NASA Electronic Parts and Packaging (NEPP) Program

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

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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 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.

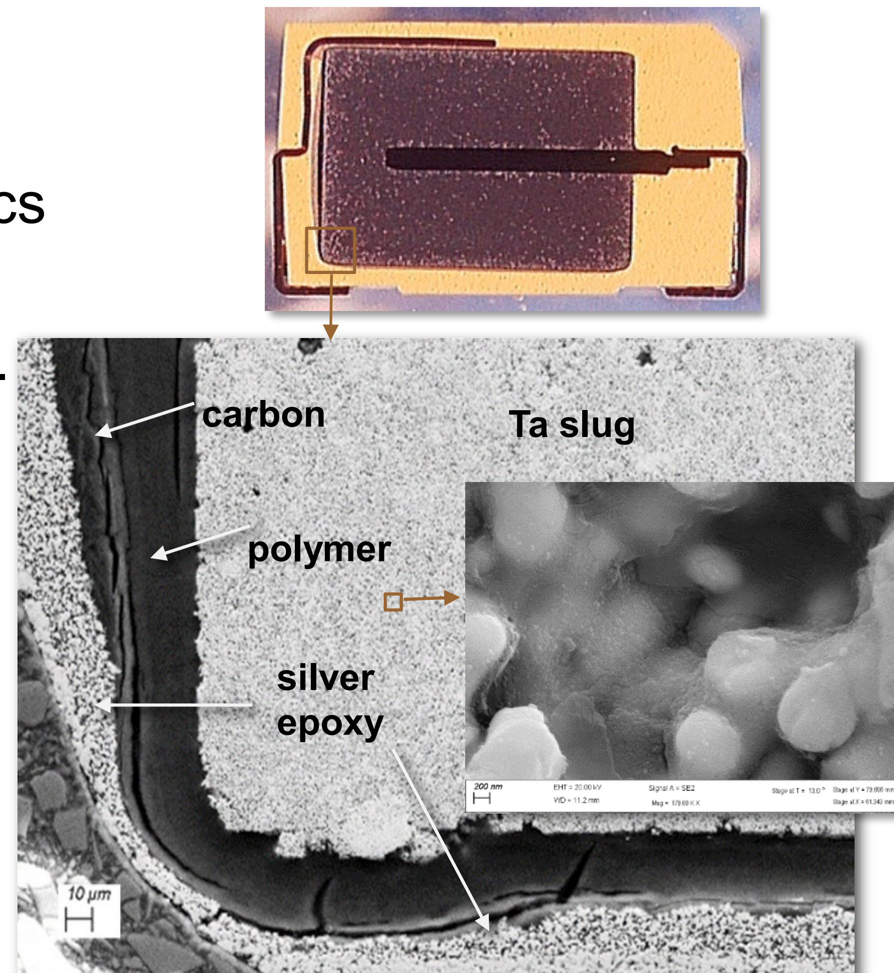
List of Acronyms

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		

Outline

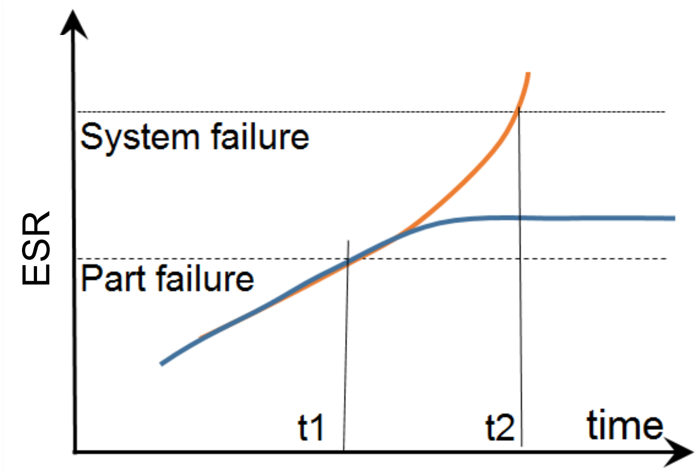
- Introduction.
- Experiment.
- Results of HTS testing.
- Sensitivity of AC characteristics to HTS.
- Specifics of ESR degradation.
- Degradation in different types of CPTCs.
- Significance of endurance testing.
- Conclusion.

Polymer Tantalum capacitors



Introduction

- One of the major benefits of CPTCs compared to MnO2 capacitors is low ESR.
- ESR in CPTCs is degrading with time of operation or storage at HT.
- Part-level ESR failures can happen with MnO2 parts, but degradation and system-level failures are unlikely.



- There is a need for a model to predict degradation of CPTCs to assess the end-of-life characteristics.
- Currently, high-quality CPTCs (auto) require HTS testing at 125 ºC for 1000 hrs with relaxed post-testing limits: $ESR \leq (2 \div 5 \times ESR_{init\ limit})$.
- The existing testing does not answer questions about long-term (years) stability of the parts at the use temperature.

✓ 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.

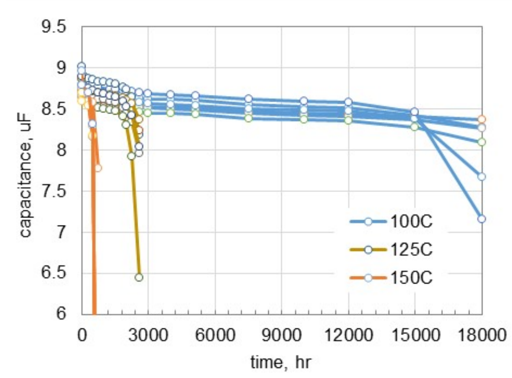
Experiment

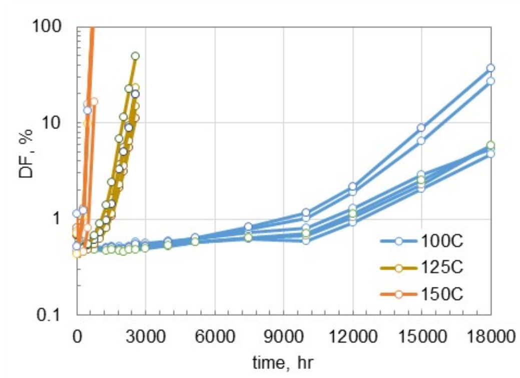
- Ten types of Mfr.A, four types of Mfr.B, and eight types of Mfr.C capacitors have been used in this study.
- Five types of the parts were general purpose, 10 types were manufactured for the automotive industry per AEC-Q200 requirements, and 7 types were hi-rel or COTS+ capacitors.
- Each group had 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: $C \le 0.8 \times C_{nom}$, $DF < DF_{limit}$, $ESR > 3 \times ESR_{limit}$
- TTF distributions were approximated with a Weibull-Arrhenius model.

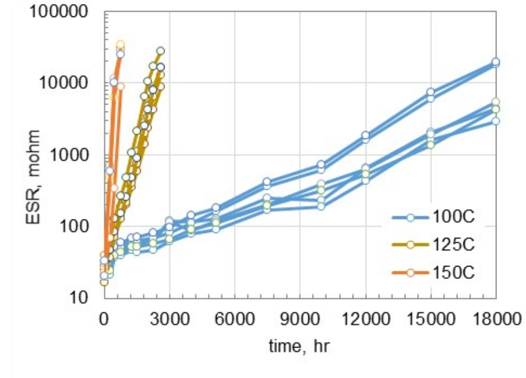
$$P(t) = 1 - \exp\left[-\left(\frac{t}{\eta}\right)^{\beta}\right] \qquad \eta = C_0 \times \exp\left(E_a / kT\right)$$

Examples of Degradation of AC Characteristics for General Purpose CPTCs

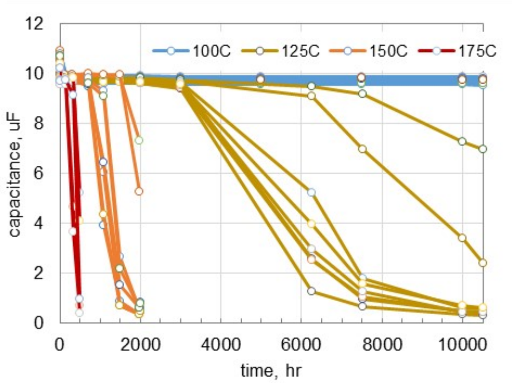
Type A7
10µF
100V

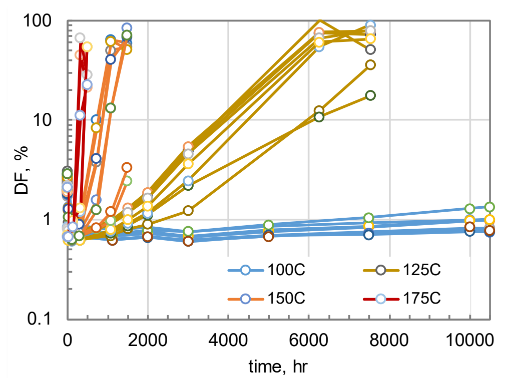


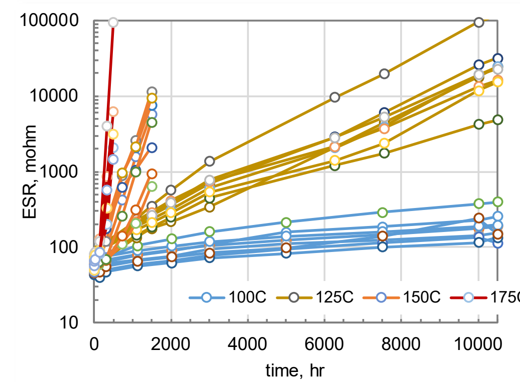




Type B1
10µF
25V

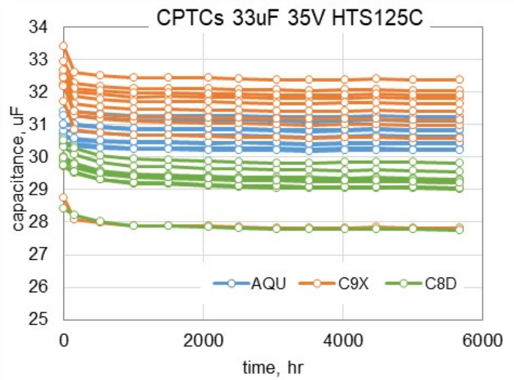


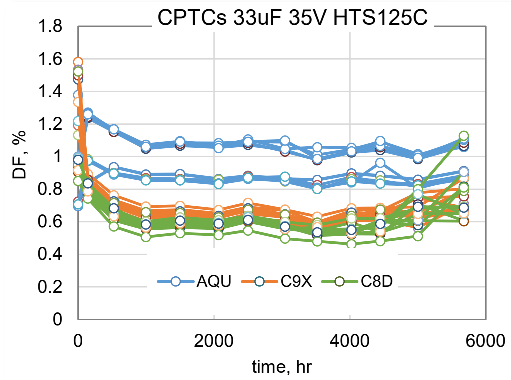


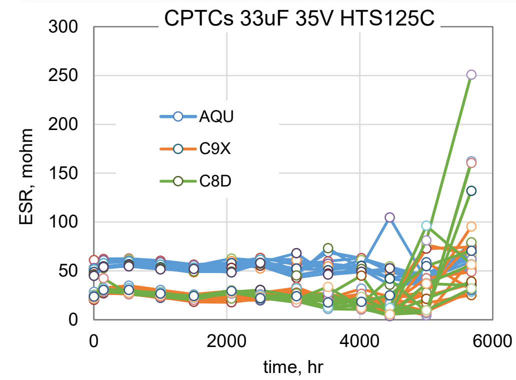


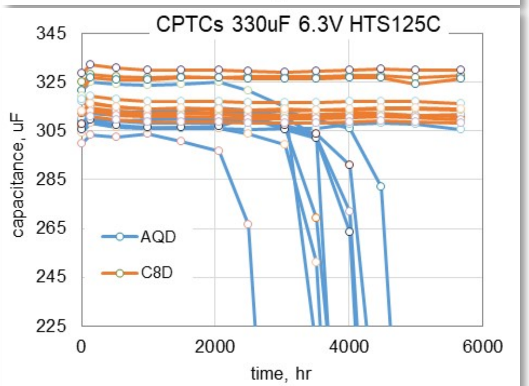
- ✓ Temperature has a strong effect on the rate of degradation.
- ✓ ESR rises with time exponentially increasing by 100× and 1000× times.
- ✓ In the general-purpose capacitors a significant degradation might occur already after 100× hours of storage at 125 ºC.

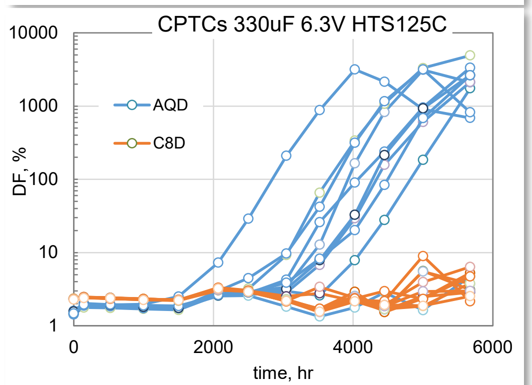
Examples of Degradation of AC Characteristics for Automotive Grade CPTCs

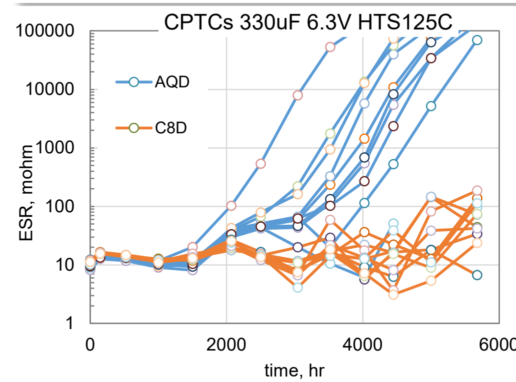








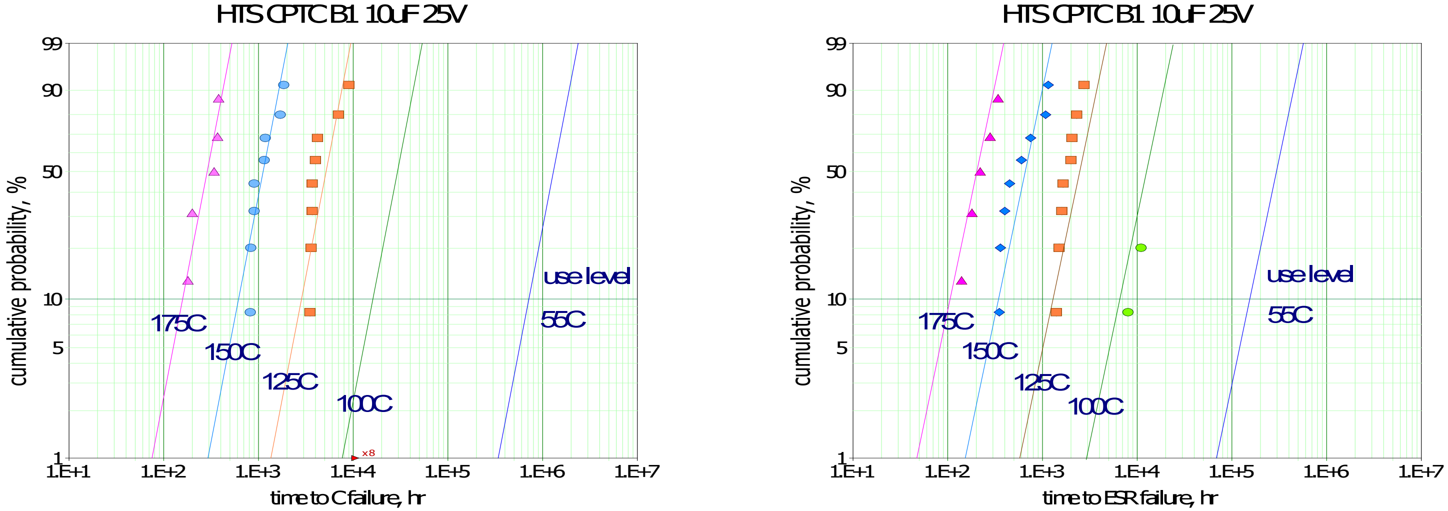




- ✓ All parts passed the required 1000hr testing at 125ºC.
- ✓ One part type degraded catastrophically after 2000hr.
- ✓ Four out of 5 automotive grade capacitors withstood 5200 hours at 125ºC.
- ✓ Capacitors that were stable at 125 ºC withstood also storage at 150ºC for 4000hr.

TTF Distributions

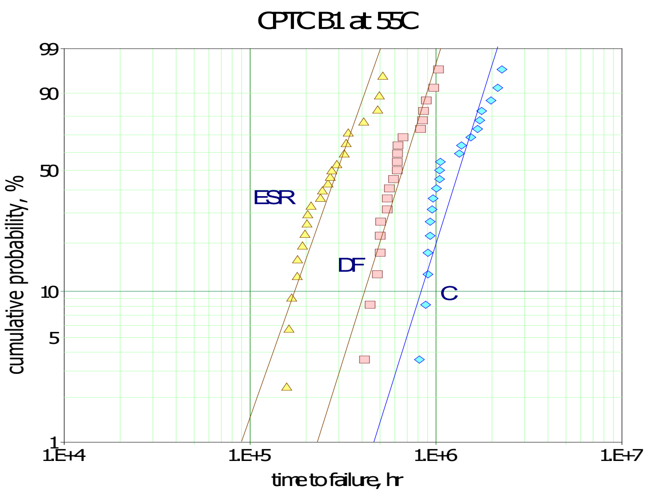
TTF distributions for C and ESR at different temperatures



- ✓ 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 Ageing

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



Ratios of median times

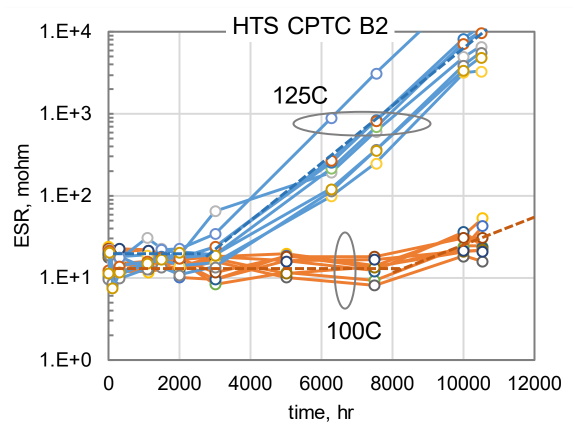
$R_C = TTF_C/TTF_{ESR}$ and $R_{DF} = TTF_{DF}/TTF_{ESR}$

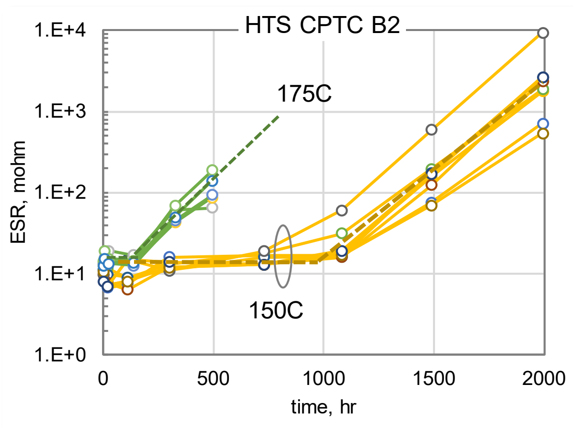
Part	A2	A3	A6	C2	B1	B2	B4
R_C	1.5	2.9	2.1	5.9	4.4	3.6	3.9
R_{DF}	1.4	3.4	1.7	1.6	2.2	2.6	1.2

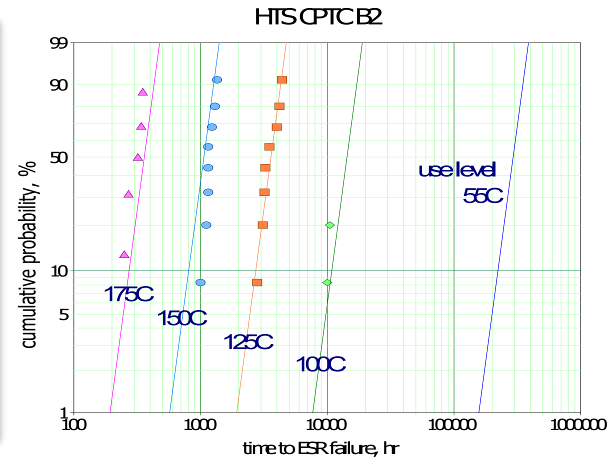
- ✓ For most tested capacitors TTF_C and TTF_{DF} values were substantially greater than TTF_{ESR}.
- ✓ On average, the times for capacitance failures (TTF_C) are ~3.5 and for DF failures (TTF_{DF}) ~2 times greater than for ESR (TTF_{ESR}).

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 with time exponentially.
- ✓ 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.

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

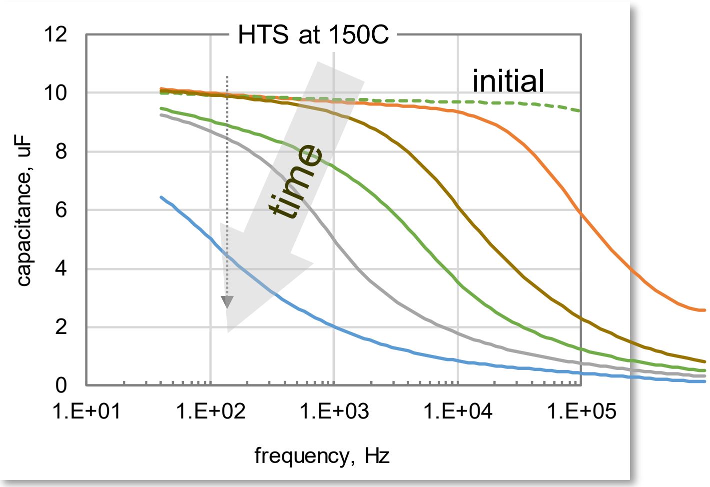
* Calculated at $\beta = 3.5$ and $E_a = 0.62$ eV

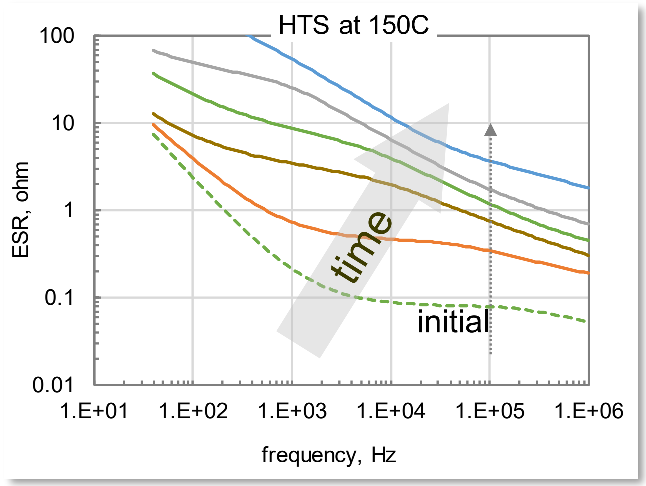
- The slopes of distributions β > 1 indicating wear-out failures.
- Calculated TTF_{50} values at operating conditions vary from a few to 471 years, and times to the failure inception ($TTF_{1\%}$) are from one to 88 years.
- E_a is varying in a wide range, from 0.38 to 0.93 eV. The average value is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

Degradation of Capacitance and DF

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

DF = ωC×ESR

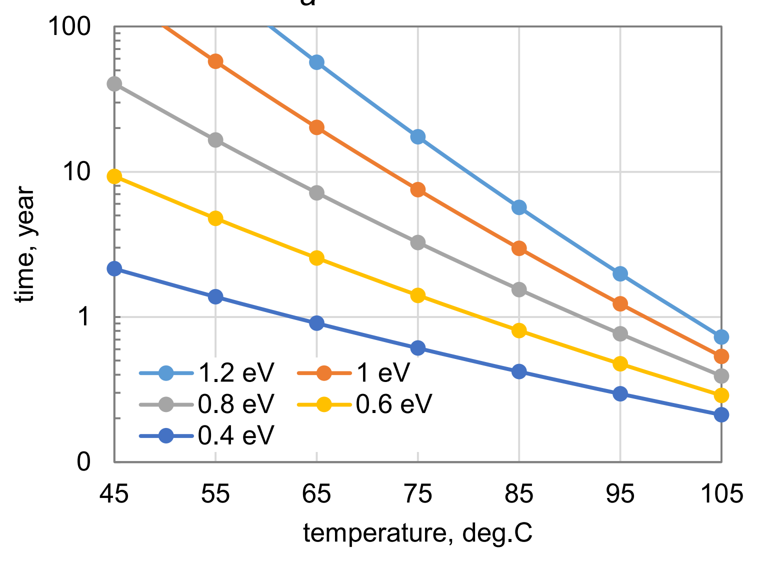




- ✓ Reduction of the roll-off frequency and degradation of capacitance is due to increasing of the resistance of cathode layers.
- ✓ Degradation of DF is mostly due to increasing ESR values.

The Significance of 125ºC/1000hr Testing

Time of storage that is equivalent to 1000 hr at 125 ºC at different E_a values



- ✓ No failures during standard HTS testing does not guarantee long-term stability of the parts during operation.
- ✓ Successful results of HTS at 125 ºC can guarantee stability of AC characteristics at relatively large E_a only.
- ✓ For lots having large enough E_a, acceptable results of HTS testing can provide more confidence that no failures will occur during use conditions.
- ✓ In the absence of air (e.g. in vacuum), E_a increases substantially.

Conclusion

- Measurements of AC characteristics of 22 types of polymer tantalum capacitors in the process of storage at temperatures from 100 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.
- Degradation of AC characteristics has been described using Weibull-Arrhenius models. In all cases, the slopes of distributions indicated 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.
- 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.
- 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. The automotive grade polymer capacitors should be the prime source for selecting components for hi-rel applications.