Evaluation of Polymer Hermetically Sealed Tantalum Capacitors

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List of Acronyms and Symbols

<table>
<thead>
<tr>
<th>AC</th>
<th>Alternative current</th>
<th>HV</th>
<th>high voltage</th>
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<tbody>
<tr>
<td>AF</td>
<td>Acceleration factor</td>
<td>LF</td>
<td>Low frequency</td>
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<tr>
<td>CCS</td>
<td>Constant current stress</td>
<td>LV</td>
<td>low voltage</td>
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<tr>
<td>CCS</td>
<td>Constant current stress</td>
<td>PEDOT</td>
<td>poly 3,4-ethylenedioxythiophene</td>
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<tr>
<td>DC</td>
<td>Direct current</td>
<td>PHS</td>
<td>polymer hermetically sealed</td>
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<tr>
<td>DCL</td>
<td>Direct current leakage</td>
<td>PWB</td>
<td>Printed wiring board</td>
</tr>
<tr>
<td>DLA L&amp;M</td>
<td>Defense Logistics Agency Land &amp; Maritime</td>
<td>RB</td>
<td>reverse bias</td>
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<tr>
<td>ESR</td>
<td>Equivalent series resistance</td>
<td>RBS</td>
<td>reverse bias stress</td>
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<tr>
<td>FIT</td>
<td>failure in time (10^9 device-hours)</td>
<td>RT</td>
<td>Room temperature</td>
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<tr>
<td>FR</td>
<td>Failure rate</td>
<td>R_{th}</td>
<td>thermal resistance</td>
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<tr>
<td>HALT</td>
<td>highly accelerated life test</td>
<td>S&amp;Q</td>
<td>screening and qualification</td>
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<tr>
<td>HF</td>
<td>High frequency</td>
<td>VBR</td>
<td>Breakdown voltage</td>
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<tr>
<td>HTS</td>
<td>high temperature storage</td>
<td>VR</td>
<td>Rated voltage</td>
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Abstract

Polymer cathode tantalum capacitors have lower ESR compared to other types of tantalum capacitors and for this reason have gained popularity in the electronics design community. Their use allows improved performance of power supply systems along with substantial reduction of size and weight of the components used. However, these parts have poor thermal stability and can degrade in humid environments. Polymer hermetically sealed (PHS) capacitors avoid problems related to environmental degradation of molded case parts and can potentially replace current wet and solid hermetically sealed capacitors. In this work, PHS capacitors manufactured per DLA LAM DWG#13030 are evaluated for space applications. Several lots of capacitors manufactured over period from 2010 to 2014 were tested for the consistency of performance, electrical and thermal characteristics, highly accelerated life testing, and robustness under reverse bias and random vibration conditions. Special attention was given to analysis of leakage currents and the effect of long-term high temperature storage on capacitors in as is condition and after hermeticity loss. The results show that PHS capacitors might be especially effective for low-temperature applications or for system requiring a cold start-up. Additional screening and qualification testing have been recommended to assure the necessary quality of capacitors for space projects.
Outline

- Introduction.
  - Benefits and drawbacks of polymer tantalum capacitors.
  - Literature review.
- Design.
  - Results of construction analysis.
  - Results of X-ray examinations.
- Specification
  - DLA DWG#13030.
  - Comparative analysis of wet and PHS capacitors.
- AC characteristics.
- DC characteristics.
  - Absorption and leakage currents at different voltages and temperatures.
  - Breakdown voltages and self-healing.
  - Comparison of DCL and VBR in wet and polymer capacitors.
- Thermal resistance.
- Random vibration testing.
- Effect of reverse bias.
- Effect of high temperature storage.
- Degradation of leakage currents at high temperatures.
- Recommendations.
- Summary.
Introduction: Benefits and Problems with Polymer Chip Tantalum Capacitors

Benefits of polymer cathode compared to MnO2 cathode tantalum capacitors:
- Low ESR and extended range of operating frequencies that allows for lower low power dissipation and higher ripple currents (The conductivity for PEDOT used as a cathode layer is in the range of 100 to 1,000 S/cm, while MnO2 is in the range of 1 to 10 S/cm) [1];
- Failures under surge current without ignition. For this reason manufacturers are suggesting only 80% voltage derating compared to 50% in MnO2 parts [2].
- It is assumed that MnO2 might cause more damage to Ta2O5 dielectric compared to softer, polymer cathodes [3] resulting in more robust components when using polymer.

Drawbacks of chip polymer tantalum capacitors:
- Although self-healing in polymer capacitors is possible due to a thermal breakdown of polymer [1], it is likely not as effective as in MnO2 capacitors;
- Unstable behavior and failures during testing at 85%RH/85°C and at T > 105°C that is related to the degradation of conductive polymers in the presence of moisture and oxygen [4, 5, 6].
- Increased leakage currents that might be related to insufficient self-healing [1];
- Polymer capacitors are specified to allow a much higher DCL limit compared to MnO2 capacitors. This might allow defective parts to pass the screening.
- ESR might increase substantially after soldering.

Use in hi-rel applications:
- Due to failures of MnO2 capacitors experienced by Raytheon and acceptable results of testing of polymer capacitors [7], DLA LAM issued drawings #04051 and 04052 for polymer chip capacitors.
- KEMET plans to start manufacturing automotive grade chip polymer capacitors [22].

Factors limiting applications of polymer capacitors for space projects:
- Sensitivity of conductive polymers to humid and high temperature environments that limits application of accelerated testing;
- Effects of long-term storage and/or operation in vacuum are unknown;
- No sufficient data on long-term reliability.
Introduction: Specifics of Polymer Tantalum Capacitors

- Low-voltage and high-voltage capacitors.
  - Historically, first polymer capacitors (late 1990’s) were manufactured using in-situ polymerization of PEDOT (poly 3,4- ethylenedioxythiophene) by chemical reaction between the oxidizer and monomer [22]. The parts had lower ESR than MnO2 capacitors, but much larger leakage currents and smaller breakdown voltages. Capacitors with cathodes formed by in-situ polymerization were found to be susceptible to anomalously high transient currents [8].
  - It is assumed that in-situ polymerization resulted in formation of defects and oxygen vacancies in the Ta2O5 film near to the Ta2O5/PEDOT interface [9]. A significant increase in VBR and reduction of DCL were achieved with the use of a pre-polymerized PEDOT suspensions. Implementation of this process in 2009 allowed for manufacturing of reliable high-voltage capacitors with low leakage currents [10].
  - Currently, HV capacitors (VR ≥ 16V) are manufactured with pre-polymerized PEDOT, while in-situ polymerization is used for LV parts (VR < 16V) [10].
  - Different types of conductive polymers or additives might be used in different part types by different vendors.
  - AVX and KEMET, are in the process of development high-voltage (up to 125V) polymer capacitors that can operate reliably at high temperatures (above 125°C) [10, 11].
Wear-out failures.

- Paulsen [12] observed wear-out failures in polymer tantalum capacitors and demonstrated the applicability of the Prokopowicz and Vaskas model for accelerated testing of these parts. Experiments show that the exponent $n$ ranged from 10.5 to 19. The $E_a$ was from 1.75 eV for $V = VR$ to 1.25 eV for $V = 2.2VR$.
- Reed [13] also observed a decrease of $E_a$ from 1.75 eV at $VR$ to 1.1 eV at 1.8$VR$ for 100 $\mu$F, 6 V polymer capacitors. The results were explained by oxygen-ion migration in the anodic oxide.
- HALT testing of 35V capacitors [14] showed that the voltage acceleration constant $18 < n < 24$ and activation energies decreasing from 1.37 eV at 1.8$VR$ to 0.87 eV at 2.1$VR$. The model predicts a median life beyond 1000 years under normal application conditions.

Failure rate assessment.

- Due to low probability of failures, the assessment of failure rate using Weibull grading test per MIL-PRF-55365 is not effective [15].
- A new FR assessment strategy developed by KEMET includes:
  - Reflow-mounting of disposable samples;
  - Testing under accelerated conditions to validate the target failure rate;
  - Sample size, accelerated test conditions, test duration, and failure criteria are chosen to matched the specific part type using equations based on the wearout mechanism.
- Unfortunately, this approach does not address the possibility of IM or random failures.
Potential Benefits of PHS Capacitors and Purpose of this Work

- Hermetically sealed capacitors should have all benefits of chip polymer capacitors, (except for size and weight) but should not be sensitive to soldering stresses and humid or vacuum conditions.
- PHS have smaller ESR and less weight (more than 20%) compared to similar size wet tantalum capacitors.
- KEMET has completed 10 khr life testing for 90 PHS capacitors at 85°C, VR without failures. At 60% confidence level this corresponds to a low failure rate of 1 FIT [8].
- DLA LAM drawing #13030 has been developed based on KEMET commercial T550 series to assure a better consistency in quality of the parts.
- AVX have demonstrated high reliability of their version of hermetic polymer capacitors, TCH series, that is manufactured using Q-process and passed 10 khr life and 85°C/85% RH testing [11]. AVX recommends this part for space applications.
- KEMET and AVX are using different types of polymers, cases, and different approaches to control moisture level inside the case.

The purpose of this work is:
- Evaluate design and performance of KEMET PHS capacitors in comparison with wet capacitors;
- Assess performance of the parts over a vide range of temperatures, under reverse bias, random vibration, and high temperature storage.
- Evaluate performance of the parts in case of hermeticity loss.
- Review DWG#13030 and based on analysis of design and performance of the parts recommend additional tests, if necessary, for capacitors to be used in space applications.
Construction Analysis

- Design of PHS is similar to the design of solid hermetically sealed capacitors manufactured per MIL-PRF-39003.
- PHS in T2 cases are ~ 25% lighter than equivalent wet tantalum capacitors.
- Capacitors are manufactured using KEMET F-tech process (includes de-carbonizing and de-oxidizing steps to provide chemical purity to the anode surface, and welded anode riser wire) and special electrolyte for electrochemical oxidation of anode pellets. Pre-polymerized PEDOT slurry was deposited on the dielectric surface by dipping pellets in the dispersion of fine polymer particles and subsequent drying in air [8].

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Results of XRF analysis:
- Case material: Cu- 85%, Zn -15%. - brass.
- Sealing solder at the case: Sn -46%, Pb – 54%.
- Internal solder: Sn – 64%, Pb – 35%.
- Solder at the anode wire: Sn -93.5%, Pb -1.3%, Sb -5.1% (DWG#13030 requires 3% Pb).

Unless special measures are taken, internal solder can reflow during soldering.
Although anode wire solder might be prone to tin whiskering, it likely would not cause catastrophic failures due to a large distance to the case and high energy stored in the parts that can blow open even relatively large size whiskers.
Materials used for PHS capacitors are similar to MIL-PRF-39003 capacitors except for a polymer cathode instead of MnO2.
DPA: Flux in the Package

- In the presence of moisture, acids in the flux inside the case can react with polymer and/or silver epoxy and degrade characteristics of capacitors.

A sample of PHS manufactured in 2010 was heated to 200°C causing solder and large amount of flux to spill over.

Presence of flux was evident during internal examination of a sample manufactured in 2013.

Small amount of flux is still present in a sample manufactured in 2014.

- Assembly process of PHS has been improved over the last few years. Still, some amount of flux remains in the case.
- Testing of samples manufactured in 2013 and 2014 did not reveal any obvious negative effects of the flux presence.
DPA: X-Ray Views of PHS 100uF 60V Capacitors Manufactured in 2014

- No excessive solder or loose solder particles. Some misalignment does not exceed M39003 requirements and is likely not a reliability concern.
- Slopes of tantalum slugs are within 15 degrees tolerance (MIL-STD-1580).
- Distribution of solder inside the case needs better control.

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Specification: DLA LAM DWG#13030

- Commercial equivalent of the part is KEMET T550 series.
- Range of capacitance: 20 μF to 820 μF; rated voltages from 6V to 75V.
- Operating temperature: -55°C to +105°C (+125°C is in the plans for near future).
- Maximum leakage currents after 5 minutes: ≤ 0.0075 CV (μA) at rated voltage and room temperature; at 105°C voltage should be derated to 78% of VR.
- KEMET manufacturing includes F-tech process for reducing oxygen level in the tantalum powder, special cleaning of the pellet, welding of the anode raiser wire, examinations of pellets to assure crystallization-free process of oxide growth, and control over moisture content in the case.
- Screening procedures include:
  - Radiographic inspection.
  - Gross leak testing.
  - Simulated Breakdown Screening™ to select parts with highest VBR (SBDS screen).
  - Constant voltage conditioning for 240 hrs at 105°C, 0.78% VR.
  - Surge current testing (10 cycles +25°C).

Manufacturing and screening processes can assure high quality of the product.

- DWG#13030 is generally in compliance with the requirements for space applications, except thermal shock testing is not required.
- Storage temperatures are not specified; however, for T550 capacitors KEMET does not recommend storage above 85°C.
Comparison of Qualification Tests for DWG#13030 and MIL-PRF-39003 Capacitors

- Catastrophic failures should not be acceptable.
- High frequency vibration as in M39003; however, random vibration is required for space applications.
- Life testing at 105°C for 2000hr, but $V=0.78VR$ (M39006 and M39003: 2000 hr at 125°C, 0.7VR).
- Reverse voltage and low temp. storage are in addition to M39003.
- Thermal shock (300 cycles) are carried out at a narrower than M39003/6 temperature range (-55°C to +105°C), whereas MIL spec requirements are M39006 (wet): -55°C to +125°C; M39003 (solid): -65°C to +125°C.

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<th>DWG#13030</th>
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<td></td>
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<tr>
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<td>12 (1)</td>
<td>Gr. I, 6 (1)</td>
</tr>
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<td></td>
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<tr>
<td>Salt atmosphere (corrosion)</td>
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<tr>
<td>Thermal shock</td>
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<td>12 (1)</td>
<td>Gr. II, 12 (1)</td>
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<tr>
<td>Resistance to solvents</td>
<td></td>
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<tr>
<td>Resistance to soldering heat</td>
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<tr>
<td>Moisture resistance</td>
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<tr>
<td>Slewing</td>
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<td><strong>Group V</strong></td>
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<td>12 (1)</td>
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<tr>
<td>Life (at +125°C)</td>
<td>12 (1)</td>
<td>Gr. 6 (at 105C), 40 (1)</td>
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<tr>
<td><strong>Group VII</strong></td>
<td></td>
<td></td>
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<tr>
<td>Life (at +85°C)</td>
<td>102 (1)</td>
<td>Gr. IV, 102 (1)</td>
</tr>
<tr>
<td><strong>Group VIII</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ripple current (CSR21 only)</td>
<td>12 (1)</td>
<td>Gr. V, 8 (1)</td>
</tr>
<tr>
<td>Reverse voltage</td>
<td>N/P</td>
<td>Gr. III (1V for 2 hr at 70°C), 12 (1)</td>
</tr>
<tr>
<td>Low temperature storage</td>
<td>N/P</td>
<td>Gr. II (per M39006 at -62°C), 12 (1)</td>
</tr>
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</table>
Comparative Analysis of Performance

- The charts below are plotted based on specifications for wet, DWG#93026, and PHS, DWG#13030, tantalum capacitors.
- Case size for PHS capacitors corresponds to case size T2 for wet capacitors.

- Maximum leakage currents in PHS capacitors are calculated as \(0.0075 \times CV\), but for wet capacitors in case T2 \(DCL_{\text{max}}\) does not depend on \(CV\). In both cases it is not clear how the maximum is determined and what is the margin between the specified and actual leakage currents.
- \(DCL_{\text{max}}\) for PHS is 10 to 100 times greater than currents in wet capacitors.
- The specified values of ESR for PHS are several times lower than for wet capacitors. However, the difference decreases for larger \(CV\) values.
- Low ESR values of PHS parts did not result in higher ripple currents. It might be due to the lack of standardization and/or poor performance of PHS at high temp.
AC Characteristics

Comparative frequency dependencies of C and ESR for 100µF 60V PHS and 470µF 75V wet tantalum capacitors (data for 470µF capacitors are normalized to the nominal value to make charts comparable).

- PHS capacitors can operate down to -140°C.
- No degradation was observed in 5 parts after testing at +-140°C.
- PHS capacitors exhibit better stability of AC characteristics even at high temperatures.
AC Characteristics, Cont’d

Temperature dependencies of C and ESR for 100μF 60V PHS and DWG93026 470μF 75V wet tantalum capacitors

Effect of exposure to cryo temperatures (-196°C) leakage currents and ESR

- PHS have much better performance at T<0°C.
- Exposure to cryogenic temperatures might cause degradation of ESR, damage to the dielectric and needs additional analysis.
At room temperature absorption currents in PHS follow power law with the exponent close to 1.

The power law (Curie-von-Schweidler behavior) describes relaxation of currents over at least five orders of magnitude, from $10^{-1}$ sec to $10^4$ sec.

Absorption currents are reproducible from sample to sample and depend mostly on the value of capacitance.
Polarization and depolarization currents in PHS capacitors

- The exponent $n$ in the power law does not change substantially with voltage.
- Absorption currents increase linearly with applied voltage.
- Polarization currents are ~50% larger than depolarization likely due to losses of the absorbed charge that might be retrapped in deeper states in the dielectric.
**DC Characteristics: Effect of Temperature on Absorption Currents**

Absorption currents in PHS prevail over intrinsic leakage currents during first few hours of electrification even at 125°C. Intrinsic leakage current at 125°C is ~ 0.1 μA.

Leakage currents measured per existing specifications (within 300 sec) have weak temperature dependence and increase linearly with voltage.
DC Characteristics: Effect of Temperature on Intrinsic Leakage Currents

Typical polarization and depolarization currents at temperatures from 22°C to 165°C

- Intrinsic leakage currents can be observed at high temperatures (>105°C) after a few hours of polarization.
- Activation energy of intrinsic leakage currents is in the range from 0.75 to 0.88 eV.
- Extrapolation to room temperatures indicates that intrinsic leakage currents are in the nanoampere range, that is more than 10⁴ times lower than DCL_{max}.
- The effective activation energy of absorption currents is much lower, from 0.03 eV to 0.16 eV.

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Absorption Capacitance

- Assuming that relaxation currents follow power law, $I = I_0 \times t^n$, in the range from 1 to 10 ksec, the absorption charge can be calculated as:

- Slopes of the $Q_t$-V lines indicate absorption capacitance $C_t = Q_t/V$.

$$Q_t = \int_{1}^{10000} I_0 \times t^{-n} \times dt = \left. \frac{I_0 \times t^{1-n}}{1-n} \right|_{1}^{10000}$$

Variations of absorption charges with voltage for wet and PHS capacitors

- Due to a linear dependence of absorption currents on voltage and $n \approx$ constant, absorption charges, $Q_t$, increase with voltage linearly.

- At room temperature absorption capacitance is in the range from 0.1×$C_0$ to 0.13×$C_0$ for both, wet and PHS.

- $C_t$ increases ~10 times as temperature rises from 22°C to 105°C and saturates at higher temperatures likely due to a limited number of available electron traps.
DC Characteristics: Progress in Quality

Variations of currents with time at RT for PHS capacitors manufactured in 2010 (top) and 2013 (bottom).

Distributions of currents measured at RT after 1000 sec in three lots from 2010, 2013, and 2014

- Lots manufactured in 2013 and 2014 had substantially lower, more reproducible and stable leakage currents.
- Based on the existing requirements, parts with anomalous and unstable leakage currents would be accepted.

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Comparison of Performance of Wet and Polymer Capacitors

PHS capacitors have lower ESR and higher roll-off frequencies.

Absorption currents are similar in PHS and wet capacitors having similar nominal values.

Currents in wet capacitors measured after 1000 sec of electrification have a good correlation with CV values and can be approximated with a power law, $n = 1.2$.

Median values of DCL measured after 1000 sec of electrification are similar for PHS13/14 and wet capacitors.

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DC Characteristics: Breakdown Voltages

- VBR in two types of PHS (100 μF 60V and 82 μF 75 V) and several types of wet tantalum capacitors were measured using a constant current stress test.
- VBR was determined as the first maximum on the V-t curve.

Typical V-t characteristics for wet and PHS capacitors

Variation of normalized to the rated voltage VBR for wet and PHS capacitors

- All wet capacitors recover (self-heal) after breakdown.
- The self-healing capability of polymer cathode capacitors is worse compared to wet and MnO2 capacitors.
- For wet capacitors, breakdown voltage margin decreases with VR substantially.
- Breakdown voltages for PHS and wet capacitors are similar. PHS capacitors have VBR two times greater than the rated voltage.
Thermal Resistance

- T550 spec.: max power dissipation ($P_{\text{max}}$) at 25°C and 60°C rise is 0.715 mW. At 45°C < $T$ ≤ 85°C $P_{\text{max}} = 0.5 \times P_{\text{max}}$, and at 85°C < $T$ ≤ 105°C $P_{\text{max}} = 0.1 \times P_{\text{max}}$.
- Max ripple current $I_{\text{max}} = (P_{\text{max}}/ESR)^{0.5}$. Considering that ESR at 40 kHz is ~0.08 Ohm, $I_{\text{max}} = 3$ A rms, which is almost two times greater than the specified value for DWG#13030 (1.66 A rms).
- MIL-PRF-39006 and DWG#93026 specify $I_{\text{max}}$, at standard conditions: 40 kHz, 2/3VR, still air, $T_{\text{amb}} = 85°C$ (temperature rise, $\Delta T = 50°C$).

Temperature rise at different ripple currents and frequencies measured as described in [23]

- At $f \geq 1$ kHz temperature stabilizes in ~4 min; at low frequencies this time is much larger, ~15 min.
- Assuming $I_{\text{max}} = 1.66$ A at 45°C, at 85°C $I_{\text{max}}$ should be 0.52 A, which is almost two times less than even for T1 case DWG#93026 capacitors ($I_{\text{max}} \sim 1$ A).
Thermal Resistance, Cont’d

Temperature rise at rated conditions (40 kHz) is ~15°C only, whereas $\Delta T = 50^\circ$C is typically assumed.

$R_{th}$ for PHS capacitors was determined as a slope of lines approximating $\Delta T(P)$ dependence $\Delta T = P \times R_{th} = I^2 \times ESR(T) \times R_{th}$, where $\Delta T$ is a steady-state temperature rise, and ESR(T) is ESR corresponding to the stabilized temperature of the case.

Temperature rise at $f \geq 1$ kHz follows a linear $\Delta T(P)$ relationship with the slope indicating $R_{th} = 52.5$ K/W.

At low frequencies (60 Hz and 120 Hz), $R_{th}$ is substantially greater, which is likely due to different temperature distributions across the slug in capacitors at low and high frequencies.
Random Vibration Testing

- Five samples were tested by step stress random vibration testing with 15 min steps at 10.76 g, 19.64 g, 34 g, and 53.44 g rms consequently.
- Leakage currents were monitored through the testing.
- No current spikes or any anomalies were observed.

As expected, solid tantalum capacitors contrary to wet capacitors are not susceptible to damage under random vibration testing even at MIL-STD-202, TM 214A, condition II-K (53.79 g rms).
Effect of Reverse Bias

- Specification DWG#13030: The parts should sustain 1V RB for 8 hrs at RT and for 2 hrs at 70°C following 125 hrs at 85°C and rated voltage.
- To assess the robustness of PHS capacitors to reverse bias, 5 samples were stressed with 10-hour cycles at RT and RB that increased incrementally from 0.25V to 5V. Each RB stress was followed by 10-hr testing at 60V forward bias.
- Forward and reverse bias currents were monitored through the cycling.

Examples of variations of currents with time under reverse bias

- Leakage currents under reverse bias conditions are reproducible.
- No degradation at 0.5V for 10 hrs. At 1V currents start increasing after ~ 5 hours, and at 2.5V after ~10 min of testing.
Effect of Reverse Bias, Cont’d

- RBS can increase currents up to 4 orders of magnitude; however, it does not cause degradation of forward currents.
- The degradation is graceful, its rate increases with voltage, and the currents are stabilizing after hours of stress.
- RB behavior for PHS is similar to MnO₂ capacitors indicating that the degradation is controlled by processes at the Ta₂O₅/Ta interface [16].
- Similar to MnO₂ capacitors, decreased breakdown voltages and increased probability of failure might be expected after RB stresses.
Effect of High Temperature Storage

- Maximum storage temperature for DLA#13030 parts is not specified; however, KEMET does not recommend storage of T550 capacitors at temperatures above 85°C.
- Operation temperature of DLA#13030 parts is limited to 105°C; however, KEMET is planning to extend it to a typical MIL standard temperature of 125°C.
- Based on 2000 hr life testing at 175°C and 0.5VR voltage, the safe working temperature of commercial hermetically sealed tantalum capacitors manufactured by AVX is 175°C [11, 17]. Degradation of C and ESR was observed during 2000 hr testing at 200°C only.
- Parts manufactured per DLA#13030 are hermetically sealed, but only gross leak testing is used to verify hermeticity. Analysis showed, that during long-term missions even for parts that passed fine leak testing the gas composition inside the case is changing, and eventually becomes similar to the outside environments.
- Considering that moisture affects performance of the parts, for space missions it is important to understand what changes in performance of capacitors are expected in case of parts loosing their hermeticity and polymer is “drying out”.
- To assure long-term stability of the parts, the degradation processes are typically accelerated by temperature. For mil-spec parts, the effect of storage is accelerated during HTS testing that is typically carried out at 150°C for 1000 hours.

To address issues related to hermeticity and stability of characteristics during long-term missions, HTS testing was carried out at 125°C for 100 hrs and 150°C for 1000 hrs using parts in “as is” condition and parts with small holes drilled and punctured at the anode end of the cases to simulate the loss of hermeticity (these parts are marked below with “h”). AC and DC characteristics of the parts were measured through the testing.
Initial Effect of Hermeticity Loss

Frequency dependencies of C and ESR and polarization and depolarization currents in PHS capacitors manufactured in 2014. Different colors correspond to parts with and without holes in the case.

- No damage to the parts by drilling and puncture.
- Hermeticity loss did not change initial AC or DC characteristics of the parts.
- Absorption currents prevail in most of hermetic and non-hermetic parts up to 10 hours of electrification.

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Effect of HTS: Storage at 125°C

Frequency dependencies of C and ESR for PHS capacitors manufactured in 2013 before and after HTS at 125°C (samples with introduced holes marked as “h_100hr”).

- Baking at 125°C for 100 hr does not affect hermetically sealed parts, but reduces capacitance and low-frequency ESR for non-hermetic parts.
- No effect on ESR measured at 100 kHz for hermetic and non-hermetic parts.
- The results might be due to changes in characteristics of the surface of Ta$_2$O$_5$ dielectric rather than degradation of the polymer.
Effect of HTS at 150°C: AC Characteristics

Typical variations of C-f and ESR-f characteristics during HTS at 150°C for hermetic and non-hermetic capacitors.

Variation of C at 120 Hz and ESR at 100 kHz during HTS.

- Hermetic parts can survive 1000 hr storage at 150°C without degradation.
- Non-hermetic parts degraded due to a substantial decrease in capacitance (down to ~ 40% of \( C_0 \)) and increase in ESR (up to 10 times).
- Degradation starts after ~200 hr and is likely due to increasing resistance of the polymer cathode layer.

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HTS: Absorption Currents in Hermetic and Non-hermetic Capacitors

Initial and pos-HTS test polarization and depolarization currents at RT

Variations of polarization and depolarization currents with time of HTS

✓ Initial leakage currents in hermetic and non-hermetic parts are similar.
✓ Absorption currents (at 1 ksec) are increasing with time of HTS in 3 to 5 times for hermetic parts and remain stable for non-hermetic capacitors.
✓ Non-hermetic parts had increased absorption currents during first 1 to 5 min, but currents measured after more than 15 min remain stable through HTS testing.
Leakage currents at $T \geq 125^\circ C$ are stabilizing after a few hours of polarization.
Different groups of PHS capacitors had similar leakage currents at HT.
Leakage currents in PHS capacitors, both hermetic and non-hermetic, had activation energies $\sim 0.77$ eV that are close to the values for wet tantalum capacitors (0.72 to 0.78 eV).
Degradation of Leakage Currents during HALT

- Step stress HALT was carried out for 100 hours at 60V consequently at 105°C, 125°C, 145°C, and 165°C.
- Between the steps, the parts were depolarized for 3 hrs at the test temperatures.

Results of HALT for PHS capacitors manufactured in 2013 and 2014

- Degradation of leakage currents in some parts was observed after a few hours at 105°C and is likely related to migration of charged oxygen vacancies [18, 19].
- Parts manufactured in 2014 appear to have somewhat greater rate of degradation compared to 2013 capacitors.
- The rate of degradation increases with temperatures. At 145°C currents appear to stabilize with time of HALT, which might be due to a limited amount of oxygen vacancies or their neutralization with time.
Degradation of leakage currents at different temperatures approximated with linear functions.

Temperature dependence of rate for two samples.

- Activation energy of the degradation rate is rather high, from 1.7 eV to 1.8 eV.
- The degradation is likely due to redistribution of positively charged oxygen vacancies and is consistent with results for chip tantalum capacitors [18].
- At $E_a \sim 1.7$-$1.8$ eV, the predicted degradation rate at 85°C is in the range from $8 \times 10^{-16}$ to $2 \times 10^{-14}$ A/sec, and the current increase over 100 years would be negligibly small, from $2 \times 10^{-7}$ to $5 \times 10^{-6}$ A.
Leakage Currents after HALT

Examples of post-HALT relaxation of leakage currents measured at 85°C and 22°C for two samples

- HALT resulted in substantial, more than 1 to 2 orders of magnitude increase in intrinsic leakage currents at low temperatures.
- The result is consistent with the charged oxygen vacancies redistribution model [16, 18].
Variations of leakage currents with time during HALT at 145°C, 60V for post HTS capacitors. PHS corresponds to non-hermetic capacitors; PHS13 were tested for 100hr at 145°C after 100hr testing at 105°C and 125°C; PHS14 capacitors were tested at 145°C for 275hr without testing at 105°C and 125°C.

- Degradation of hermetic PHS14 parts after HTS starts later (after ~10 hr at 145°C) compared to the parts not stressed by HTS, but occurs at a higher rate.
- Contrary to parts not stressed by HTS, there was no evidence of current saturation during 275 hr testing at 145°C.
- Two post-HTS PHS parts manufactured in 2013 failed short circuit after 60 and 100 hrs at 145°C, three more failed at 165°C.
- One PHS capacitor manufactured in 2014 failed after 40 hr, and another after 60 hr. The second part self-healed after a few hours but failed again after 270 hr.
- No degradation in post-HTS non-hermetic capacitors was observed.
The most intriguing results of this study are related to the effect of high-temperature storage, in particular:

- A ~10% decrease of C at low frequencies, below ~3 kHz that was noticeable already after 100 hrs at 125°C (p.33) or 24hrs at 150°C (p.34).
- No degradation of AC characteristics for hermetic capacitors and significant degradation for non-hermetic parts (p.34).
- Gradual increase of absorption currents with time of HTS for hermetic parts and stable behavior for non-hermetic capacitors. In the latter case, increasing absorption currents were observed only within first 100 to 1000 sec of electrification (p.35).
- Substantial degradation of leakage currents during HALT for hermetic and decreasing leakage currents with time for non-hermetic capacitors (p.40).

Although more analysis is necessary to understand this behavior, some results might be explained assuming that charge absorption processes and leakage currents in the capacitors are controlled by migration of charged oxygen vacancies in the dielectric and electron trapping processes at the cathode/polymer interface.

- Absorption currents are related to trapping and release of electrons under voltage variations (polarization and depolarization currents during current transient measurements).
- Intrinsic leakage currents that prevail after a few hours at high temperatures are likely due to a Schottky-like transport of electrons across the barrier at the Ta2O5/polymer interface [18-20]. The barrier height is controlled by the trapped negative charge and positive charge of ionized oxygen vacancies (\(V^{++}\)) that migrate with time under bias through the dielectric layer.
- Negative charges increase the barrier and reduce the current, while accumulation of the charged oxygen vacancies acts in the opposite direction.
Changes of AC characteristics.

- A decrease of capacitance (~10%) during initial stages of HTS for non-hermetic capacitors can be explained using a sleeping cells model [25] assuming that polymer does not cover the entire surface of the Ta2O5 pellet, and ~ 10% of the surface remains uncovered. In the presence of moisture, the surface conductivity of the dielectric is sufficient to assure that the AC signal is applied along a large proportion of the uncovered surface. At high temperatures, moisture desorbs from the non-hermetic parts and increases surface resistance, thus decreasing capacitance.

- Degradation of C and ESR at 150°C after ~ 200 hr for non-hermetic occurs gradually, and is likely due to increasing resistance of the polymer that raises ESR at 100 kHz and reduces substantially the roll-off frequency, hence, capacitance of the part.

- Because no significant changes in AC characteristics happen during HTS for hermetic parts, the observed degradation for non-hermetic capacitors might be related either to variations in the concentration of absorbed moisture or to the irreversible thermal degradation of the polymer. However, additional experiments with the non-hermetic parts exposed to humid environments (48hr at 85°C, 85% RH) did not change values of C and ESR any substantially thus indicating irreversible degradation.

- The results show that the observed degradation is not due to just drying-out of the polymer cathode, but rather to a thermal decomposition that is likely accelerated substantially in the absence of moisture. This means that operation of PHS capacitors in vacuum at relatively low temperatures (below 85°C) even in the event of hermeticity loss most likely will not cause catastrophic failures.
Absorption currents.

- Increasing absorption currents for hermetic capacitors and stable behavior for non-hermetic devices indicates that moisture at high temperatures can create surface states with a wide range of relaxation times at the Ta2O5/polymer interface. It is possible that a similar effect occurs in wet tantalum capacitors resulting in a substantial increase of transient currents after HTS.

- For non-hermetic capacitors, an increase in absorption currents was observed only during initial period of polarization indicating that surface states with relatively fast relaxation times might be introduced by the conductive polymer even without moisture. These relaxators can be also responsible for anomalous transient currents in the parts.

Degradation of leakage currents at high temperatures.

- In hermetically sealed capacitors that passed HTS the on-set of degradation occurs after ~ 10 hr at 145°C, 60V and results in DCL increasing more than two orders of magnitude. Similar effects were observed in MnO2 capacitors and were explained by migration of $V^{++}_o$ in the dielectric [18, 19].

- Assuming that during HTS the oxygen diffuses from the dielectric to Ta [9], the concentration of $V^{++}_o$ at the anode interface should increase. In this case, post-HTS HALT would result in a delayed, but more significant rate of degradation compared to parts that did not pass HTS.

- The most surprising result is that leakage currents in non-hermetic parts after HTS continue decreasing even after 275 hrs of HALT at 145°C, 60V. It is possible that in the absence of moisture, changes at the interface allow positive charges to be neutralized by electrons injected from the cathode.
Design.
- Design and materials used in PHS, DWG#13030, capacitors are similar to the design of parts manufactured per MIL-PRF-39003 except for using a conductive polymer instead of MnO2 layer.
- DPA requirements used for M39003 capacitors are applicable to DWG#1303 parts.
- The presence of near-eutectic solder inside the part limits maximum case temperature during assembly.

DLA DWG#13030 specification.
- Thermal shock and fine leak hermeticity testing are not included in the screening process.
- The specified leakage currents are more than 2 orders of magnitude larger than actual leakage currents allowing defective parts passing the screening.
- In spite of lower ESR values, the specified ripple currents for PHS are substantially less than for similar wet tantalum capacitors. Requirements for ripple currents should be revised.

Performance.
- PHS capacitors have a better stability of AC characteristics compared to wet capacitors, and contrary to wets can operate down to -140°C.
- Exposure to cryogenic temperatures (-196°C) can cause degradation of ESR and damage to the dielectric. Additional testing is necessary if parts are to be used below -55°C.
- Absorption currents prevail over intrinsic leakage currents up to 105°C during first several hours of electrification. These currents depend mostly on the value of capacitance, increase linearly with voltage and practically do not depend on temperature. Absorption capacitance at RT is ~10% of $C_0$, but increases substantially with temperature.
- Activation energy of intrinsic leakage currents in PHS is similar to wet capacitors and is in the range from 0.75 eV to 0.88 eV. Estimations show that intrinsic leakage currents at room temperature are in the nanoampere range that is more 4 orders of magnitude below the specified limit.
- Breakdown voltages of PHS and wet capacitors are similar. However, self-healing in PHS capacitors is much less effective compared to wets.
Summary, Cont’d

- **Thermal resistance.**
  - Thermal resistance of PHS capacitors in T2 size cases is ~52.5 K/W, but is likely to increase to ~100 K/W in vacuum. At frequencies below ~1 kHz thermal resistance might be much greater.
  - Rather low ripple currents specified for PHS are likely related to a limited maximum operation temperature of the parts. This reduces substantially the effectiveness of using low ESR PHS capacitors compared to wet capacitors. Based on results of HTS testing, the limit to maximum ripple currents can be increased.

- **Random vibration.**
  - The parts passed random vibration testing up to 53.4 g rms (cond. II-K per MIL-STD-202, TM214). The existing requirements in DWG#13030 should be revised.

- **Effect of reverse bias.**
  - Reverse bias degradation at room temperature can be observed at 1V after a few hours of testing. This degradation is similar to MnO2 cathode devices [24] and most likely is reversible (after storage and/or forward bias operation).

- **Effect of high temperature storage.**
  - No degradation of capacitance or ESR was observed during 1000 hour storage at 150°C for hermetically sealed capacitors.
  - Absorption currents for hermetically sealed parts after 1000 hrs of testing increased 3 to 5 times remaining still well below the limit.
  - High-temperature storage of non-hermetic parts resulted in a substantial degradation of C (decrease to below 40% of the initial value) and ESR (increase up to 10 times) likely due to increasing resistivity of the polymer.
  - The results indicate an important role of moisture (hence, hermeticity testing) in assurance of thermal stability of the parts.
Summary, Cont’d

- Although no catastrophic failures are expected in PHS capacitors operating in vacuum at relatively low temperatures after hermeticity loss, more data on thermal degradation of the polymer and the role of moisture are necessary to explain behavior of the parts in vacuum and/or at high temperatures.

Effect of HALT.

- For hermetic capacitors, HALT resulted in degradation of leakage currents that can be observed after a few hours at 105°C and 60V. Temperature increases the rate of degradation substantially. The activation energy of the degradation is \( \sim 1.7 \) eV suggesting that the process is likely due to migration of positively charged oxygen vacancies in the dielectric.

- The degradation process might cause wear-out failures of the parts; however, due to a high activation energy, acceleration factors are large, and the predicted time to failure at 85°C is greater than 100 years, which corresponds to the results reported in [13, 14].

- For capacitors with a relatively small concentration of oxygen vacancies in the dielectric, the degradation process saturates and the level of current that is necessary to cause thermal runaway, and hence failures, might never be reached. This reduces the risk of failure even below the level estimated based on the acceleration factors. Concentration of oxygen vacancies in the dielectric should be under tight manufacturing control.

- Long-term exposure of the parts to high temperatures appeared to raise the time to degradation onset, but it also increased the rate of degradation. This might be due to diffusion of oxygen into Ta anode during HTS, thus increasing concentration of the vacancies at the anode interface that migrate to the cathode during HALT.

- Surprisingly, no degradation was observed during HALT at 145°C, 60V for 275 hr in non-hermetic devices. Instead, the currents keep decreasing with time slowly. It is possible that the absence of moisture allows for a better charge compensation of oxygen vacancies; however, more analysis is necessary to understand this phenomenon.
Recommendations

- PHS capacitors have lower weight and ESR compared to similar case size wet tantalum capacitors and their application in power lines can assure better filtering and lower ripple currents.
- Polymer capacitors would mostly benefit low-temperature applications (below 0°C) or systems where a cold start-up is required. However, additional application-specific testing are required if the parts are to be used at T < -55°C.
- Self-healing capability of PHS is much worse than wet capacitors and flaws in the dielectric that might be forgiven in wet capacitors might cause catastrophic failures in PHS. This requires a close attention to the results of S&Q, specifically, to measurements of leakage currents through the testing.
- Capacitors manufactured per DLA LAM DWG#13030 can be used in L2 and L3 space projects after additional screening that includes:
  - 10 temperature cycles between -55°C and +105°C before voltage conditioning and DCL measurements;
  - DCL measurements after 15 min electrification and selection parts based on $3\sigma$ criterion;
  - Fine leak testing (according to recent KEMET information, this test is included in the screening process).
- Qualification requirements:
  - Thermal shock and life testing should be specified in the purchase order.
  - Catastrophic failures should not be acceptable during qualification tests.
- Derating requirements:
  - Voltage derating should be similar to MIL-PRF-93006 capacitors (60%);
  - Maximum case temperature for long-term storage and operating conditions is limited to 85°C.
- During assembly, the case temperature should not increase above 180°C to avoid internal solder reflow.
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