c, d) capacitors.

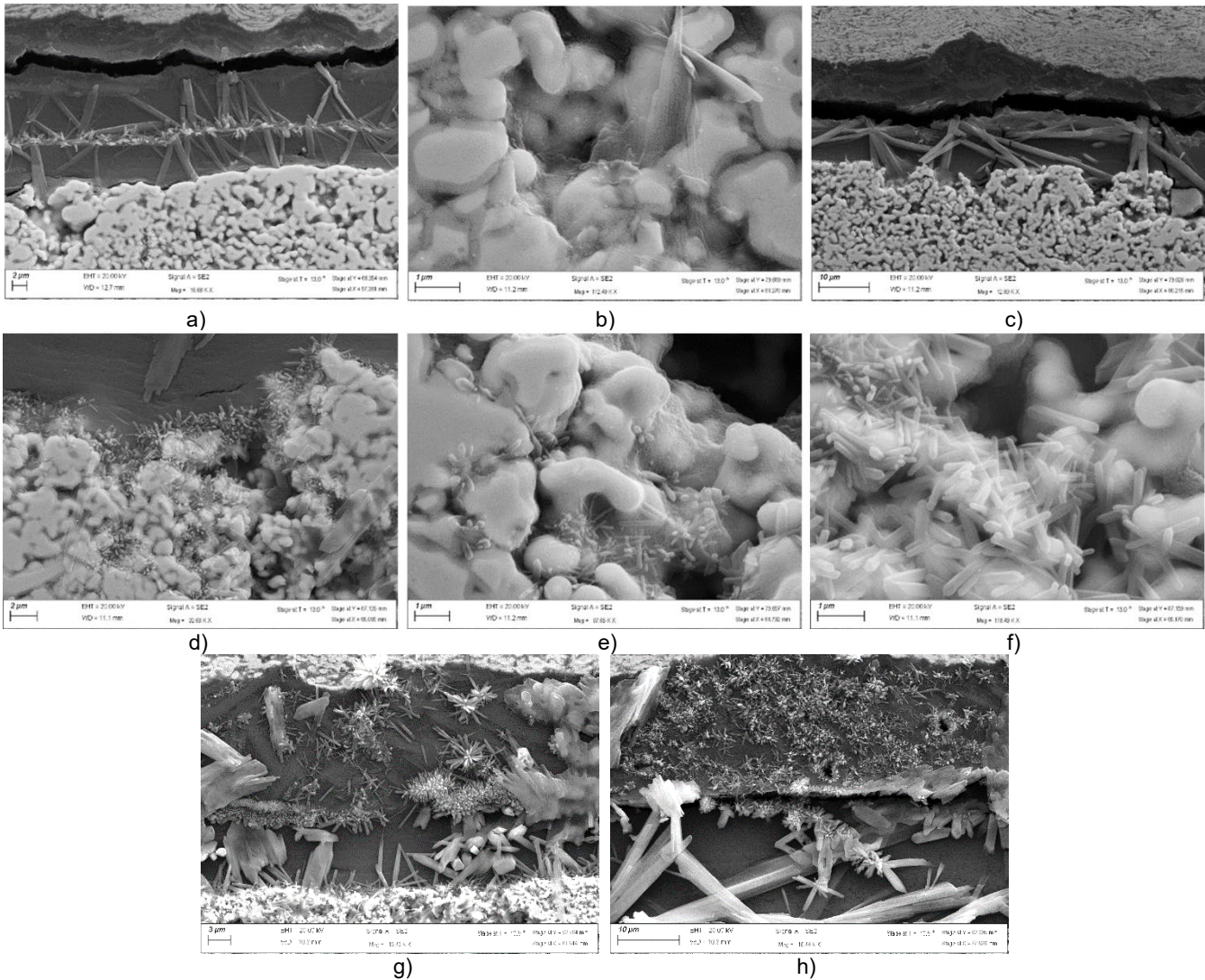


Figure 13. Examples of calcium sulfate ( $\text{CaSO}_4$ ) crystals formed on the surface of conductive polymer in A1 (top row) and A3 (second and third rows) capacitors after HTS150.

## Discussion

Degradation of capacitance and dissipation factor during HTS is due to a substantial increase of *ESR*. Figure 14 shows typical variations of *C* and *ESR* with frequency for CPTCs in the process of aging at 150 °C. During HTS, 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 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 [14].

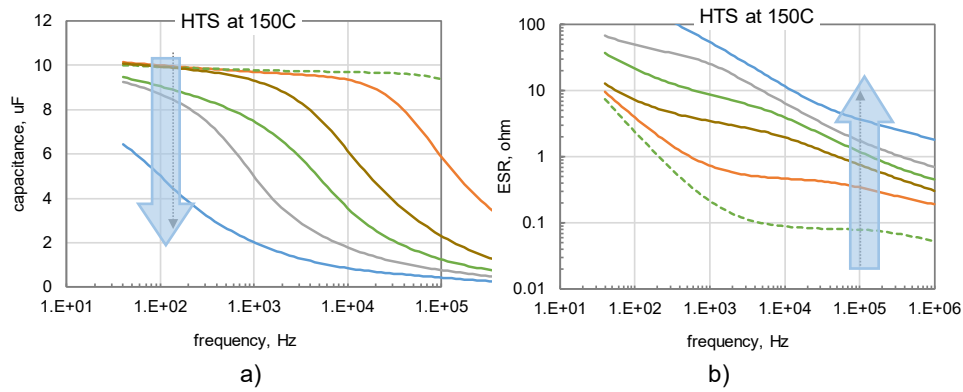


Figure 14. Frequency dependencies of capacitance (a) and ESR (b) for a 10  $\mu$ F CPTC during HTS at 150  $^{\circ}$ C. Dashed lines indicate initial characteristics, and arrows indicate degradation of characteristics with time at the specified frequencies (120 Hz for capacitance and 100 kHz for *ESR*).

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 [15]. Thermal and thermo-oxidative degradation kinetics of poly(3-hexyl thiophene) (P3HT) conducting polymers in nitrogen and air medium was investigated in [16]. The activation energy of degradation of P3HT was  $\sim 2$  eV in nitrogen, while in air  $E_a$  varied with the extent of the thermo-oxidative conversion from  $\sim 0.5$  eV to 1.5 eV. Direct measurements of the sheet resistance for in-situ polymerization PEDOT films in [17] showed that the resistance increased from 64 ohm to more than  $10^6$  ohm after 16 hours of storage in air at 175  $^{\circ}$ 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.

The structure of PEDOT:PSS polymers can be described as conductive PEDOT-rich grains that are enclosed in insulating PSS-rich shells (conductive grains in insulative matrix). The mechanism of conductivity of PEDOT:PSS polymers is a hopping transport of carriers between PEDOT conductive grains that are electrostatically attached to insulating PSS chains [18, 19]. The charge transport between segments and grains requires thermal activation over certain potential barriers. Aging at high temperatures increases distances between the grains and potential barriers thus reducing the conductivity of cathode layers and increasing *ESR*. A similar explanation of degradation of conductivity of polypyrrole (PPy) polymers in the process of ageing was given in [20]. The inter-grain separation was found to increase from 3 to 30  $\text{\AA}$  after one month of aging at 120  $^{\circ}$ C. The evolution of conductivity with time was described by a stretched exponential function. According to this mechanism, even relatively minor changes in the structure of conductive polymers during HTS can result in a substantial rise of *ESR*.

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.

*ESR* failures can be model based on analysis of distributions of times to failure (TTF), but this approach requires extended testing until a sufficient number of failures occurs. At temperatures close to operational, a very long time might be necessary to precipitate failures. Considering specifics of *ESR* variations with time, it is possible to simulate *ESR* degradation and predict possible *ESR* values at the end of the mission before a formal failure happens.

In a general case, degradation of ESR during storage can be described as an exponential growth with time that begins after an incubation period  $t_i$ . The rate of ESR degradation can be described using a characteristic time  $\tau$ .

$$\left. \begin{aligned} ESR &= ESR_0 \times \exp\left(\frac{t-t_i}{\tau}\right) && \text{at } t > t_i \\ ESR &= ESR_0 && \text{at } t \leq t_i \end{aligned} \right\}, \quad (2)$$

where  $ESR_0$  is the initial value of  $ESR$ .

Both parameters,  $\tau$  and  $t_i$ , are assumed to reduce exponentially with temperature and their distributions can be approximated with the Weibull-Arrhenius models. The major parameters of these models are activation energies, scale factors, and slopes of the distributions:

$$P(\tau) = 1 - \exp\left[-\left(\frac{\tau}{\eta_\tau}\right)^{\beta_\tau}\right], \quad \eta_\tau = \eta_{\tau 0} \times \exp\left(\frac{E_{a_\tau}}{kT}\right), \quad (3)$$

$$P(t_i) = 1 - \exp\left[-\left(\frac{t_i}{\eta_i}\right)^{\beta_i}\right], \quad \eta_i = \eta_{i 0} \times \exp\left(\frac{E_{a_i}}{kT}\right), \quad (4)$$

where  $\eta_\tau$  and  $\eta_i$  are the scale parameters,  $\beta_\tau$  and  $\beta_i$  are the slopes of the relevant distributions, and  $\eta_{\tau 0}$  and  $\eta_{i 0}$  are constants.

## Qualification Testing

The focus of the existing quality assurance system for MnO<sub>2</sub> capacitors described in MIL-PRF-55365 is mostly on elimination of infant mortality (IM) failures and does not address parametric degradation of AC characteristics sufficiently. In particular, there is no requirements for HTS endurance testing. However, due to the intrinsic degradation of conductive polymers, HTS testing is necessary to assure that the time of inception of ESR failures at operating temperatures is greater than the intended mission time for the system. A common standard for HTS testing is 1000 hours at 125 °C as it is described in AEC-Q200 requirements for automotive industry.

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 °C without failures (ESR remains below  $3 \times ESR_{\text{limit}}$ ) would be equivalent to more than one year of storage or operation at 55 °C if  $E_a = 0.4$  eV, and to more than 20 years at  $E_a = 0.8$  eV.

Considering that these failures are due to wear-out processes, a relatively small number of samples would be sufficient to assure that the time to failure inception is greater than the mission time. However, the presence of defects in the case (cracks or LF/MC delamination) or their development with time of storage can reduce this time substantially. To assure low probability of  $ESR$  failures for terrestrial applications a relatively large sample size is necessary. Considering uncertainties in stability of the materials and production processes during manufacturing of CPTCs, all lots should be tested using 77 samples (as per AEC-Q200) to qualify a specific lot of capacitors for hi-rel applications. Note that testing of 77 samples with no failures can assure that the probability of failure is likely below 1.5% which might be not sufficient for some hi-rel applications. Additional assurance can be achieved by a thorough visual examination during screening of the parts and after their soldering onto the boards.

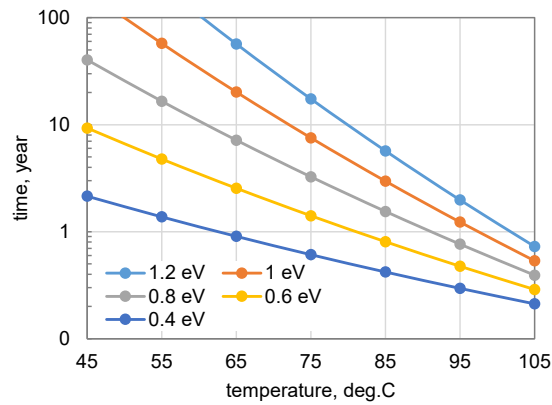


Figure 15. Time in years during storage or operation in the range of temperatures from 45 °C to 105 °C that is equivalent to 1000 hours testing at 125 °C.

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 [21]. 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 N<sub>2</sub> to 0.7 eV in air for PE, from ~2.0 eV in N<sub>2</sub> to 0.87 eV in air for PP, and from ~2.1 eV in N<sub>2</sub> to 1.1 eV in air for PS [22].

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 [15]. Thermal and thermo-oxidative degradation kinetics of poly(3-hexyl thiophene) (P3HT) conducting polymers in nitrogen and air medium was investigated in [16]. 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 [9] showed that 2000 hours storage at 100 °C 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 [17] 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.

## 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 °C to 175 °C 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,  $E_a = 0.62 \pm 0.17$  eV.
3. Median times to failure at operating conditions (55 °C) for different part types vary from 3.9 to 471 year, but the times to failure inception (1% of failures) are much less, from 1 to 88 years. Successful results of qualification testing at 125 °C 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 1000hr testing at 125 °C 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 °C and 4 types remained stable for 4000 hours at 150 °C. The automotive grade polymer capacitors should be the prime source for selecting components for space applications.
5. Equivalent series resistances of CPTCs are increasing exponentially with time of storage after a certain incubation period. This increase is due to thermo-oxidative processes in conductive polymers that result in structural changes and increase of energy barriers for the transport of charge carriers along the cathode layer. The major path for oxygen penetration to the tantalum slug is along the molding compound/lead-frame interfaces or through the cracks in the package. The incubation period corresponds to the time necessary to form delamination or cracks in the case.

## References

- [1] J. Young, "Polymer Tantalum Capacitors for Automotive Applications," in *CARTS International*, Santa Clara, CA, 2014, March 31- April 3, pp. 297-311.
- [2] J. Lewis. (2013). *Considerations for Polymer Capacitors in Extreme Environments*. Available: [www.kemet.com/ExtremePolymerPaper](http://www.kemet.com/ExtremePolymerPaper)
- [3] S. Zedníček, J. Petržílek, P. Vanšura, M. Weaver, and C. Reynolds. Conductive Polymer Capacitors. Basic Guidelines. *AVX Technical information*. 2015, Available: <http://www.avx.com/docs/techinfo/PolymerGuidelines.pdf>
- [4] J. Petržílek, M. Biler, and T. Zednicek, "Hermetically Sealed Conductive Polymer Tantalum Capacitors," in *CARTS International*, Santa Clara, CA, 2014, March 31- April 3, pp. 287-292.
- [5] J. Ye, C. Stolarski, M. Yuan, and C. MotaCaetano. (2016). *Conductive polymer based tantalum capacitors for automotive applications*, KEMET. Available: <https://ec.kemet.com/knowledge/detailed-data-for-automotive-polymer-capacitors>
- [6] M. Cozzolino, "Evaluation of Polymer Counter-Electrode Tantalum Capacitors for High Reliability Airborne Applications," in *CARTS International*, Las Vegas, NV, 2012, March 26-29, pp. 13-22.
- [7] Y. P. Wen and J. K. Xu, "Scientific Importance of Water-Processable PEDOT-PSS and Preparation, Challenge and New Application in Sensors of Its Film Electrode: A Review," *Journal of Polymer Science Part a-Polymer Chemistry*, vol. 55, pp. 1121-1150, Apr 2017
- [8] M. Giannouli, V. M. Drakonakis, A. Savva, P. Eleftheriou, G. Florides, and S. A. Choulis, "Methods for Improving the Lifetime Performance of Organic Photovoltaics with Low-Costing Encapsulation," *ChemPhysChem Reviews*, vol. 16, pp. 1134-1154, 2015
- [9] A. Teverovsky, "Evaluation of 10V chip polymer tantalum capacitors for space applications," presented at the ESA 2nd International Symposium - Space Passive Component Days, Noordwijk, The Netherlands, 2016. <https://ntrs.nasa.gov/archive/nasa/casi.ntrs.nasa.gov/20160010399.pdf>
- [10] C. MotaCaetano, "Polymer Tantalum Capacitors Continue to Toughen Up to Meet Automotive Demands," *KEMET Engineering Center*, June 2019 <https://ec.kemet.com/polymer-tantalum-capacitors-continue-to-toughen-up-to-meet-automotive-demands>

- [11] A. Teverovsky, "Degradation and ESR Failures in MnO<sub>2</sub> Chip Tantalum Capacitors," in *Components for Military and Space Electronics, CMSE'17*, Los Angeles, CA, 2017, April 11-13. <https://ntrs.nasa.gov/archive/nasa/casi.ntrs.nasa.gov/20170003492.pdf>
- [12] A. Teverovsky, "Effect of Moisture on AC Characteristics of Chip Polymer Tantalum Capacitors," *IEEE Transactions on Components, Packaging and Manufacturing Technology*, vol. 9, pp. 2282-2289, 2019
- [13] S. G. Hong, "The thermal-oxidative degradation of an epoxy adhesive on metal substrates -XPS and RAIR analyses," *Polymer Degradation and Stability*, vol. 48, pp. 211-218, 1995 <Go to ISI>://WOS:A1995RM94700002
- [14] A. Teverovsky, "Performance and reliability of solid tantalum capacitors at cryogenic conditions," in *7th International workshop on low temperature electronics, WOLTE-7*, ESTEC, Noordwijk, The Netherlands, 2006, pp. 165-172.
- [15] V. Singh, S. Arora, M. Arora, V. Sharma, and R. P. Tandon, "Characterization of doped PEDOT: PSS and its influence on the performance and degradation of organic solar cells," *Semiconductor Science and Technology*, vol. 29, p. 045020, 2014 <http://stacks.iop.org/0268-1242/29/i=4/a=045020>
- [16] R. Ramani, J. Srivastava, and S. Alam, "Application of model-free kinetics to the thermal and thermo-oxidative degradation of poly(3-hexyl thiophene)," *Thermochimica Acta*, vol. 499, pp. 34-39, 2010/02/20/ 2010 <http://www.sciencedirect.com/science/article/pii/S0040603109003864>
- [17] Y. Jin, Q. Chen, and P. Lessner, "Thermal Stability Investigation of PEDOT Films from Chemical Oxidation and Prepolymerized Dispersion," *Electrochemistry*, vol. 81, pp. 801-803, 2013
- [18] E. Vitoratos, S. Sakkopoulos, E. Dalas, N. Paliatsas, D. Karageorgopoulos, F. Petraki, *et al.*, "Thermal degradation mechanisms of PEDOT:PSS," *Organic Electronics*, vol. 10, pp. 61-66, 2009 <http://www.sciencedirect.com/science/article/pii/S1566119908001791>
- [19] E. Vitoratos, S. Sakkopoulos, N. Paliatsas, K. Emmanouil, and S. A. Choulis, "Conductivity Degradation Study of PEDOT: PSS Films under Heat Treatment in Helium and Atmospheric Air," *Open Journal of Organic Polymer Materials*, vol. 2, pp. 7-11, January 2012
- [20] B. Sixou, N. Mermilliod, and J. P. Travers, "Aging effects on the transport properties in conducting polymer polypyrrole," *Physical Review B*, vol. 53, pp. 4509-4521, 02/15/ 1996 <https://link.aps.org/doi/10.1103/PhysRevB.53.4509>
- [21] P. Gijssman, "Review on the thermo-oxidative degradation of polymers during processing and in service," in *e-Polymers* vol. 8, 2008, p. 727, <http://www.degruyter.com/view/j/epoly.2008.8.issue-1/epoly.2008.8.1.727/epoly.2008.8.1.727.xml>.
- [22] J. D. Peterson, S. Vyazovkin, and C. A. Wight, "Kinetics of the Thermal and Thermo-Oxidative Degradation of Polystyrene, Polyethylene and Poly(propylene)," *Macromolecular Chemistry and Physics*, vol. 202, pp. 775-784, 2001 [http://dx.doi.org/10.1002/1521-3935\(20010301\)202:6<775::AID-MACP775>3.0.CO;2-G](http://dx.doi.org/10.1002/1521-3935(20010301)202:6<775::AID-MACP775>3.0.CO;2-G)





