Anomalous Transients in Chip Polymer Tantalum Capacitors

Alexander Teverovsky

ASRC, NASA/GSFC code 562, Greenbelt, MD20771, USA
Alexander.A.Teverovsky@nasa.gov

ABSTRACT

Contrary to MnO2 tantalum capacitors, transient processes in polymer tantalum capacitors after voltage application might result in anomalously high, ampere-level currents when a capacitor might appear as a short circuit for a time that is much greater than a transient time in MnO2 capacitors. In this work, conditions that cause anomalous transients in different types of polymer tantalum capacitors have been analyzed. Related phenomena that included increasing of capacitance and dissipation factors with voltage, parametric surge current test failures without damage to capacitors, and increasing leakage currents at low temperatures are described. It has been shown that anomalous transients increased substantially with applied voltage and with reduction of moisture content in capacitors caused by storage or operation at high temperatures and/or in vacuum. Different types of capacitors exhibited different level of transients and modification of conductive polymers or process of their application might decrease transient leakage currents substantially. For space applications, the risk of failures related to anomalous transients can be mitigated by special testing procedures to select parts with an acceptable level of transients and by voltage derating.

CONTENTS

ABSTRACT 1
CONTENTS 1
INTRODUCTION 1
EXPERIMENT 3
TEST RESULTS 3
- Effect of Preconditioning 3
- Effect of Temperature 4
- Effect of Voltage 6
- Effect of Vacuum 7
- Anomalies in AC Characteristics 9
- Effect of Part Type 10
- Effect of HALT 11

DISCUSSION 11
- Mechanisms of anomalous transient currents 12
- C-V and Transient AC Characteristics 13
- Temperature Transients and Reliability under Power Cycling 13

SUMMARY 14
- Recommendations 14

ACKNOWLEDGMENT 15
REFERENCES. 15

INTRODUCTION

Due to a low equivalent series resistance (ESR) and relatively safe failure mode of chip polymer tantalum capacitors (CPTC), compared to traditional MnO2 cathode capacitors, there is a strong pressure from electronic designers to use these parts in hi-rel systems. Reliability concerns related to CPTCs are mostly due to the sensitivity of conductive polymers to environmental stresses. Both high humidity conditions and dry high-temperature environments are detrimental for polymer capacitors resulting in increased ESR or leakage currents. Long-term biased operation in humid environments is a serious concern for the automotive industry, and for this reason substantial efforts have been made by manufacturers to improve moisture resistance of CPTCs [1-3].

Reliability of components in humid environments is not the major concern for space applications. A more important factor is vacuum that depending on the mechanism of degradation can be a benefit or a hazard. Our previous studies of CPTCs [4] have shown that ESR failures during high-temperature operation or storage that are due to oxidative degradation of polymers are less probable in vacuum than in air. However, insufficient self-healing that is likely less effective in vacuum might result in increased probability of current spiking and noise generation in capacitors.

Vacuum conditions might also result in a substantial increase of charging currents in CPTCs when a capacitor appears as a short circuit for a relatively short period of time, so-called anomalous charging currents [2, 5]. Excessive charging currents that are increased after reflow soldering might cause failures in some applications. This phenomenon has not been investigated sufficiently and requires a more detailed analysis.

Normally, charging processes caused by application of a step voltage, *V*, from a voltage supply with low internal resistance, e.g. a battery, to a tantalum capacitor of value *C* result in a current spike with an amplitude and width that are determined by the value of ESR of the capacitor. The amplitude of the spike and characteristic relaxation time can be estimated as $I_{sp} = V/ESR$ and $\Delta t_{sp} = ESR \times C$. For low ESR capacitors (ESR ≤ 0.1 ohm) rated from 10 to 50 V I_{sp} might exceed hundreds of amperes, but the width is less than 100 μsec. Actual values of I_{sp} are lower and values of Δt_{sp} are larger due to the presence of inductance and resistance of connecting wires and internal resistance of the power supply. After the spike, currents in MnO2 cathode capacitors typically reduce to below milliamperes within a few milliseconds and continue decreasing with time according to a power law, $I \sim t^{-n}$ where $n \approx 1$. This process is due to charge absorption (e.g. electrons' trapping at the interface states) that is common for most types of capacitors, including wet tantalum [6], CPTCs [4], and MLCCs [7]. These transient currents are stabilized eventually at a level corresponding to intrinsic leakage currents after minutes or hours of electrification.

Contrary to MnO2 capacitors, currents in polymer tantalum capacitors after the initial spike might remain high, exceeding dozens of milliamperes and even amperes for a period substantially exceeding relaxation times for similar value MnO2 capacitors. These currents gradually decreasing with time, but for a long period, that might last tens of minutes, remain orders of magnitude higher than the intrinsic leakage currents and even exceed the specified limits resulting in parametric failures.

This phenomena was first described for low-voltage (rated to 6.3 V) polymer capacitors by Y.Freeman and co-workers in 2013 [5]. It has been shown that anomalous transient currents are smaller for capacitors with polymers formed by in-situ polymerization (polymerization of 3,4-ethylenedioxythiophene in the presence of iron (III) toluenesulfonate) compared to hybrid capacitors with in-situ polymers used inside the porous tantalum pellet and pre-polymerized PEDOT:PSS polymers used on the external surface of the pellet. High-voltage capacitors that employed pure pre-polymerized PEDOT/PSS systems had no anomalies. For hybrid capacitors, the currents increased substantially at lower temperatures -200 ºC). After application of a 6.3 V pulse, the currents exceeded 1 A for ~300 msec at room temperature and for ~ 1.2 sec at -200 ºC. No excessive currents were observed after exposure of the parts to environments with 70% RH humidity, but drying at 125 ºC for 24 hours restored anomalous transients.

If moisture is essential to suppress anomalous transients, this phenomenon might appear with time of operation in space due to a gradual moisture release in vacuum. Unfortunately, there is a very limited information about the internal (technology, part type, manufacturing processes and materials) and external (test voltage and temperature, duration of storage in different environments, etc.) factors affecting anomalous charging currents. In addition, the existing screening and qualification procedures during manufacturing of hi-rel tantalum capacitors had been developed for MnO2 technology and do not address parametric failures associated with anomalous transients.

In this work, transient currents in the range from microseconds to hours have been analyzed for different types of CPTCs to reveal common features in their behavior and compare with the behavior of similar value MnO2 capacitors. Transient currents have been measured at different temperatures and voltages after different preconditioning including storage in humidity chamber, in vacuum, and in air temperature chamber. Anomalies in AC characteristics of dry CPTCs have been revealed and possible mechanisms are discussed. Screening and qualification procedures to constrain anomalous transients are suggested.

EXPERIMENT

Transient currents have been monitored for periods from microseconds to hours after step voltage application using three techniques covering different time intervals. A set-up for surge current testing with a current probe and an oscilloscope was used for times between 1 μs and 1 msec (short-term transients). The circuitry used a power FET as a switch and a 18.6 mF bank capacitor as a power source. No limiting resistors was used, so mostly the ESR of capacitors and connecting wires limited the amplitude and width of the current spikes. A power SMU in Agilent Precision Semiconductor Analyzer 4156A was used to measure currents in the range from 1 msec to 10 sec (middle-term transients). The SMU clamped currents at 1 A for voltages below 20 V and at 0.5 A for voltages up to 50 V. In the time range from 10 sec to hours (long-term transients) leakage currents were monitored using a PC-based system and Agilent scanners that measured voltage drop across 1 kohm or 10 kohm resistors connected in series with each capacitor. Unless specified, transient currents were measured after application of rated voltages. Variations of capacitance and ESR with voltage and time under bias were measured at different frequencies using Agilent 4294A impedance analyzer.

More than 20 different types of capacitors from three manufacturers were used in this study to reveal common features in transient behavior of CPTCs in comparison to MnO_2 capacitors. The rating voltages of capacitors varied from 6.3 V to 35 V and capacitance from 10 μF to 330 μF. Most parts had case size D.

The parts were used in "as is" condition (virgin) within ~1 week of removal from dry bags, after soaking in humidity chamber at 85 ºC and 85% RH (marked below as "HUM" condition), or after storing at 125 ºC ("bake" condition). Preliminary experiments have shown that moisture content in CPTCs is typically stabilized after 100 to 200 hours of exposure in humidity chamber or at 125 ºC. For this reason, the duration of soaking or baking of the capacitors was from 1 week to 10 days. Typically, groups from 5 to 10 samples of each type were used for the testing described below.

Some part types have been tested after long-term, typically 1000 hr, high-temperature storage (HTS) at 100 or 125 ºC. Thirteen part types were stored in vacuum at 3×10^{-6} torr for 2000 hours before measurements. Leakage currents in nine groups of capacitors have been monitored with time directly in vacuum chamber at temperatures from -50 ºC to +85 ºC during voltage cycling test: one hour ON and one hour OFF (long-term transients). The currents during these tests were limited by 1 kohm resistors connected in series with each capacitor.

TEST RESULTS

Effect of Preconditioning

Fig.1 shows transient currents in different types of capacitors preconditioned by soaking in a humidity chamber or by drying at 125 ºC. Results show that moisture content affected transients occurring in CPTCs in a wide range of times from dozens of microseconds to hours. Anomalously high currents occurred in low-voltage (6.3 V, 10 V) as well as in high-voltage capacitors rated to 35 V. The difference between currents measured at the same time in parts after bake and after humidity chamber can exceed two orders of magnitude.

Both, medium-term and long-term transients are plotted for 10 μF 35 V capacitors on the same chart (Fig. 1c). For MnO_2 capacitors with any preconditioning and for moisturized CPTCs the current decay in the range from milliseconds to hours followed a general power law rule with the exponent close to 1, which is likely due to absorption processes in the Ta_2O_5 dielectric. For these parts, depolarization currents measured at 0 V are close by absolute value, but different by sign to the currents measured at 35 V. Although decay in dry CPTCs appeared to have a similar slope, depolarization currents are much lower compared to the electrification currents. This indicates that transients in dry CPTCs are likely due to increased conduction of the dielectric that is decreasing with time under bias.

Transient currents in "virgin" capacitors are between the currents for humidified and baked parts, and depending on the part type are closer to the one or another group. As manufactured, the parts are relatively dry, but their moisture content can be further decreased by additional baking or long-term operation in vacuum.

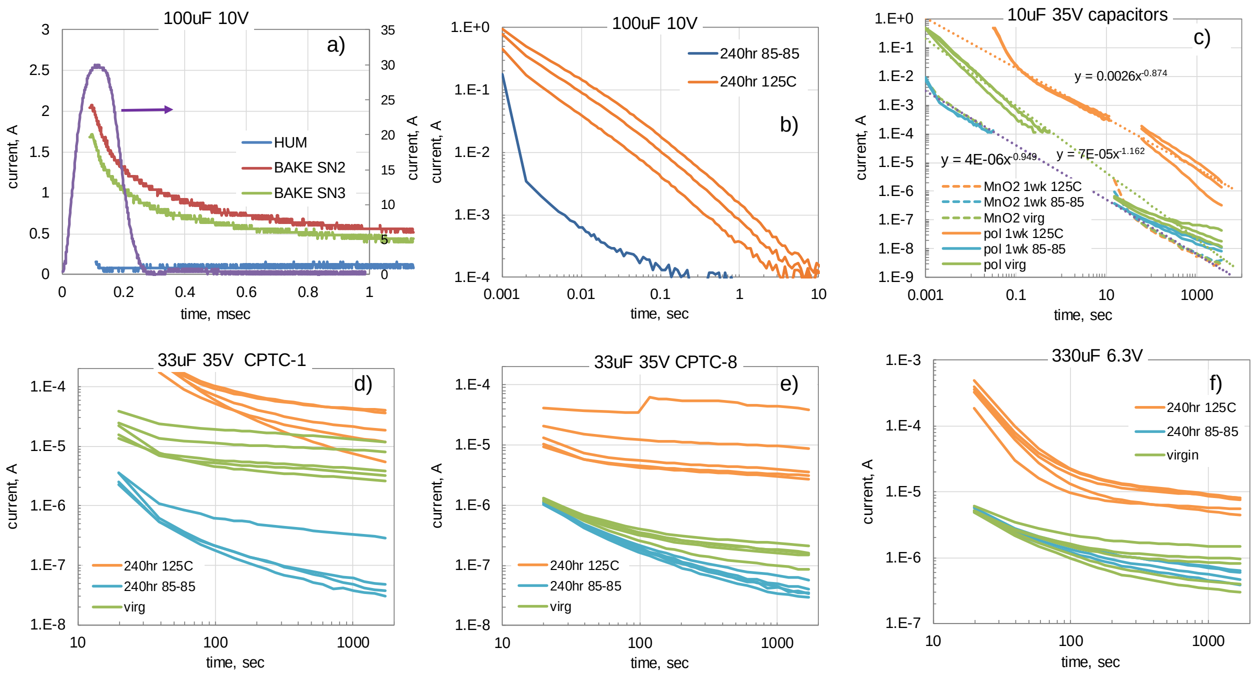


Figure 1. Short- (a), medium- (b, c), and long-term (c-f) transient currents in different types of CPTCs in "as-received" (virgin) condition, after bake at 125 ºC for 240 hr and after humidifying at 85 ºC 85% RH for 240hours.

Effect of Temperature

Long-term transients in dry 220 µF 16 V polymer capacitors (Fig. 2a) show that decreasing temperature to -50 ºC increases leakage currents more than two orders of magnitude compared to room temperature, and the current decay at -50 ºC occurs much slower than at higher temperatures.

Temperature dependencies of currents measured after 1000 sec of electrification depended strongly on preconditioning (Fig. 2 b, c), and the difference between humidified and dried capacitors reached six orders of magnitude. Temperature dependencies of the currents have extremum at a temperature T_{max} that depends on moisture content. For example, for 22 µF 25 V dry capacitors have T_{max} at -20 ºC, for virgin parts it is at -50 ºC, and for wet capacitors it is likely below -70 ºC (Fig. 2c). At relatively high temperatures (above ~ 20 ºC) leakage currents in humidified capacitors follow Arrhenius law (Fig. 2b) with activation energy of 0.2 eV. Calculations showed that humidified 22 µF 25 V capacitors (Fig. 2c) had also a relatively low value of activation energy of 0.25 eV.

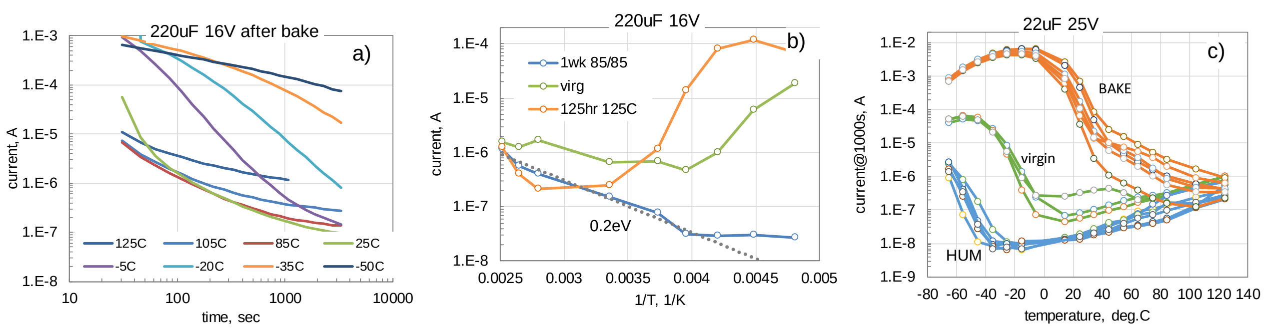


Figure 2. Effect of temperature on leakage currents in 220 µF 16 V and 22 µF 25 V capacitors. (a) typical long-term transients at temperatures between -50 ºC and +125 ºC in dry capacitors; (b) typical temperature dependencies of leakage currents measured after 1000 sec of electrification for 220 µF 16 V capacitors in Arrhenius coordinates; (c) variations of 1000-sec currents in 22 µF 25 V capacitors with different preconditioning.

Similar results were obtained for 10 µF 35 V capacitors (Fig. 3). At -45 ºC currents in dry CPTCs were substantially larger than at room temperature or at +85 ºC. At low temperatures, dried capacitors had up to 5 orders of magnitude higher leakage currents compared to MnO2 or humidified polymer capacitors. Currents for humidified and MnO2 capacitors at all temperatures were similar, and the current decay at room and lower temperatures for these parts followed a power law with the exponent close to 1.

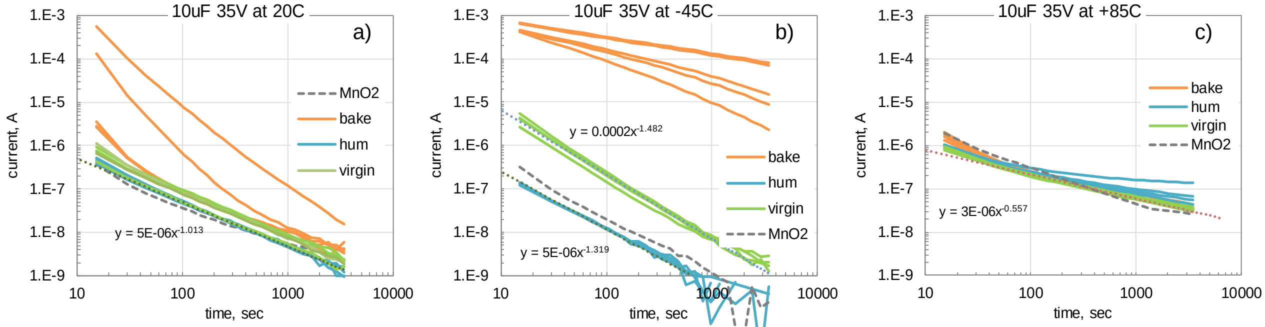


Figure 3. Long-term transients in 10 µF 35 V capacitors with different preconditioning at +20 ºC (a), -45 ºC (b), and +85 ºC (c). Dashed lines correspond to 10 µF 35 V MnO2 capacitors.

Fig. 4 shows Arrhenius plots for different types of 35 V capacitors with different preconditioning. Results suggest that temperature dependence of leakage currents in all CPTCs varies with the moisture content, and the activation energy can be determined for humidified part at relatively high temperatures only. At these conditions, all CPTCs have a relatively low activation energy, from 0.2 eV to 0.3 eV.

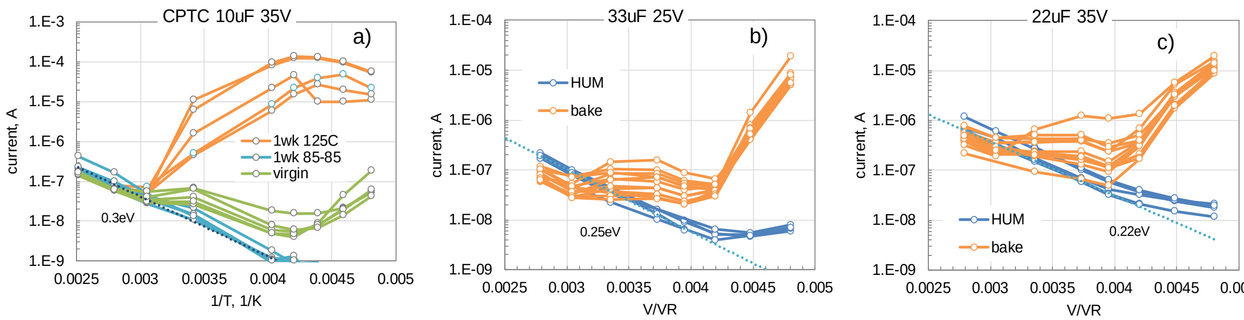
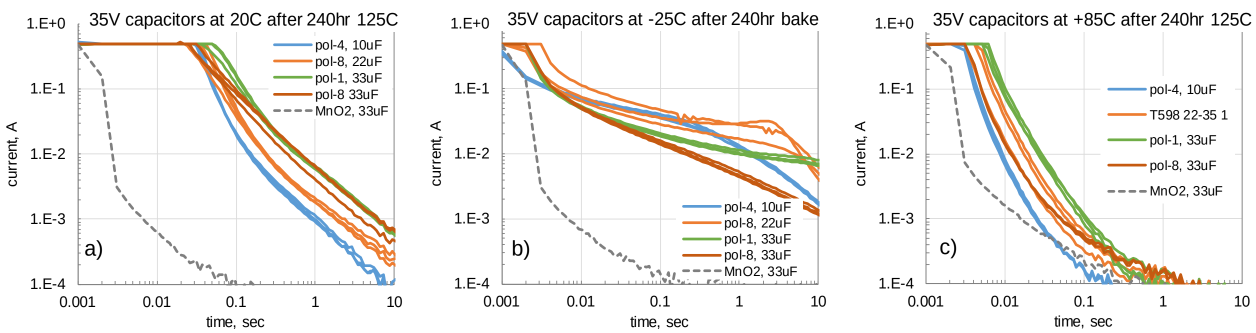


Figure 4. Arrhenius plots of leakage currents measured after 1000 sec of electrification for 10 µF 35 V (a), 33 µF 25 V (b), and 22 µF 35 V (c) capacitors preconditioned by bake and exposure to high humidity.

Similar to long-term, the medium-term transients measured at +20 ºC, -25 ºC, and +85 ºC for different types of dry 35 V and 6.3 V capacitors (Fig.5) also showed increasing currents at low temperatures. However, compared to long-term transients temperature variations depended strongly on the elapsed time. For example, 35 V capacitors at +20 ºC have currents above 0.5 A up to 30 msec. This time interval decreases to 2 to 5 msec at -25 ºC, and then increases to 4 to 8 msec at +85 ºC. The one-second currents increased several times as temperature decreased from 20 ºC to -25 ºC and almost an order of magnitude when it rises to +85 ºC. It is possible that different mechanisms control processes during short- and long-term relaxation. Results also indicated that different types of similar value capacitors might have substantially different transients.



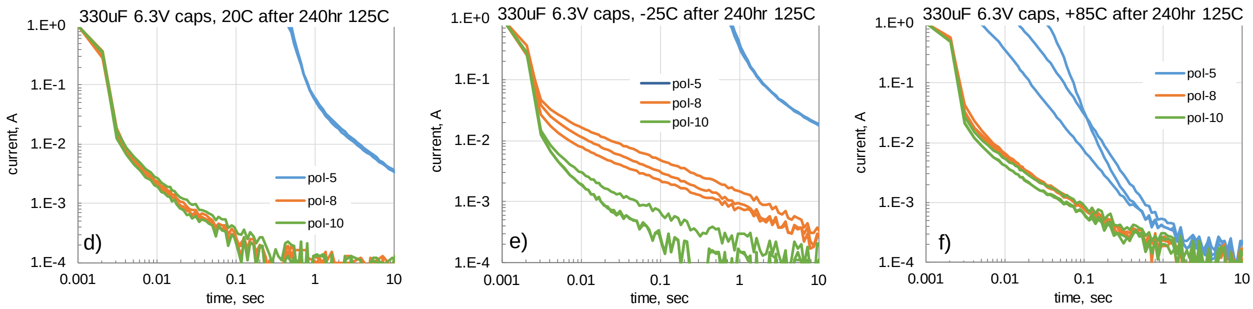


Figure 5. Medium-term transient currents in different types of capacitors rated to 35 V, type -1, type-4, and type-8 (a-c), and 6.3 V capacitors, type -5, type-8 and type-10, (d-f) at 20 ºC (a, d), -25 ºC (b, e), and +85 ºC (c, f).

Effect of Voltage

Results of surge current testing for 220 µF 16 V and 33 µF 35 V capacitors after high temperature storage (Fig. 6 a, b) showed that the amplitude of spikes that is controlled by displacement currents in the dielectric is similar for virgin and humidified capacitors and increased practically linearly with voltage. However, currents measured after a few milliseconds have a much sharper voltage dependence. Transient currents might exceed 1 A after 1 msec, which is currently used as a failure criteria for surge current testing for MnO2 capacitors in MIL-PRF-55365. Additional testing, during which the parts were stressed by 100 surge current cycles have shown that CPTCs with high 1 msec currents are not damaged, can withstand multiple cycling and operate normally under steady-state conditions.

Measurements of medium-term transients for other types of capacitors after HTS (Fig. 6 c–f) at different voltages also resulted in a sharp (orders of magnitude) increase of currents with voltage. Variations of currents measured after 100 msec with applied voltage (Fig.7) in all cases confirmed a near exponential dependence of currents with voltage. A reduction of voltage by 50% would reduce transient currents by approximately two orders of magnitude. This indicated that voltage derating is an effective means to constrain anomalous transients.

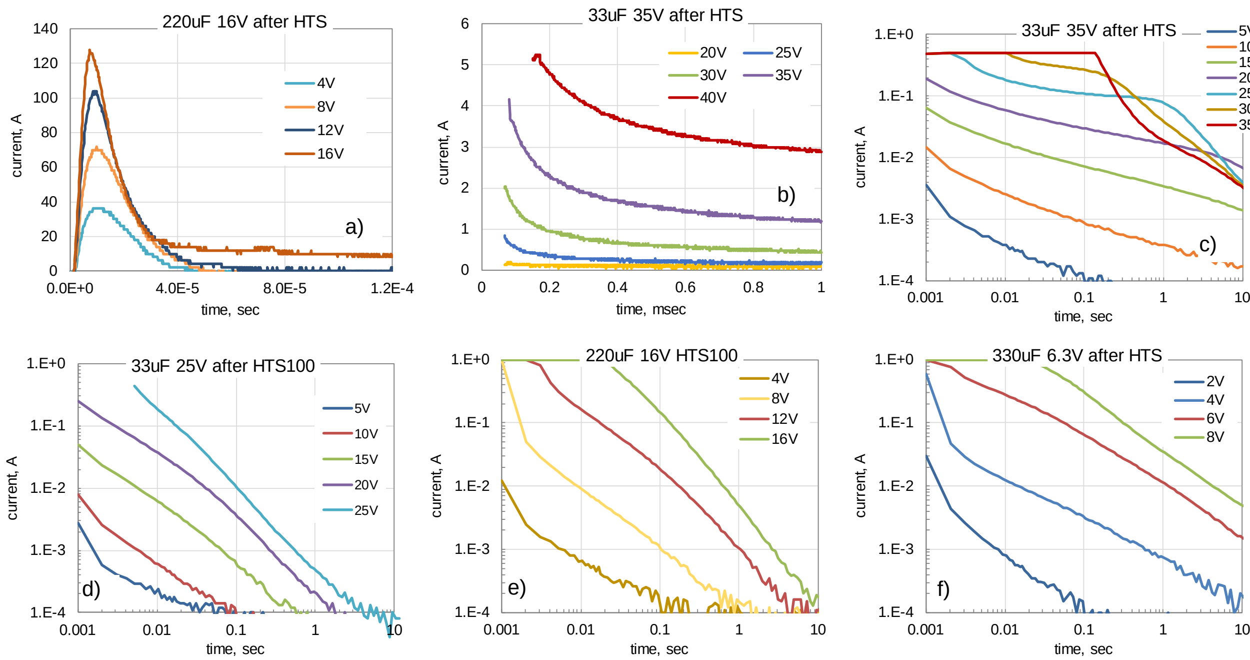


Figure 6. Effect of voltage on short-term (a, b) and medium-term (c-f) transient currents in different types of capacitors.

Note, that due to a relatively slow voltage rise during turning-on in most of power supplies, the shape of transients might differ from results shown above. Fig. 8 shows voltage and current transients in a 22 µF 25 V capacitor during turning-on of a 300V/5A Keysight model 5771A power supply. The first current maximum is observed in a few msec, has a linear dependence on voltage and can be explained by displacement currents in the capacitor. The voltage is stabilized after ~ 20 msec and at this time the currents have a secondary, much larger maximum that has a sharp voltage dependence and is likely due to the anomalous conductivity of the dielectric.

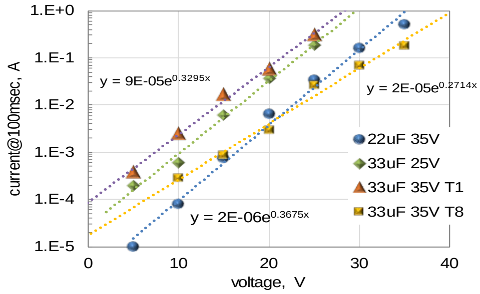


Figure 7. Voltage dependency of currents measured at 100 msec after step voltage application in different types of 35 V capacitors.

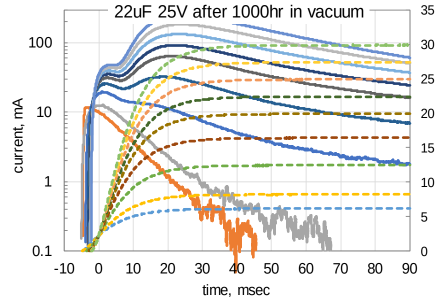


Figure 8. Transient currents in 22 μF 25 V capacitors after drying in vacuum for 1000 hours measured using a 300V/5A Keysight power supply model 5771A. Dashed lines correspond to voltage turn-on transients and solid lines to current transients.

An example of long-term transients in dry 22 μF 25 V capacitors at different voltages is shown in Fig.9. Currents measured at 10 sec and 25 V are approximately four orders of magnitude higher than at 5 V. However, this difference decreases with time under bias, and is about two orders of magnitude after 1 hour of electrification.

Temperature dependencies of leakage currents measured in dry 33 μF 25 V and 22 μF 35 V capacitors at different voltages (Fig. 10) indicate that as voltage decreased to 50% of the rated, anomalous currents at low temperatures decreased almost four orders of magnitude. This trend is especially evident in Fig.11 that shows voltage dependencies of leakage currents measured at -65 ºC. Leakage currents increased near exponentially with voltage in both, humidified and dry conditions, $I \sim e^{(\alpha \times V/VR)}$, where α is a constant. However, α remained constant for humidified capacitors in the whole range of voltages, from 0.2×VR to 1.2×VR, whereas a substantial increase in α occured for dry capacitors after ~ 0.6×VR. Note that at high temperatures (>~ 85 ºC) α does not change substantially in the whole range of voltages even in dry capacitors (Fig. 11c).

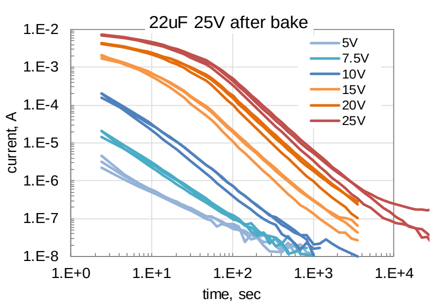


Figure 9. Relaxation of leakage currents at different voltages in 22 μF 25 V capacitors after bake.

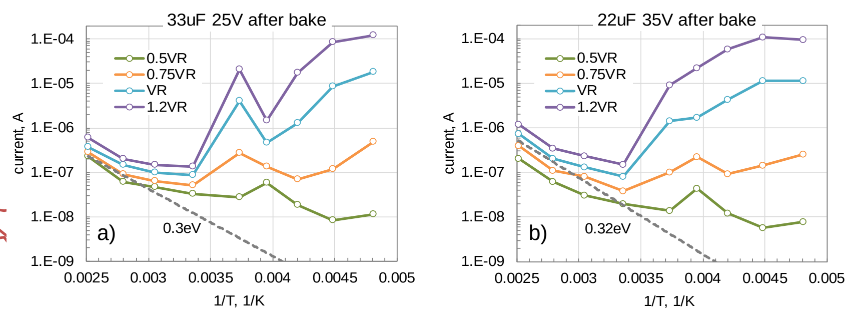


Figure 10. Temperature dependencies of leakage currents measured after 1000 sec of electrification in dry 33 μF 25 V (a) and 22 μF 35 V (b) capacitors at different voltages (0.5VR, 0.75VR, VR, and 1.2VR)

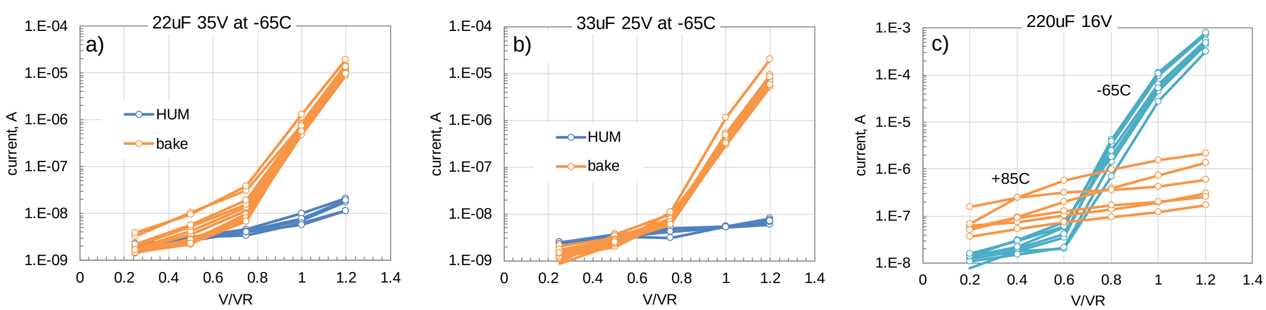


Figure 11. Voltage dependencies of leakage currents measured after 1000 sec of electrification for 22 μF 35 V (a), 33 μF 25 V (b), and 220 μF 16 V (c). (a, b) results at -65 ºC for parts with different preconditioning (bake at 125 ºC or humidification at 85 ºC, 85%RH). (c) results at 85 ºC and -65 ºC for dry capacitors.

Effect of Vacuum

Measurements of transient currents at different temperatures in capacitors dried by storing in vacuum for 2000 hours (Fig. 12) showed a significant change in the shape of transients, which is similar to air baking at 125 ºC. Alike to air baking, temperature dependences of transient currents differ for different elapsed times, but in all cases have a maximum that might be more than two orders of magnitude greater than currents at high or low temperatures (Fig.13). Contrary to CPTCs, currents in MnO2 capacitors increase gradually with temperature (Fig. 13 c).

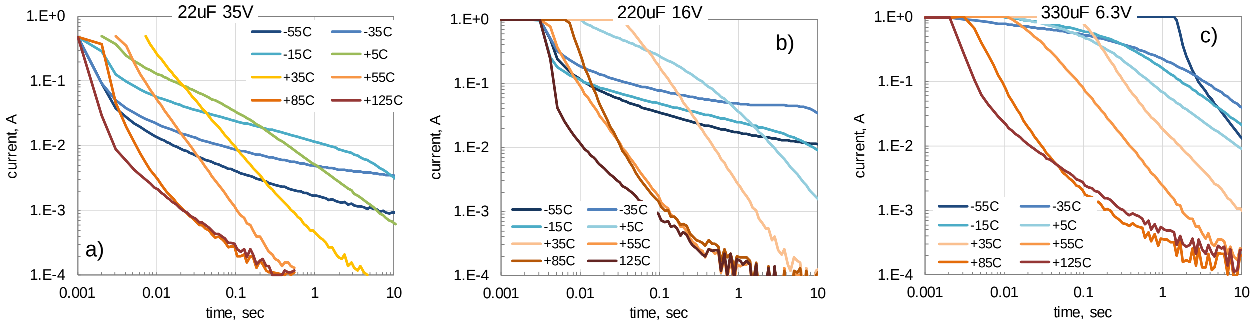


Figure 12. Medium-term transient currents in 22 μF 35 V (a), 220 μF 16 V (b), and 330 μF 6.3 V (c) capacitors after 2000 hours storage in vacuum. The transients were measured in the range of temperatures from +125 ºC to -55 ºC.

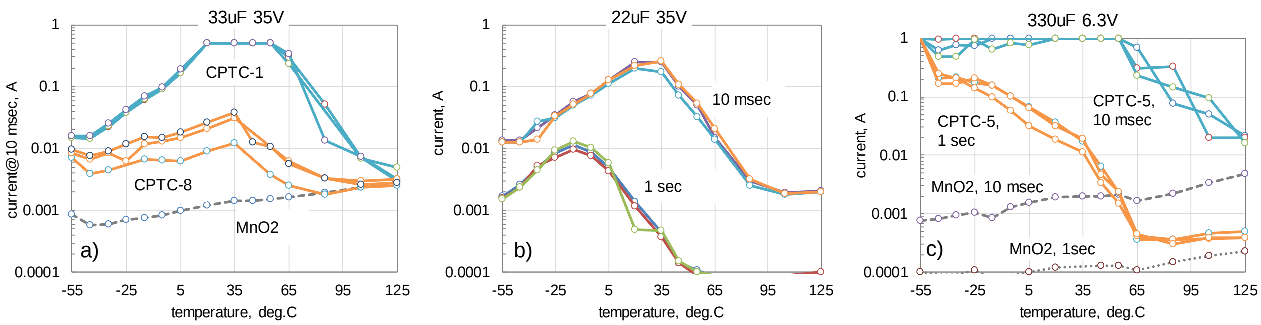


Figure 13. Temperature dependencies of currents measured after 10 msec (a) and after 10 msec and 1 sec (b, c) in different types of capacitors. Note, that currents for 33 μF 35 V capacitors (a) were clamped at 0.5 A and for 330 μF 6.3 V capacitors (c) were clamped at 1 A by the power supply.

Long-term (one-hour) transient currents in CPTCs measured in vacuum after 2000 hours of testing are shown in Fig. 14. In all cases, currents decreased gradually as temperature rose from -50 ºC to +85 ºC. In some part types, currents at temperatures from 0 to -50 ºC remained above 1 mA for up to 5 minutes and then gradually decreased to the microampere level after hours of electrification (Fig. 14 b, c). Note that MnO2 capacitors had much lower currents that slightly increased with temperature and decreased with time according to a power law indicating absorption processes at the MnO2/Ta2O5 interface.

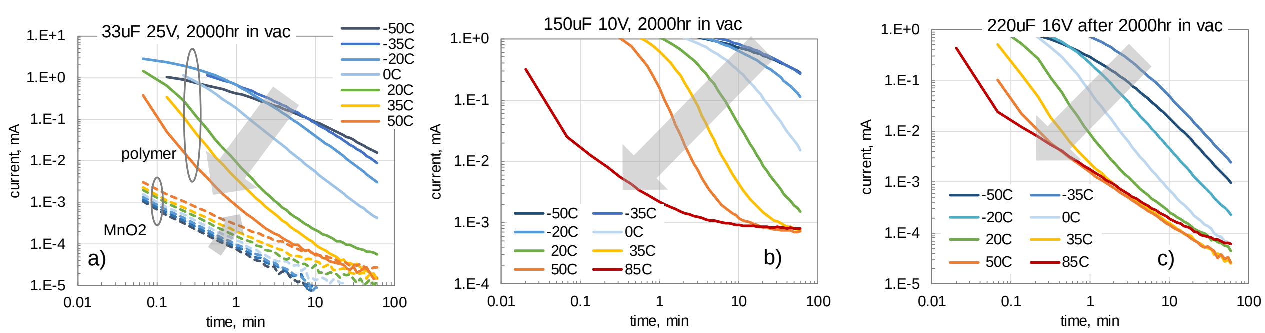


Figure 14. Long-term relaxation of leakage currents measured in vacuum after 2000 hours of testing at temperatures from +85 ºC to -50 ºC for 33 μF 25 V (a), 150 μF 10 V (b), and 220 μF 16 V (c) capacitors. Gray arrows indicate directions of temperature increase.

Transient currents measured at 20 ºC are changing with time of operation in vacuum. Storage in vacuum during 100 hours did not cause any significant variations in the transients (Fig. 15). However, a substantial increase of currents occurred after 610 hours, out of which the parts were at 85 ºC for 260 hours. The currents increased even more after 1100 hours in vacuum (700 hours at 85 ºC). At this condition, some parts (e.g 150 μF 10 V capacitors, Fig. 15 c) had currents exceeding 1 mA for more than 10 minutes.

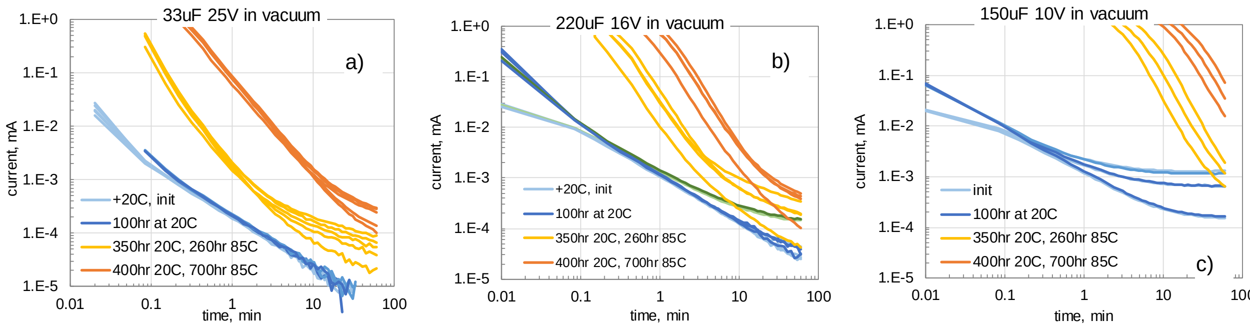


Figure 15. Long-term transient currents measured after different times during vacuum testing for 33 μF 25 V (a), 220 μF 16 V (b), and 150 μF 10 V (c) capacitors. The legends indicate accumulated times of exposure to vacuum at 20 ºC and 85 ºC.

Anomalies in AC Characteristics

AC characteristics of MnO2 capacitors are stable and contrary to ceramic capacitors, the values of capacitance (C), dissipation factor (DF), or ESR do not change with voltage. However, a voltage dependence of these characteristics for CPTCs changes substantially with preconditioning (Fig. 16). For dry capacitors, the values of C, ESR, and DF ($DF = \omega \times C \times ESR$) increased with voltage significantly (dozens of percent for capacitance and more than an order of magnitude for DF), whereas characteristics remained stable for humidified capacitors. Anomalous behavior of CPTCs is most evident at low frequencies and variations with voltage become negligible at $f > 10$ kHz (Fig. 17).

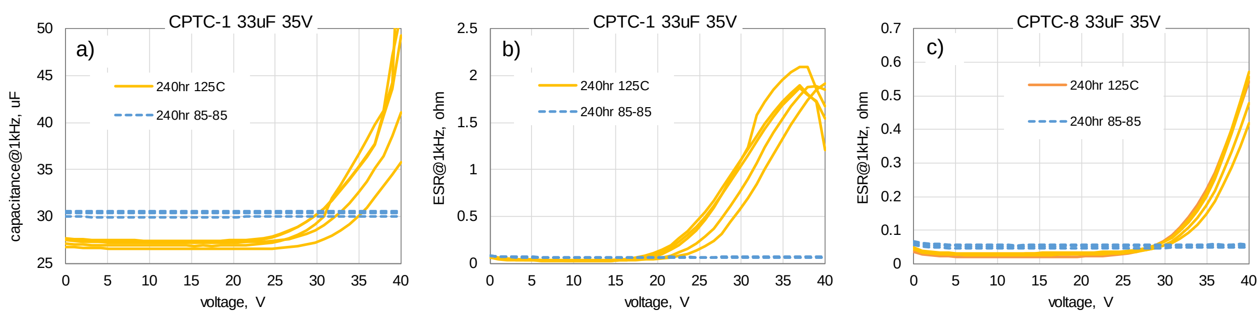


Figure 16. Voltage dependencies of capacitance (a) and ESR (b, c) measured at 1 kHz for 33 μF 35 V capacitors of type 1 (a, b) and type 8. Dotted lines correspond to capacitors humidified at 85 ºC 85% RH for 240 hours, and solid lines to capacitors baked at 125 ºC for 240 hours.

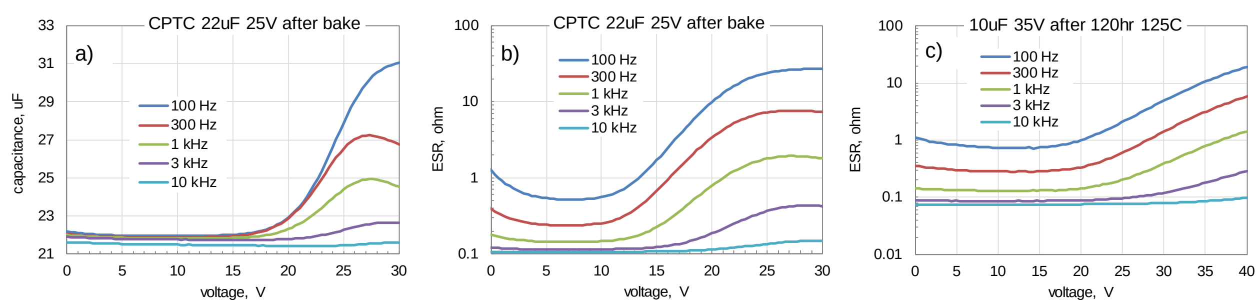


Figure 17. Voltage dependencies of capacitance (a) and ESR (b, c) measured at different frequencies (from 100 Hz to 10 kHz) for 22 μF 25 V (a, b) and 10 μF 35 V (c) capacitors after bake.

The values of AC characteristics measured in dry CPTCs changed with time under bias (Fig. 18) resulting in transients similar to current transients discussed above. Dissipation factors in dry CPTCs measured at 120 Hz and rated voltages exceeded substantially a typical limit of 10%, reaching up to 100% initially, but decreasing gradually with time under bias and stabilizing after dozens of minutes of testing. Note that this relaxation occured only at relatively high DC voltages, close to the rated, whereas unbiased dry capacitors or capacitors measured at 2.2 V as required by MIL-PRF-55365 specification have stable characteristics (Fig. 18 c).

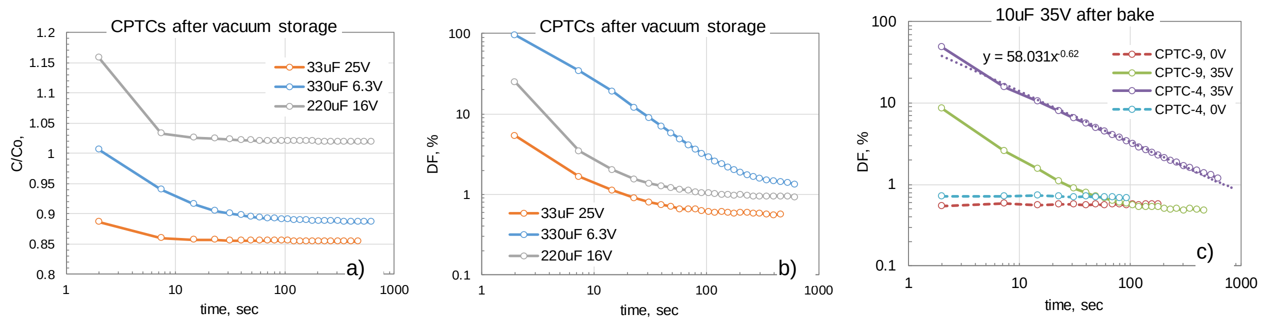


Figure 18. Relaxation of normalized capacitance (a) and dissipation factors (b, c) measured at 120 Hz in different types of capacitors after vacuum storage (a, b) and bake (c). Note, that charts (a, b) show characteristics measured at rated voltages whereas characteristics on chart (c) were measured for both, unbiased and biased capacitors.

Effect of Part Type

To reveal the effect of part types on anomalous transients, Fig.19 displays short-term and medium-term transients in different CPTCs that passed the same testing or the same preconditioning. For different part types at the same condition, the difference in transient currents can vary substantially, orders of magnitude, even within the same voltage group of capacitors. This difference might be attributed to variations in the process of oxide formation and treatment, or to differences in conductive polymers or processes of their application used by different vendors, or even by the same vendor but for different types of capacitors.

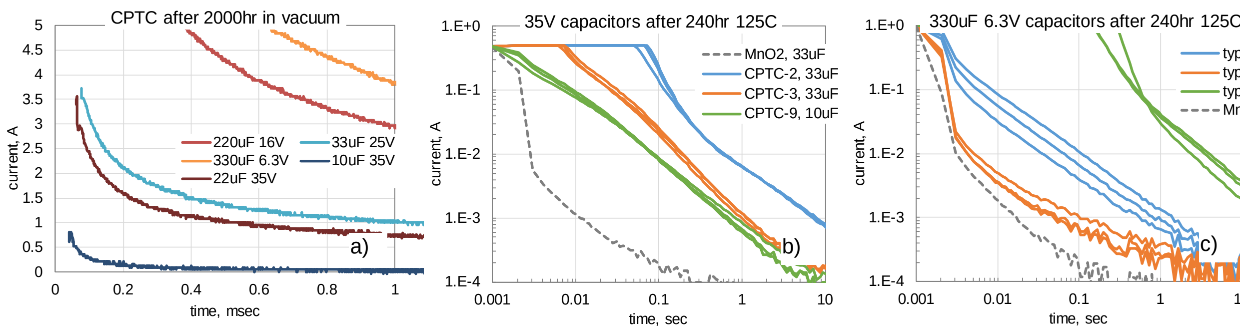


Figure 19. Short-term (a) and medium-term (b, c) transient currents in different types of capacitors after the same preconditioning.

The effect of the type of conductive polymers can be illustrated by comparing transients in 10 µF 35 V capacitors manufactured by AVX using their “standard” and “modified” polymers [2] and processes of application (Fig. 20). Samples with modified polymers had practically no anomalous transients and behaved after bake similar to the parts after humidification. Long-term testing in vacuum confirmed that a substantial improvement in quality of CPTCs can be achieved by a proper selection of materials and processes of their application.

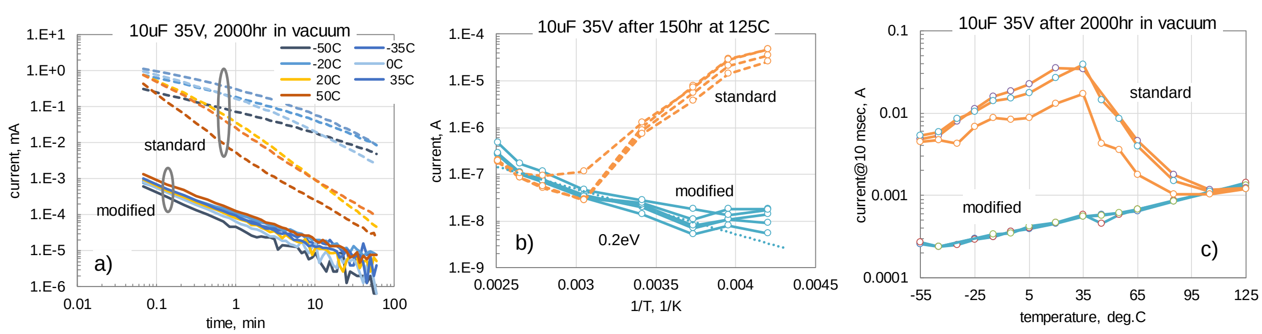


Figure 20. Transient currents after 2000 hours operation in vacuum (a) and temperature dependencies of currents measured after 1000 sec (b) and 10 msec (c) of electrification for two groups of dry 10 µF 35 V capacitors having different types of conductive polymers, one is a standard and another was modified to reduce anomalous transients.

Effect of HALT

So far, we considered mostly the effect of unbiased storage of CPTCs at high temperatures. To verify that anomalous transients can occur also after high-temperature biased operation, transient currents were measured in several types of CPTCs after highly accelerated life testing (HALT) carried out at rated voltages and 165 ºC for 200 hours. After HALT, the parts were depolarized for one hour, and then leakage currents were monitored with time at room temperature. Fig. 21 shows results of these testing. Behavior of CPTCs during HALT (Fig 21 a-c) is similar to what was observed for MnO2 capacitors [8]; an initial decrease of currents that is due to absorption processes is followed by a stabilization period with currents determined by intrinsic conduction of the dielectric. By the end of testing, currents are increasing most likely due to redistribution of oxygen vacancies and modification of the barrier at the MnO2/Ta2O5 interface. Note that testing of CPTCs at high temperatures did not result in short circuit failures thus indicating a high reliability of the parts under steady-state bias conditions.

Currents measured at room temperature after HALT during first few minutes exceeded by orders of magnitude the level of currents at 165 ºC and then decreased two (Fig. 21e) to four orders of magnitude (Fig. 21d) after 10 hours of electrification. This behavior can be explained by anomalous transients similar to the effect of unbiased storage at high temperatures.

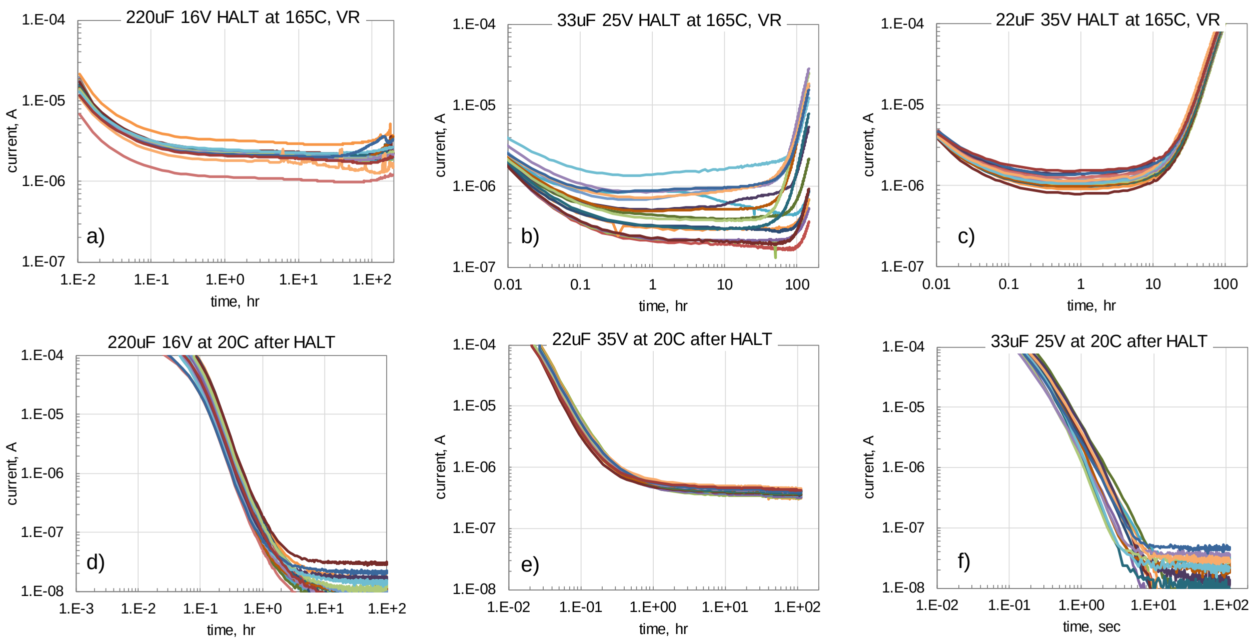


Figure 21. Variations of leakage currents with time during HALT at 165 ºC and rated voltages (a-c) and post-HALT relaxation of currents at room temperature measured after 1 hour of depolarization (d-f) for 220 µF 16 V (a, d), 33 µF 25 V (b, e), and 22 µF 35 V (c, f) capacitors.

DISCUSSION

Results of testing described above can be summarized as follows.

- Anomalous transients can occur in low-voltage that are typically using a hybrid technology, as well as in high-voltage polymer tantalum capacitors that might be manufactured using pre-polymerized PEDOT:PSS polymers only, and can be observed in a wide range of times, from milliseconds to hours. The major factor that affects transients is moisture content in polymers, which is consistent with works carried out by AVX [9] and KEMET [5]. More analysis is necessary to determine kinetics of moisture sorption and desorption in CPTCs at different temperatures. However, existing data indicate that substantial changes in the moisture content occur during baking for more than 100 hours at 125 ºC or by exposure to vacuum at relatively low temperatures (20 ºC to 85 ºC) for more than 1000 hours.
- No high currents during transients were observed in dry CPTCs at temperatures above ~ +65 ºC, but currents increased substantially (up to 6 orders of magnitude) at low temperatures, in the range from +20 ºC to -65 ºC. Temperature dependencies of transient currents have a maximum, position of which depends on moisture content and elapsed time under bias.

- CPTCs exhibiting anomalous transient currents have anomalies in AC characteristics measured under bias. In particular, application of rated voltage increased capacitance up to dozens of percent and DF or ESR up to 2 orders of magnitude. These variations were especially noticeable at relatively low frequencies (below 10 kHz) and similar to leakage currents, C and DF gradually decreased with time under bias.
- Different part types with similar ratings can have substantially different transient currents after drying. A proper selection of conductive polymers and processes of application can suppress anomalous transients substantially.
- Anomalous transient phenomena are observed in CPTCs only, and because MnO2 cathode capacitors do not exhibit these phenomena, the existing system of screening and qualification used for MnO2 military grade tantalum capacitors requires additional tests to constrain transients of DC and AC characteristics to the acceptable level.

Mechanisms of anomalous transient currents

Anomalous charging currents were explained in [5] by reorientation of polar macromolecules comprising conductive polymers. This reorientation of the polymer chains under pulse field results in building up of charges at the polymer/Ta2O5 interface that changes the barrier height at the interface with time and respectively, the charge transport through the dielectric. Moisture plays a role of a plasticizer allowing for a faster and to a greater degree reorientation of dipoles under the field, thus eliminating anomalous charging in wet capacitors. In dry capacitors, relaxation occurs much slower and results in significant charging currents. Temperature can also change the mobility of polymer chains, so at low temperatures dipole reorientation occurs much slower, which explains larger charging currents.

The resistivity of conductive polymers is likely more than nine orders of magnitude less than of Ta2O5 dielectric, so the voltage applied to a capacitor drops mostly across the dielectric, and the electric field in the polymer is negligibly small except for initial moments after step voltage application. These initial moments are associated with displacement currents and are significant during likely less than 100 μsec, so a field that might polarize polymer chains exists for a very short period of time and in the shell area around the slug only. This does not explain experimentally observed transients after minutes and hours of electrification and decreasing of transient currents after reaching maximum when the temperature decreases to lower values.

PEDOT:PSS polymers are highly hygroscopic and even at room conditions free films can absorb up to 25% of water resulting in a substantial swelling [10, 11]. At a higher humidity (95% RH) the sorption might increase to 87% and contraction caused by loss of water during heating might reach 4.5%. This effect indicates substantial structural changes in polymers and results in changes of most mechanical [12] and electrical [13] characteristics of the films. There are even attempts to use it for development of actuators or artificial muscles [13].

Changes in the microstructure of PEDOT:PSS films with temperature and moisture content has been studied in [10] by using electronic and atomic force microscopy combined with electron energy loss spectroscopy. Results confirmed that PEDOT:PSS is a granular material with a core-shell structure of the grains. The conductive core is a PEDOT-rich nanocrystal and the isolative shell has a PSS-rich composition. An average diameter of the grain is from 30 to 60 nm, and the shell thickness is of 5-10 nm. Low temperatures (-177 ºC) induce structural changes in PEDOT:PSS grains resulting in practically disappearing of the core-shell structure likely due to a reduction of concentration of PSS in the shell compared to room temperature. At room temperature, swelling by water sorption reduces the conductivity of the film, but at high temperatures (100 ºC) the water concentration is reduced and PEDOT:PSS grains became connected to each other and the boundaries are overlapping. Water removal changes interconnection of PSS chains by increasing hydrogen bonding between the adjacent PSS chains (inter-molecular) or within different parts of the same chain (intra-molecular) resulting in a better interconnection of the grains and increasing conductivity of the polymer.

It is quite possible that variations in the microstructure of PEDOT:PSS due to the effect of both external factors, moisture content and temperature, are also causing changes in the band structure of the polymer. Shifting positions of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) might change currents in CPTCs by changing the barrier height at the interface similar to the PEDOT:PSS/SiO2/Si structure considered in [14]. This hypothesis is supported by direct measurements of the work function in PEDOT:PSS films using scanning Kelvin probe microscopy in [11]. The removal of water and sorbitol (a solvent that was used to increase conductivity of the polymer) during annealing enabled rearrangement of PEDOT and PSS clusters to a more compact morphology. The work function decreased from 5.1 eV in pristine PEDOT:PSS sample to 4.8 – 4.9 eV after sorbitol treatment. The effect was attributed to a removal of the PSS-rich surface layer that exists in pristine PEDOT:PSS films.

Reduction of currents with time during transients might be due to changes in the electronic structure of polymers caused by injection of electrons and holes similar to the processes occurring in organic memory elements employing PEDOT:PSS polymers [15, 16]. Electrons injected into the polymer film lead to reduction of the oxidized PEDOT:PSS chains and can cause substantial increase in the resistivity of the film and also change the barrier at the polymer/Ta2O5 interface.

A review of literature data shows that conductive polymers in CPTCs under electrical and environmental stresses might experience a wide range of chemical and electrochemical reactions that affect the structure of the polymer and cathode-dielectric interface. The latter is likely responsible for the anomalous transients in polymer capacitors. A further analysis is necessary to get a better understanding of the mechanism of these phenomena.

C-V and Transient AC Characteristics

Increased conductivity of Ta2O5 in dry polymer capacitors is likely responsible for anomalies in AC characteristics under bias. A simple C-R-r model of a capacitor can be used to illustrate the effect of high conductivity of the dielectric. Let us consider a circuit having a resistor *r* connected in series with a capacitor C_0 and a resistor *R* connected in parallel to C_0 and representing conductivity of the dielectric. The values of experimentally measured capacitance and ESR at a frequency ω can be calculated as:

$$C = C_0 \times \left[1 + \frac{1}{(R\omega C_0)^2}\right], \qquad ESR = r + \frac{R}{1 + (\omega CR)^2} \qquad (1)$$

For a typical case of a capacitor having C_0 = 100 μF and *r* = 0.1 or 0.01 ohm, frequency variations of *C* and ESR are shown in Fig. 22. At 100 Hz capacitance increases noticeably at resistances *R* below ~ 100 ohm, and ESR rises more than an order of magnitude for *r* = 0.1 ohm and more than 2 orders of magnitude for *r* = 0.01 ohm. Note that currents of more than 1 A during anomalous transients in 6.3 to 35 V capacitors correspond to values of *R* in the range from below 6 to below 35 ohm. This model shows that variations of ESR (or DF) are more sensitive compared to variations of *C*, and the effect is more significant at low frequencies. It also explains the presence of maximum on ESR – V characteristics for dry capacitors.

Temperature Transients and Reliability under Power Cycling

A substantial amount of power that is dissipated in a part during anomalous transients results in temperature spikes. Fig. 23 displays temperature transients in a 330 μF 6.3 V capacitor detected by an infrared camera. A temperature spike exceeded 50 ºC less than a second following voltage application. An insert shows an oscillogram of the voltage and current variations during the test and indicates that the currents exceeded 2 A during first 250 msec. It is possible that due to a relatively low rate of sampling (~ 30 msec) the actual temperature rise occured faster and reached higher values.

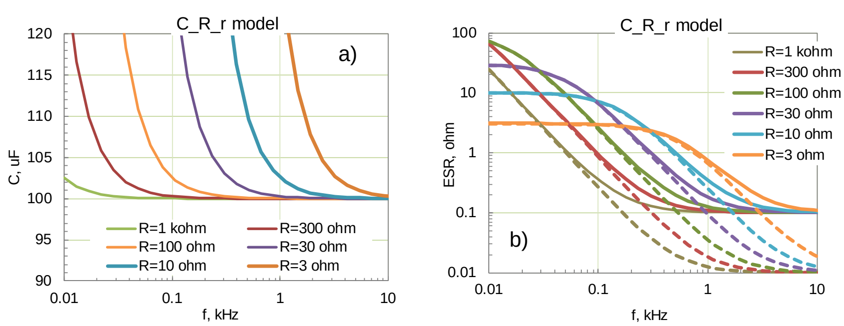


Figure 22. Frequency dependencies of capacitance (a) and ESR (b) for a 100 μF capacitor having ESR = 0.1 ohm (solid lines) or 0.01 ohm (dashed lines) at different levels of leakage currents representing by resistance R connected in parallel with the capacitor. The data are calculated per Eq. (1).

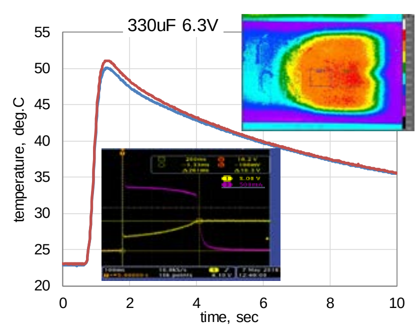


Figure 23. Variations of temperature in a 330 μF 6.3 V capacitor during transients. Inserts show *I-t* and *V-t* characteristics and a temperature distribution on the surface.

Considering that during transients the current remains high for a relatively short period of time, *Δt*, and most dissipated energy remains in the slug, we can use an adiabatic assumption to estimate the temperature rise:

$$\Delta T = \frac{I \times V \times \Delta t}{c \times m} \qquad (2)$$

where, *V* and *I* are voltage and current in the capacitor, *c* = 140 J/(K-kg) is the specific heat capacity, and *m* is the mass of the slug. At *m* ~ 0.1 g, calculations yield *ΔT* ~ 180 ºC.

The actual temperature rise will be less than the calculated rise due to the heat release through the leads, but temperature spikes up to 100 ºC can be expected. These spikes might create substantial thermo-mechanical stresses in the part and cause cracking of the dielectric, which is a reliability concern. Power cycling test following baking of the parts might be necessary for capacitors operating in power systems under cycling conditions. The power supply for this testing should allow a sharp, less than a millisecond, voltage rise at loaded conditions.

SUMMARY

1. Anomalous transients in CPTCs after step voltage application include:
   a. Ampere-level currents for up to dozens of milliseconds resulting in a temporary shorting of the part. High dissipated power during transients results in temperature spiking that might create significant thermo-mechanical stresses in the slug and affect reliability of CPTCs.
   b. Anomalous temperature dependence of leakage currents measured after minutes of electrification when currents are increasing more than 3 to 4 orders of magnitude at low temperatures reaching maximum in the range from -10 ºC to -60 ºC.
   c. Increasing capacitance and ESR with voltage at low frequencies (below 10 kHz).
   d. A gradual relaxation of a dissipation factor measured under bias from more than 10% initially to below 1% after several minutes of electrification.
2. Anomalous transients can be observed in low-voltage (rated to 6.3 V and 10 V) and high-voltage (>10 V) capacitors in dry conditions, e.g. after long-term exposure to vacuum or baking at 125 ºC for more than 100 hours. Moisture sorption, e.g. exposure to 85% RH at 85 ºC for a few days, practically eliminates anomalous transients and humidified CPTCs behave similar to MnO2 capacitors.
3. The level of transients depends on the type of capacitors even for parts with the same rating. A proper selection of polymers as a cathode material and optimization of application conditions might practically eliminate anomalies in behavior of CPTCs.
4. The increase in conductivity of Ta2O5 dielectric in dry CPTCs is most likely due to structural changes in PEDOT:PSS polymers that are strongly affected by temperature and the moisture content. Both factors result in variations in the core-shell structure of the polymer and interactions between the grains that affect electronic structure of the polymer and the barrier height at the polymer/Ta2O5 interface. Injection of electrons and holes under bias might further change the barrier by oxidation/reduction reactions in the polymer resulting in a gradual decrease of leakage currents with time.
5. Anomalies in behavior of AC characteristics are due to increased conductivity of the oxide during initial moments after step voltage application. This behavior can be explained using a simple C-R-r model of capacitors with leakage.
6. Anomalous transients are most noticeable during sharp voltage rise and might not affect performance of CPTCs in applications when power turning-on occurs relatively slowly. Polymer tantalum capacitors can be used in space applications at the following conditions:
   a. circuit designers and parts engineers are aware of potential anomalies in behavior of CPTCs;
   b. a 50% voltage derating is applied;
   c. the level of anomalous transients is limited by special screening and qualification procedures.

Recommendations

1. Surge current testing (SCT).
   This test for MnO2 capacitors is used to reveal and screen-out weak parts that can fail short circuit. SCT for polymer capacitors should be used to select parts with the acceptable level of transient currents. The existing MIL-PRF-55365 requirements limiting maximum current after 1 msec can be used for CPTCs. The acceptance level can be set in the range from 0.5 to 1 A. As a part of gr. B testing, this test should be carried out at room and -55 ºC after baking of the parts (168 hours at 125 ºC).
2. Stability at low and high temperatures.
   Leakage currents in MnO2 capacitors are decreasing substantially at low temperatures, and for this reason, DCL measurements at -55 ºC are not required. In dry CPTCs, leakage currents can increase orders of magnitude at low temperatures and for this reason, DCL should be measured at low temperatures after baking as a gr. B of testing. Considering that DCL can have maximum at temperatures lower than -55 ºC, additional measurements should be carried out at -25 ºC.
3. Biased AC characteristics.
   Contrary to MnO2 parts, capacitance, and especially dissipation factor, in dry CPTCs can increase substantially with DC bias. Stability of *C* and *DF* should be controlled by delta analysis between 2.2 V and rated voltage. These measurements should be carried out as a gr.B test after baking. Acceptable lots should have $\Delta C/C_0$ < 20% and $\Delta DF/DF_0$ < 100%.
4. Qualification tests.
   SCT and biased AC characteristics should be measured within 24 hours after life testing (following 1 hour depolarization) and after high temperature storage test (2000 hr at 125 ºC).

ACKNOWLEDGMENT

This work was sponsored by the NASA Electronic Parts and Packaging (NEPP) program. The author is thankful to Michael Sampson, NEPP Program Manager, for support of this investigation and discussions, Bruce Meinhold, ASRC Federal Space and Defense, Group Lead, for a review and recommendations.

REFERENCES.

[1] 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

[2] M. Weaver, "Attributes and Challenges of Polymer Electrolytic Capacitors in High Reliability Applications, AVX " in *Components for Military and Space Electronics, CMSE'18*, Los Angeles, CA, 2018, pp. 3-2.

[3] J. Young, "Polymer Tantalum Capacitors for Automotive Applications," in *CARTS International*, Santa Clara, CA, 2014, pp. 297-311.

[4] 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.

[5] Y. Freeman, G. F. Alapatt, W. R. Harrell, I. Luzinov, P. Lessner, and J. Qazi, "Anomalous Currents in Low Voltage Polymer Tantalum Capacitors," *Ecs Journal of Solid State Science and Technology*, vol. 2, pp. N197-N204, 2013.

[6] A. Teverovsky, "Leakage currents and gas generation in advanced wet tantalum capacitors," NASA/GSFC, Greenbelt, MD, 2015.

[7] A. Teverovsky, "Insulation Resistance and Leakage Currents in Low-Voltage Ceramic Capacitors With Cracks," *Components, Packaging and Manufacturing Technology, IEEE Transactions on*, vol. 4, pp. 1169-1176, 2014.

[8] A. Teverovsky, "Degradation of leakage currents in solid tantalum capacitors under steady-state bias conditions," in *Electronic Components and Technology Conference (ECTC), 2010 Proceedings 60th*, 2010, pp. 752-757.

[9] J. Petrzilek, M. Biler, and T. Zednicek, "Hermetically Sealed Conductive Polymer Tantalum Capacitors," in *CARTS International*, Santa Clara, CA, 2014, pp. 287-292.

[10] J. Zhou, D. H. Anjum, L. Chen, X. Z. Xu, I. A. Ventura, L. Jiang, *et al.*, "The temperature-dependent microstructure of PEDOT/PSS films: insights from morphological, mechanical and electrical analyses," *Journal of Materials Chemistry C*, vol. 2, pp. 9903-9910, 2014.

[11] A. M. Nardes, M. Kemerink, M. M. de Kok, E. Vinken, K. Maturova, and R. A. J. Janssen, "Conductivity, work function, and environmental stability of PEDOT : PSS thin films treated with sorbitol," *Organic Electronics*, vol. 9, pp. 727-734, Oct 2008.

[12] U. Lang, N. Naujoks, and J. Dual, "Mechanical characterization of PEDOT:PSS thin films," *Synthetic Metals*, vol. 159, pp. 473-479, 3// 2009.

[13] H. Okuzaki, K. Hosaka, H. Suzuki, and T. Ito, "Electrically driven PEDOT/PSS actuators," 2010, pp. 76422U-76422U-8.

[14] S. Demtchenko, N. G. Tarr, and S. McGarry, "Effect of PEDOT band structure on conductive polymer-insulator-silicon junctions," *Journal of Applied Physics*, vol. 122, p. 065502, 2017.

[15] L. M. Y. Yang, J. Ouyang, J. He, H. M. Liem, C.-W. Chu, A. Prakash, "Organic Nonvolatile Memories," in *Materials for Information Technology : Devices, Interconnects and Packaging*, C. W. a. T. M. E. Zschech, Ed., ed: Springer, 2006.

[16] S. Smith and S. R. Forrest, "A low switching voltage organic-on-inorganic heterojunction memory element utilizing a conductive polymer fuse on a doped silicon substrate," *Applied Physics Letters*, vol. 84, pp. 5019-5021, Jun 2004.