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

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List of Acronyms

AC	alternating current	ESR	equivalent series resistance
C	capacitance	HT	high temperature
CPTC	chip polymer tantalum capacitor	HTS	high temperature storage
DCL	direct current leakage	TTF	time to failure
DF	dissipation factor		

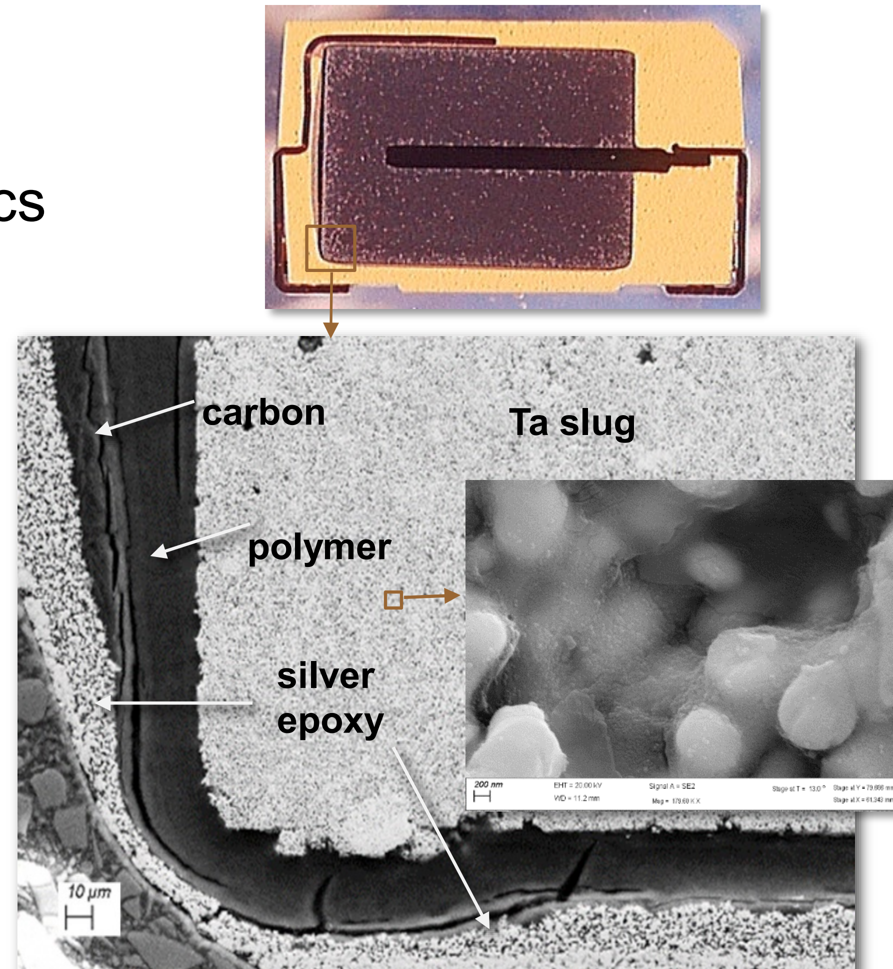
Abstract

Replacement of MnO_2 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 parameter to degradation. 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 increase of the resistivity with time of aging. 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.

Outline

- Introduction
- Experiment
- Results of HTS testing
- Sensitivity of AC characteristics to HTS
- Specifics of ESR degradation
- Degradation in different types of CPTCs
- Significance of endurance testing
- Conclusion

Polymer Tantalum capacitors



Introduction

- Contrary to MnO_2 capacitors, AC characteristics in CPTCs can degrade substantially with time at high temperatures.
- Currently, high-quality CPTCs (auto) require HTS testing at 125 ºC for 1000 hours with relaxed post-testing limits: $ESR \le (2 \div 5 \times ESR_{init\ limit})$.
- There are no requirements for military grade MnO_2 tantalum capacitors and in the draft "MIL-PRF-POLY".
- The existing testing does not answer questions about stability of the parts at usage conditions.
- There is a need for a model to predict degradation of CPTCs to assess the end-of-life characteristics.

✓ To develop reliability models, different types of CPTCs from three manufacturers have been tested periodically during long-term storage at temperatures from 100 ºC to 175 ºC.

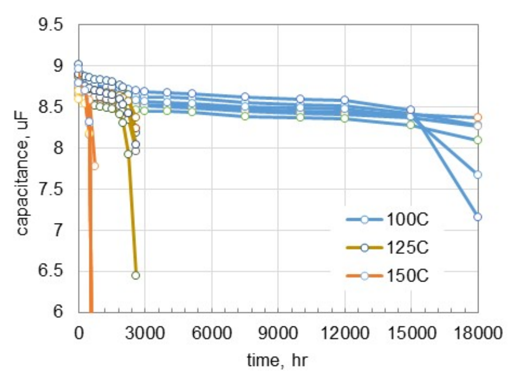
Experiment

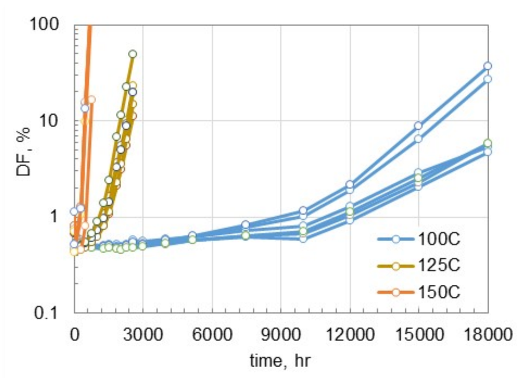
- Ten types of Mfr.A, four types of Mfr.B, and eight types of Mfr.C capacitors have been used in this study.
- Five types of the parts were general purpose, 10 types were manufactured for the automotive industry per AEC-Q200 requirements, and 7 types were hi-rel or COTS+ capacitors.
- Each group had 5 to 20 samples in each (typically 10 samples).
- The parts have been stored at 100 ºC, 125 ºC, 150 ºC, and 175 ºC for several thousand hours, and their AC characteristics (C, DF, and ESR) were measured periodically.
- Failure criteria: $C \leq 0.8 \times C_{nom}$, $DF < DF_{limit}$, $ESR > 3 \times ESR_{limit}$
- TTF distributions were approximated with a Weibull-Arrhenius model.

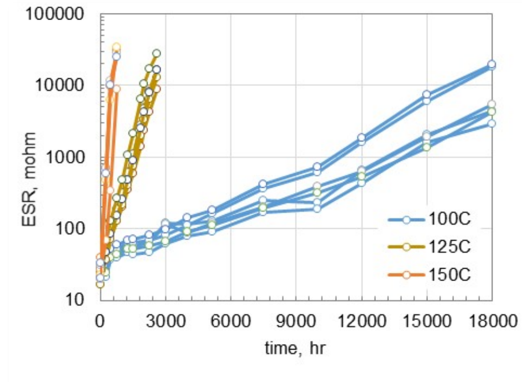
$$P(t) = 1 - \exp\left[-\left(\frac{t}{\eta}\right)^{\beta}\right] \qquad \eta = C_0 \times \exp\left(E_a / kT\right)$$

Examples of Degradation of AC Characteristics for General Purpose CPTCs

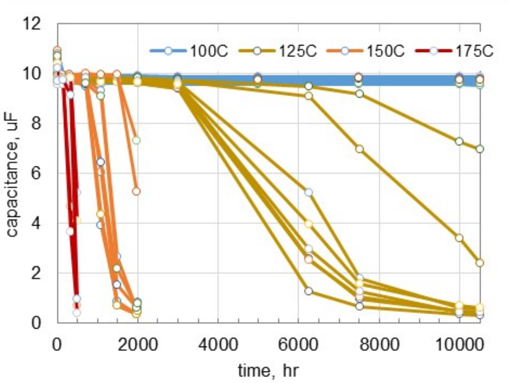
Type A7
10µF
100V

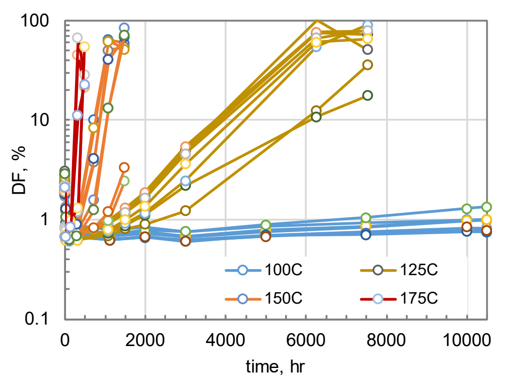


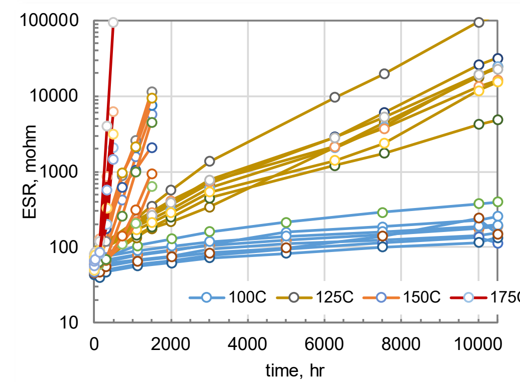




Type B1
10µF
25V

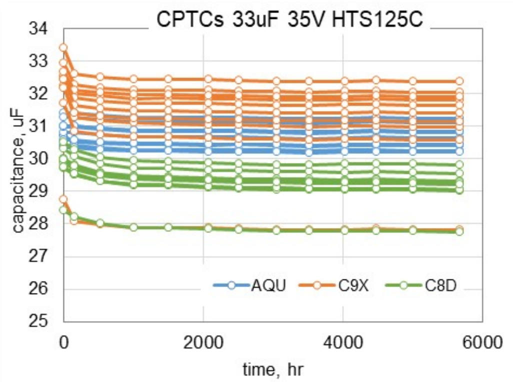


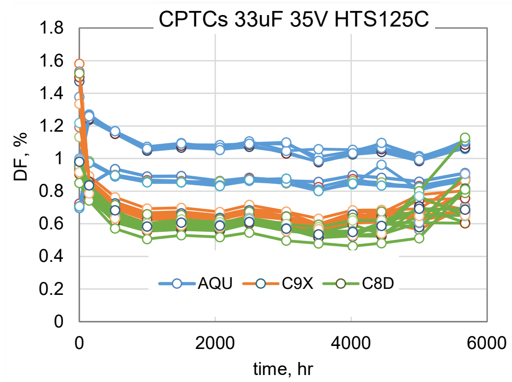


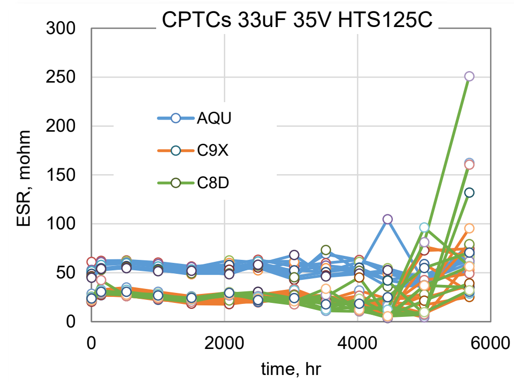


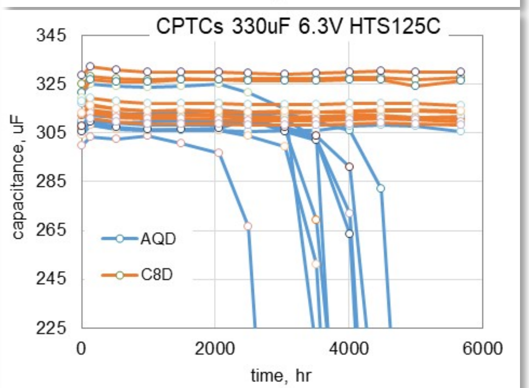
- ✓ Temperature has a strong effect on the rate of degradation.
- ✓ ESR rises with time, exponentially increasing by 100 and 1000 times.
- ✓ In the general-purpose capacitors a significant degradation might occur already after 100+ hours of storage at 125 ºC.

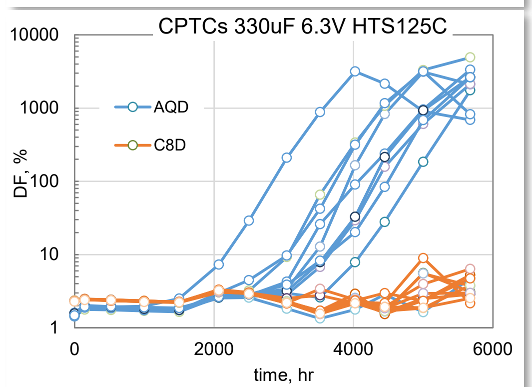
Examples of Degradation of AC Characteristics for Automotive Grade CPTCs

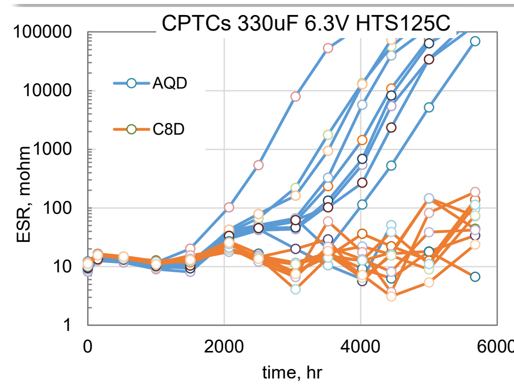








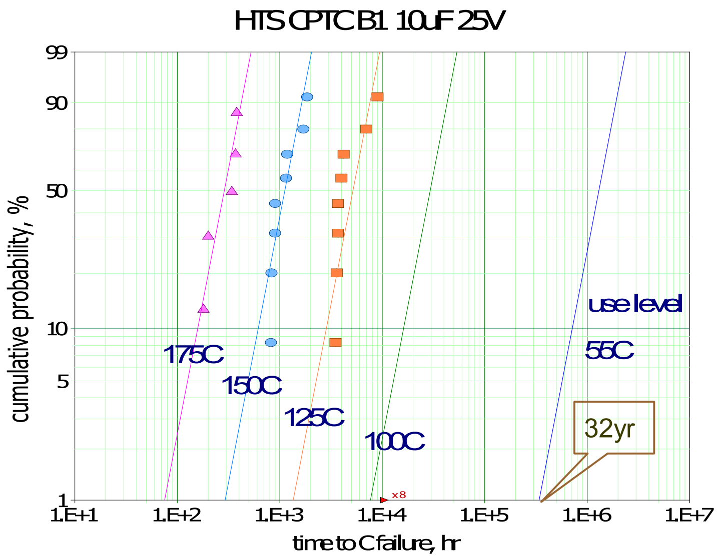


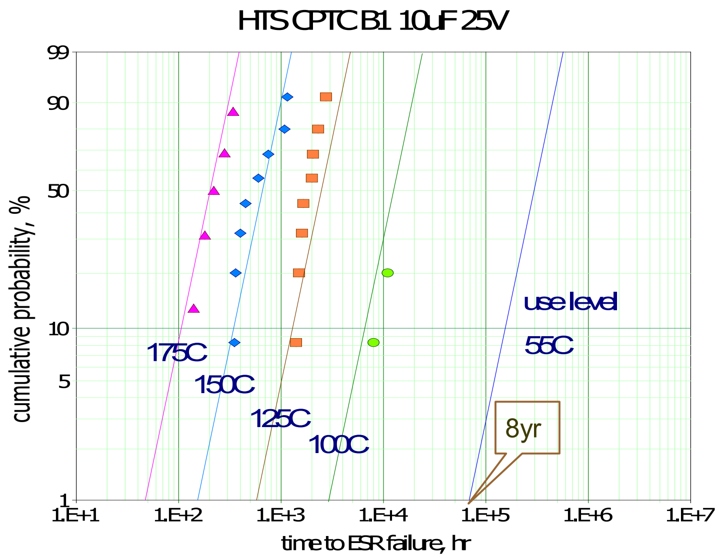


- ✓ All parts passed the required 1000hr testing at 125ºC.
- ✓ One part type degraded catastrophically after 2000hr.
- ✓ Four out of 5 automotive grade capacitors withstood 5200 hours at 125ºC.
- ✓ Capacitors that were stable at 125 ºC also withstood storage at 150ºC for 4000hr.

TTF Distributions

Examples of TTF distributions for C and ESR during HTS at different temperatures

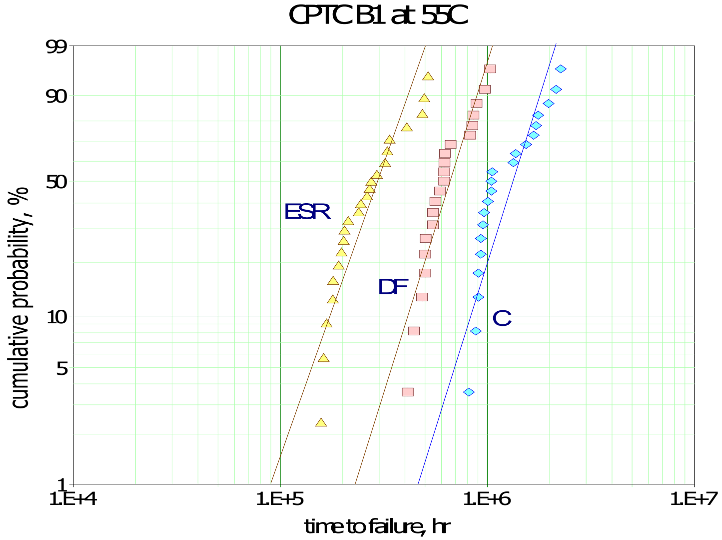




- ✓ Experimental data follow the Weibull-Arrhenius model.
- ✓ Similar slopes indicate same mechanism of degradation.
- ✓ The model allows for prediction of the failure inception time, TTF_i, and the probability of failure at operating conditions.

Sensitivity of AC Characteristics to Aging

Comparison of TTF distributions for C, DF, and ESR at the use temperature



Ratios of median times

$R_C = TTF_C/TTF_{ESR}$ and $R_{DF} = TTF_{DF}/TTF_{ESR}$

Part	A2	A3	A6	C2	B1	B2	B4
R_C	1.5	2.9	2.1	5.9	4.4	3.6	3.9
R_{DF}	1.4	3.4	1.7	1.6	2.2	2.6	1.2

- ✓ For most tested capacitors TTF_C and TTF_{DF} values were substantially greater than TTF_{ESR}.
- ✓ Similar slopes of distributions indicate the same mechanism of failures.
- ✓ On average, the times for capacitance failures (TTF_C) are ~3.5 and for DF failures (TTF_{DF}) ~2 times greater than for ESR (TTF_{ESR}).

Degradation in Different Part Types

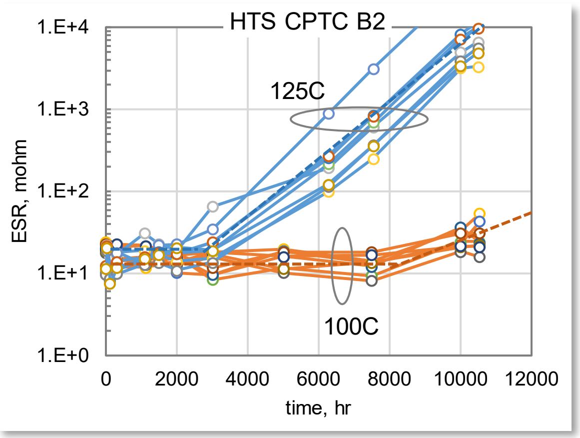
Part type	Qual. level	β	E_a eV	TTF_{50} use, yr.	$TTF_{1\%}$ use, yr.	TTF_{50} 125C, khr	P_{125} 1000hr, %
A1 10-35	COTS+	2.09	0.48	7.6	1.0	3.4	5.3
A2 10-35	COTS+	3.47	0.46	6.2	1.8	3.1	1.3
A3 15-25	COTS+	2.49	0.45	5.4	1.0	2.9	4.5
A4 15-25	COTS+	4.43	0.38	3.9	1.5	3.1	0.4
A5 100-10	auto	10.2	0.43	4.8	3.2	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

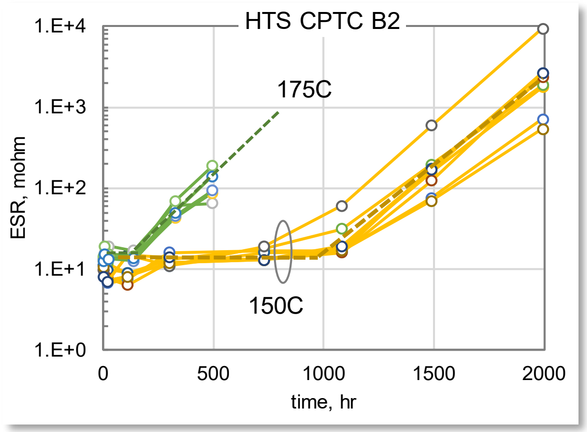
* Calculated at $\beta = 3.5$ and $E_a = 0.62$ eV

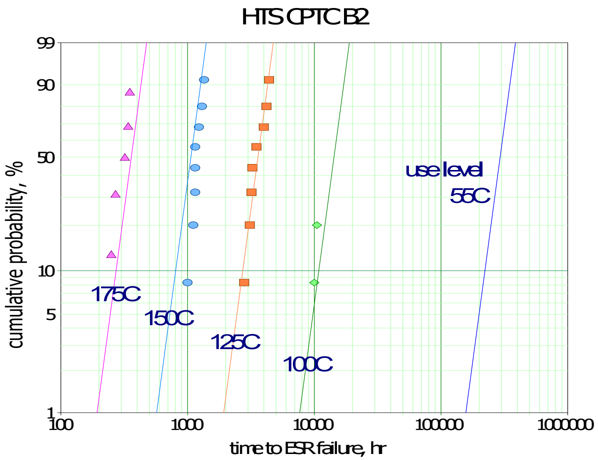
- The slopes of distributions β>1 indicate wear-out failures.
- Calculated TTF_{50} values at operating conditions vary from a few to 471 years, and times to the failure inception ($TTF_{1\%}$) are from one to 88 years.
- E_a is varying in a wide range, from 0.38 to 0.93 eV. The average value is 0.62 ±0.17 eV.
- Some automotive industry CTPCs showed exceptional results during HTS; however, variations between part types might be significant.
- The standard HTS testing is not sufficient to assure long-term stability of AC characteristics at HT.

Specifics of ESR Degradation

HTS of B2 220 μF 10 V capacitors



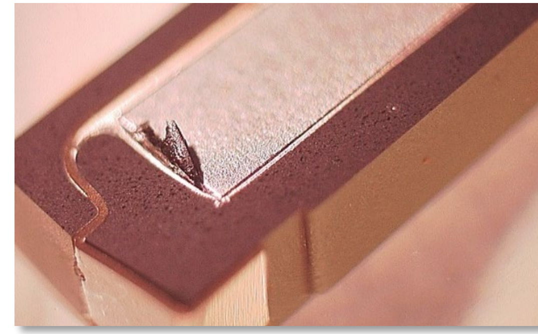




- ✓ There is a certain incubation period, t_i, before the inception of ESR growth.
- ✓ After t_i, ESR increases exponentially with time.
- ✓ Both, incubation periods and characteristic times of degradation are decreasing with temperature.
- ✓ Degradation of *ESR* in CPTCs is due to thermo-oxidative processes in conductive polymers.
- ✓ Permeability of air depends on packaging quality that affects the rate of ESR degradation and times-to failure.

Failure Analysis

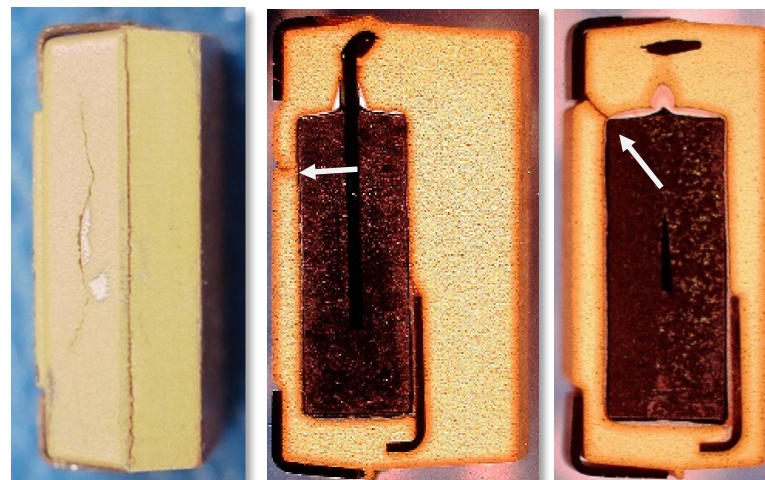
Extrusion of polymer due to moisture sorption



- X-sectioning after HTS shows discoloration of MC that indicates the path of oxygen towards PEDOT:PSS cathode.
- More discoloration around the slug corresponds to greater degradation of ESR.

Parts with delamination

Parts with cracks

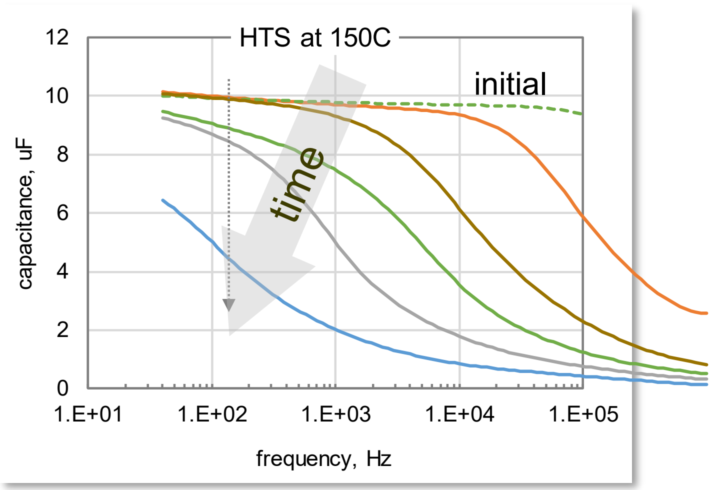


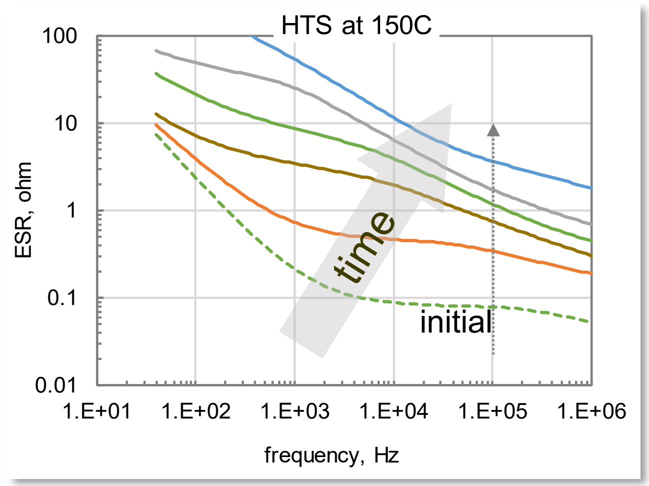
✓ Cracks and LF/MC delamination provide a path for oxygen penetration to the slug and accelerate degradation processes substantially.

FA: Degradation of Capacitance and DF

Frequency dependencies of C and ESR for 10 μF CPTC during HTS at 150 ºC.

$DF = \omega C \times ESR$

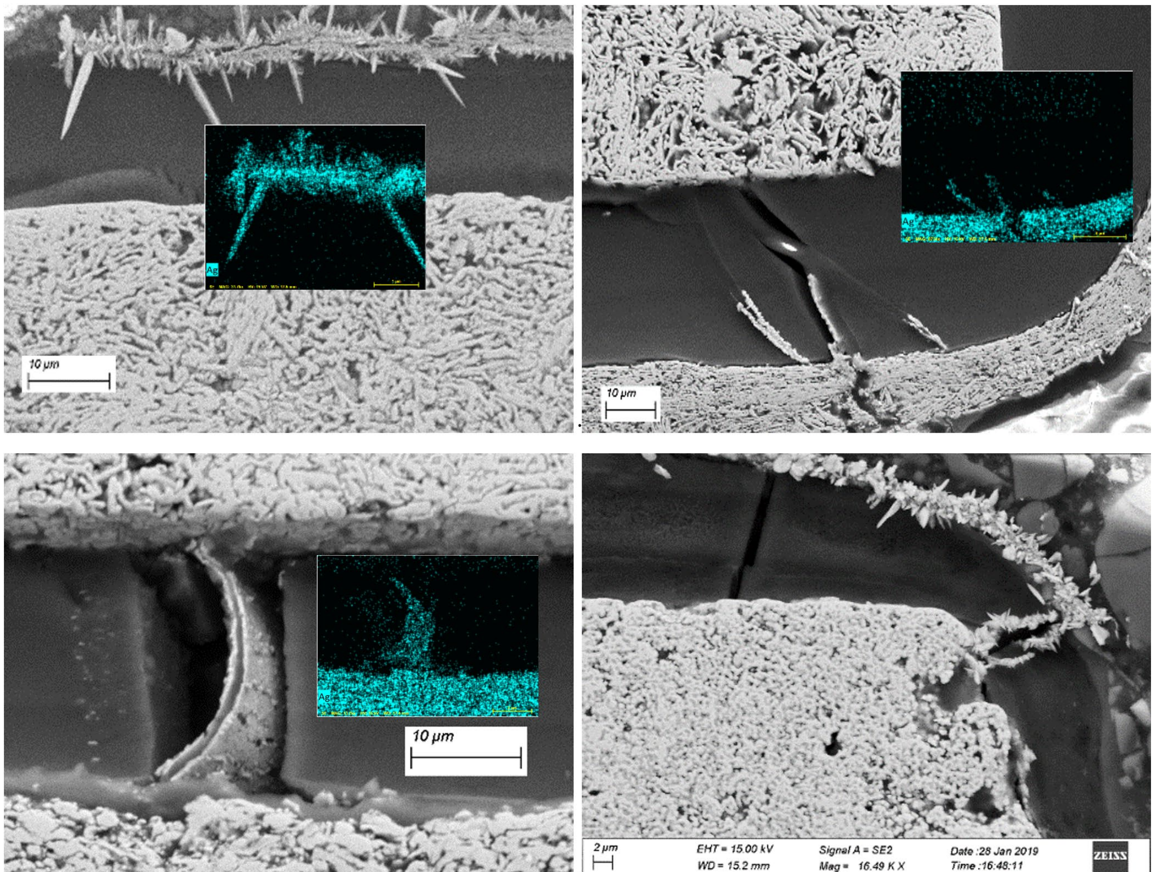




- ✓ Reduction of the roll-off frequency and degradation of capacitance is due to increase of the resistance of cathode layers.
- ✓ Degradation of DF is mostly due to increasing ESR values.

FA: Ag Compositions

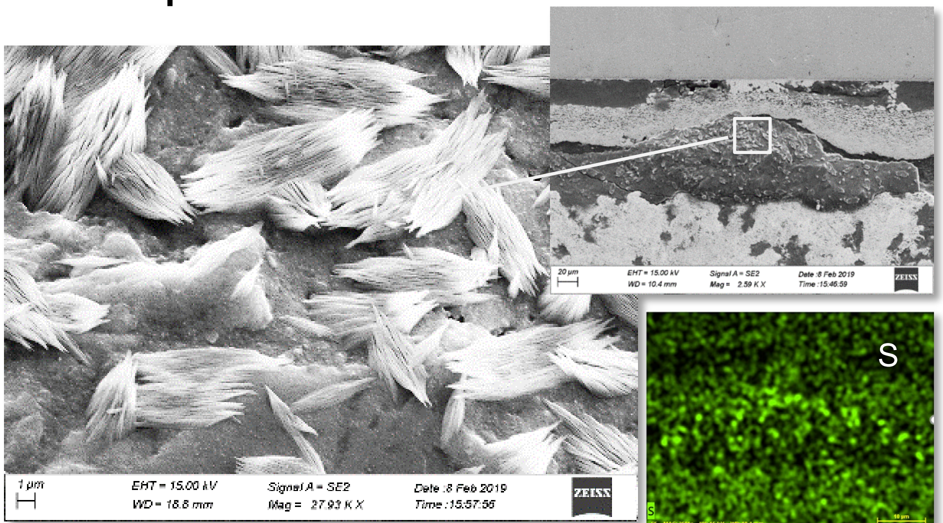
Examples of Ag-containing crystals on silver epoxy in virgin and post-HTS capacitors.

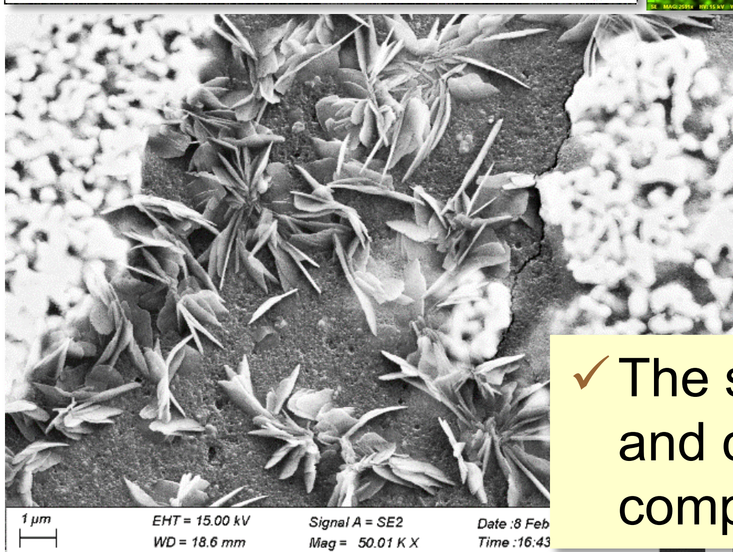


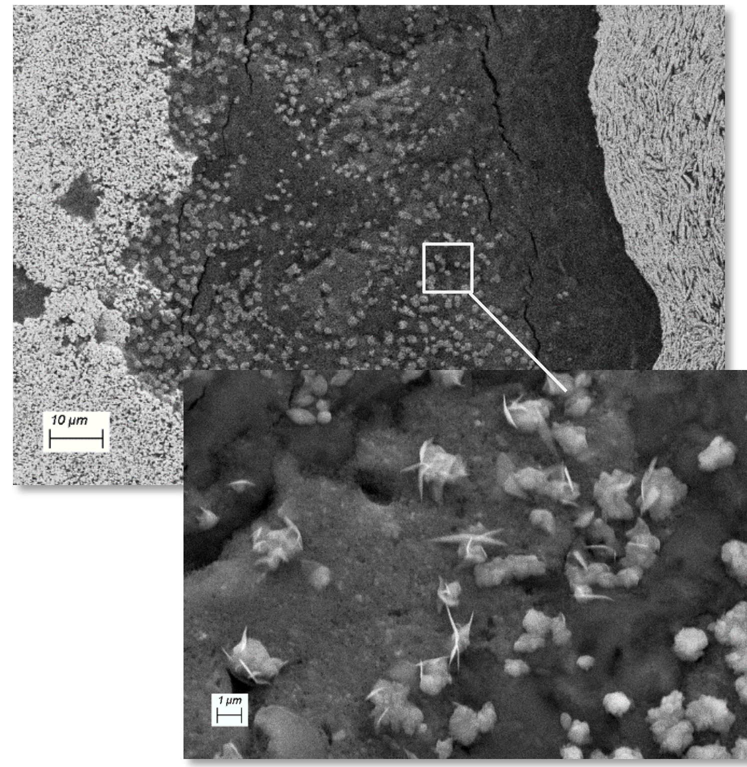
- ✓ Ag-containing crystals were formed at the Ag-epoxy and PEDOT interface in the presence of water.
- ✓ Similar crystals might be formed after moisture sorption in cracks caused by HTS.
- ✓ Due to a small size, these crystals most likely will burn-out after voltage applications and are unlikely to cause catastrophic failures.

FA: Sulfur Compositions

Compositions formed on 6.3V in-situ polymerization cathode layers

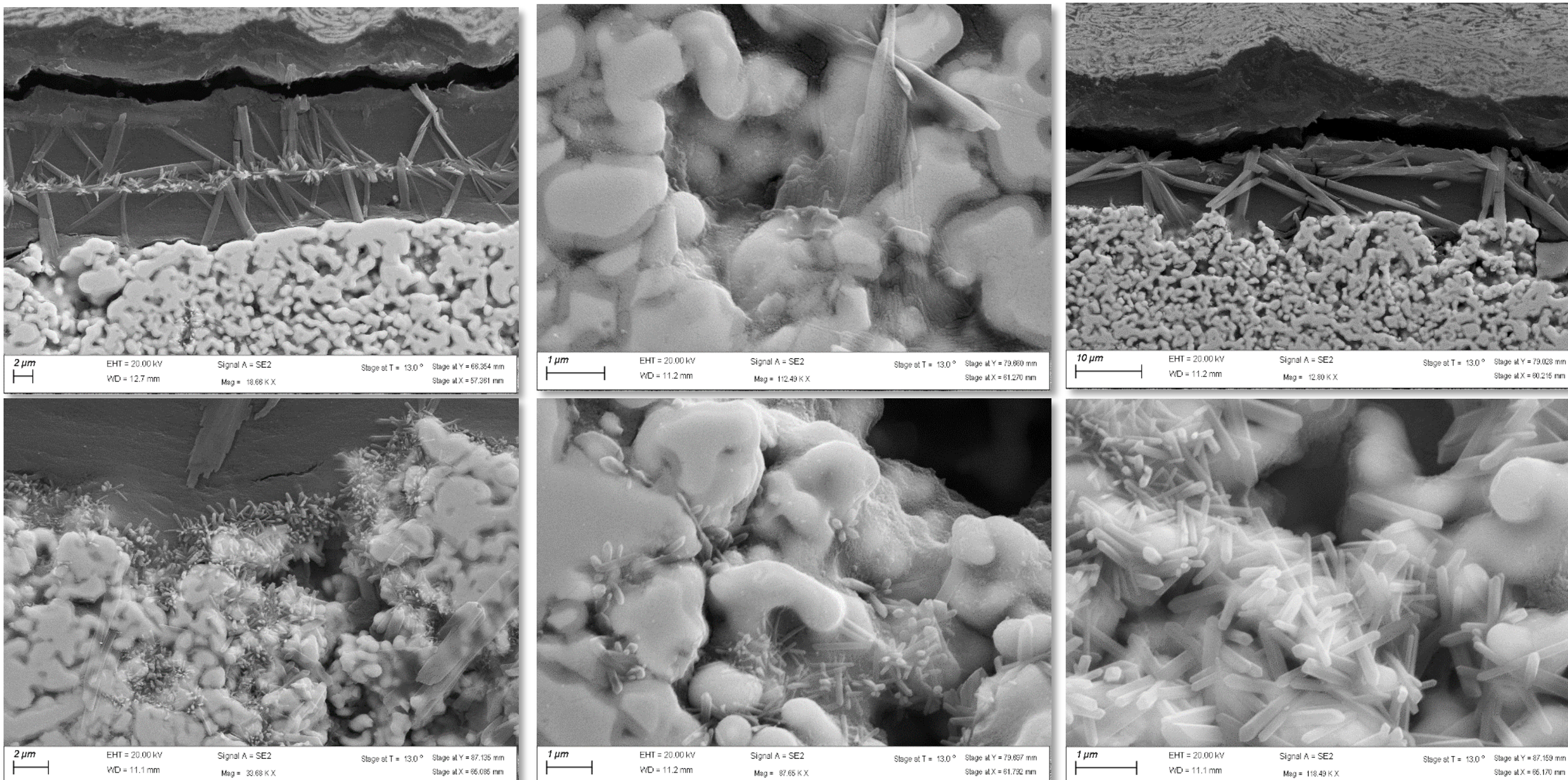






✓ The surface of PEDOT:PSS is chemically active and can form different types of S-containing compositions in the presence of moisture.

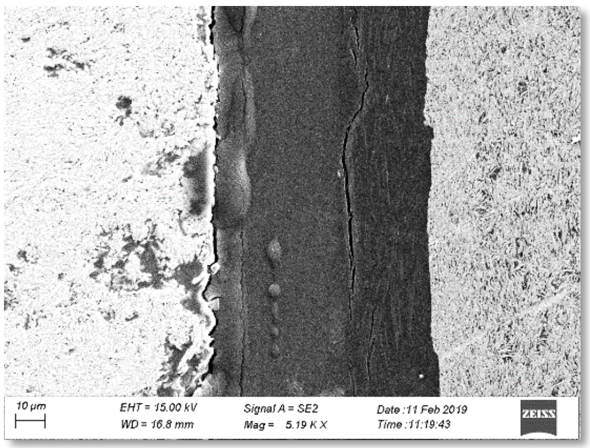
FA: Ca Compositions

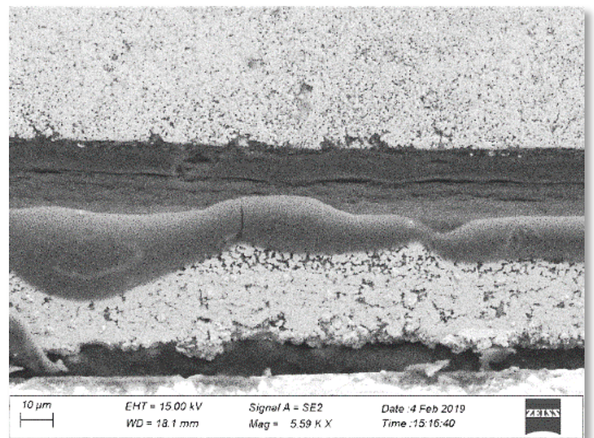


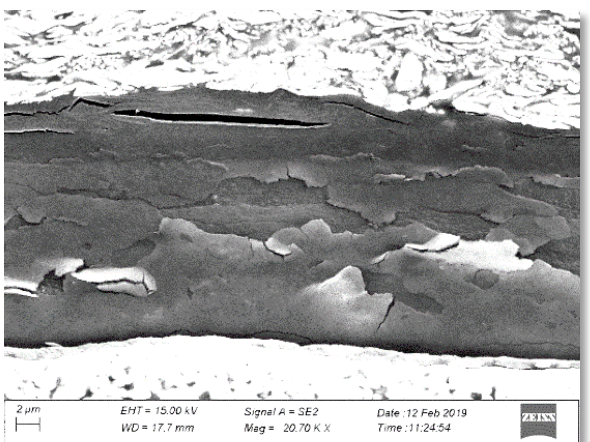
- ✓ Ca most likely originates from the fabrication process of PEDOT:PSS and crystals are growing in the presence of moisture.
- ✓ Calcium sulfate ($CaSO_4$) crystals are formed in the presence of moisture.

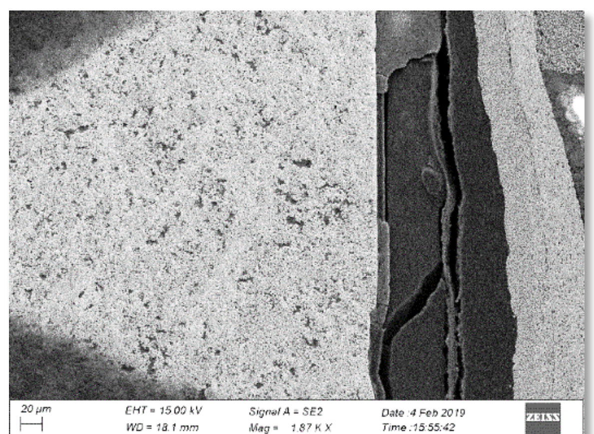
FA: Liquids in Cathode Layers

Liquid polymer oozed from the cathode shell after cross-sectioning for virgin and post-HTS capacitors





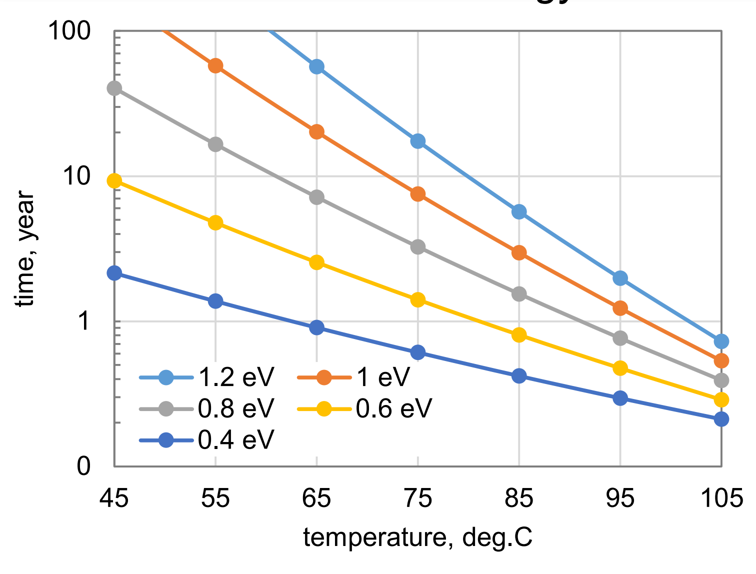




- ✓ The liquid is likely a polymer solution in water formed during cross sectioning.
- ✓HTS does not remove soluble polymers.
- ✓ Drying of the solution formed a thin and fragile layer on the surface of the shell.
- ✓ The presence of the soluble polymers is most likely not a reliability concern.

The Significance of 125ºC/1000hr Testing

Time of storage that is equivalent to 1000 hr at 125 ºC varies substantially with activation energy



- ❑ Possible presence of defects (cracks) in the case requires relatively large SS.
- ❑ Testing 77 samples with no failures can assure that the probability of defect is below 1.5%.
- ❑ E_a for thermal degradation of polymers in vacuum is substantially greater than in the presence of oxygen.
- ❑ Experimental data suggest a better stability of ESR in vacuum.

- ✓ Successful results of HTS at 125 ºC can guarantee stability of ESR during operations at relatively large activation energy of degradation only.
- ✓ Increasing E_a from 0.6 eV that is typical for in-air conditions even to 1 eV in vacuum for capacitors that are stable at 125 °C for 1000 hours would increase their operational life in space at 65 °C from 2 years to more than 20 years.

Conclusion

- Testing of 22 types of polymer tantalum capacitors during HTS at temperatures from 100 to 175 ºC showed that *ESR* is the most sensitive parameter to degradation that can increase dozens and thousands times.
- 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 caused by thermo-oxidative processes in conductive polymers.
- Degradation of AC characteristics has been described using Weibull-Arrhenius models. The slopes of TTF distributions indicate 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.
- Successful results of qualification testing at 125 ºC for 1000 hours can guarantee stability of parts at operating conditions only for lots with relatively high activation energies that is typical for space applications.
- All tested automotive grade CPTCs can withstand more than 1000 hours at 125 ºC and 4 types remained stable for 4000 hours at 150 ºC. Automotive grade polymer capacitors should be the prime source for selecting components for space applications.