2017 NEPP Tasks Update for Ceramic and Tantalum Capacitors

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# List of Acronyms

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<th>Acronym</th>
<th>Description</th>
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<tbody>
<tr>
<td>AF</td>
<td>acceleration factor</td>
<td>MLCC</td>
<td>multilayer ceramic capacitor</td>
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<tr>
<td>BME</td>
<td>base metal electrode</td>
<td>MOR</td>
<td>modulus of rupture</td>
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<tr>
<td>DCL</td>
<td>direct current leakage</td>
<td>PME</td>
<td>precious metal electrode</td>
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<tr>
<td>ESR</td>
<td>Equivalent series resistance</td>
<td>QA</td>
<td>quality assurance</td>
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<tr>
<td>FPGA</td>
<td>field-programmable gate array</td>
<td>RB</td>
<td>reverse bias</td>
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<tr>
<td>HALT</td>
<td>highly accelerated life testing</td>
<td>S&amp;Q</td>
<td>screening and qualification</td>
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<td>HT</td>
<td>High temperature</td>
<td>SMT</td>
<td>surface mount technology</td>
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<td>HTS</td>
<td>high temperature storage</td>
<td>TC</td>
<td>temperature cycling</td>
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<td>IDC</td>
<td>inter-digitated capacitor</td>
<td>VH</td>
<td>Vickers hardness</td>
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<td>IFT</td>
<td>Indentation Fracture Test</td>
<td>WTC</td>
<td>wet tantalum capacitor</td>
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Outline

- Update on tantalum capacitors.
  - Leakage currents, gas generation and case deformation in wet tantalum capacitors.
  - MnO2 chip capacitors:
    • ESR degradation.
    • Acceleration factors for DCL degradation and failures.
    • Effect of moisture on degradation of reverse currents.
  - Polymer capacitors.
  - Future work.

- Update on ceramic capacitors.
  - Mechanical properties of MLCCs.
  - Failures in BME capacitors with defects.
  - Effect of cracking on degradation of MLCCs at HT.
  - Future work.

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Leakage Currents, Gas Generation and Case Deformation in Wets

NEPP report (https://nepp.nasa.gov/) contains:
- Part I. Analysis of leakage currents;
- Part II. Gas generation, hermeticity, and pressure in the case.
- Part III. Electrolyte at the glass seal.
- Part IV. Deformation of cases in high capacitance value wet tantalum capacitors.

**Anomalies in leakage currents indicate presence of defects**

- Risks of internal leaks: non-oxidized surfaces; corrosion of welds; excessive leakage currents and gas generation.
- To reduce failures a special conditioning at HT is recommended.
Multiple (1650) transients did not cause case bulging likely due to H₂ outdiffusion through tantalum case.

TC can result in irreversible lid deformation and excessive DCL.

To assure reliable operation in vacuum, HTS testing at 150 ºC for 1000 hours is recommended.

Glass seal protection in button case capacitors is less effective compared to the cylinder case parts.
ESR Degradation in MnO2 Capacitors

A report (https://nepp.nasa.gov/) includes analysis of environmental factors: vacuum, high temperature storage, temperature cycling, moisture, and soldering.

Examples of ESR variations during HTS and humidity testing

- Most parametric ESR failures are due to insufficient margin to ESR_{limit}.
- MnO2 caps can withstand 1000 hr at 150 °C and at 85 °C/85% RH.
- AEC-Q200 requirements are much more severe compared to M55365.
- Compressive stresses after bake reduce delaminations and squeeze microcracks in cathode layers resulting in reduction of ESR.
- Swelling of MC and stress relaxation in moisture have opposite effects.
Acceleration Factors for DCL Degradation and Failures

A report ([https://nepp.nasa.gov/](https://nepp.nasa.gov/)) describes catastrophic and parametric failures in Ta capacitors, their mechanisms and AF.

$$AF_T = \exp \left[ B \times \left( \frac{V_{\text{test}}}{V_R} - 1 \right) \right]$$

$$AT_T = \exp \left[ -\frac{E_a}{k} \times \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \right]$$

- Analysis showed that $5.5 < B < 10.3$, $1.42 < E_a < 1.66$ eV.
- Parametric degradation is reversible and can be annealed at HT.
- The mechanism of degradation is attributed to migration of oxygen vacancies in the dielectric with $E \sim 1.1$ eV.

Kinetics of Moisture Sorption in MnO2 Capacitors

Moisture sorption can be characterized by two time constants

\[ C(t) = C_{\text{min}} + (C_{\text{max}} - C_{\text{min}}) \times \left[ 1 - \exp\left(-\frac{(t-t_D)}{\tau}\right) \right] \]

\[ t_D = \frac{d^2}{6 \times D} \]

\[ \tau = \frac{d}{\gamma \times \bar{p} \times S} \]

- Slugs in tantalum chip capacitors can be used as moisture sensors.
- A model for \( C-t \) variations has been developed.
- Bake-out times can be selected based on the characteristic times of the desorption process.
Effect of Moisture on Degradation of Reverse Currents in MnO2 Capacitors

\[
H_2O + V_{O^*} \rightarrow 2H^* + O^x_O
\]

\[
H_2O + V_{O^*} + O^x_O \rightarrow 2OH^*_O
\]

- Degradation under RB strongly depends on presence of moisture in environments and preconditioning.
- Oxygen vacancies play important role in formation of protonic species.
Polymer Capacitors


- Parametric failures are likely to be major issues with polymer caps.
- QA system developed for MnO2 capacitors is not applicable.
- Unstable leakage currents that might be more significant in vacuum.
- Significant degradation of ESR during HTS.
One of the most intriguing problems: anomalous transients after HTS

- Moisture plays an important role in the mechanism of transients.
- Anomalies in long-term transient currents might be due to changes in the trap system of Ta2O5.
- More analysis necessary.

Future Work on Tantalum Capacitors

- MnO2 chip capacitors.
  - Complete current tasks.
  - Reliability acceleration factors for automotive grade capacitors.
- Advanced wet capacitors.
  - Effect of HT storage on performance and reliability.
  - Evaluation of SMT wet tantalum capacitors.
- Polymer capacitors.
  - Degradation models for HTS and recommendations for S&Q.
- Super-capacitors for space application.
Mechanical Properties of MLCCs

- Can mechanical characteristics predict robustness of MLCCs under soldering stresses?

- Report that is available at https://nepp.nasa.gov/ includes:
  - Flexural Strength Testing of MLCCs.
  - Vickers Hardness Testing.
  - Indentation Fracture Test (IFT).

\[ MOR = \frac{3FL}{2bd^2} \]

- Flexural strength method determines tensile strength at the surface.
- No substantial difference between mechanical characteristics of BME and PME capacitors.
- Smaller size MLCCs have greater strength – Benefits of BMEs.
- Same size capacitors can be used for comparative analysis of the lots.
- Variations of MOR values from lot to lot might exceed 50%.
Vickers Hardness

- Hardness is a resistance to indentation.

In-situ VH measurements are possible using MLCCs with relatively thick cover plates. $P$ should be low so the depth of the indentation is $< 2x$ the thickness of the cover plate.

- No significant difference between PME and BME capacitors.

- Improvements to reduce errors might allow for revealing differences in lots.

$VH = \frac{1.854 \times P}{D^2}$

Vickers Hardness Test for PME and BME Capacitors

Cumulative probability, %

90% confidence

BME

PME

Load, N

Vickers test, LT capacitors

$y = 191.65x$

$D^2, \text{um}^2$

$VH, \text{GPa}$

SN1

SN2

SN3

SN4

SN5

Indentation Fracture Test

- Fracture Toughness: the ability of a material to withstand stresses in the presence of cracks.
- IFT technique is the most controversial.

IFT can provide useful information regarding robustness of capacitors under soldering conditions, but additional analysis is necessary.

Mechanical testing might be useful for selecting robust parts for manual soldering, but more work is necessary to reduce errors and select criteria.

For critical applications a combination of assembly simulation and special testing might be recommended.

\[ IFT = \xi_{JM} \left( \frac{E}{VH} \right)^{0.5} \left( \frac{P}{C^{1.5}} \right) \]

- PME_L capacitors
- PME_V capacitors

Failures in BME Capacitors with Defects

- Migration of VO$^{++}$ is enhanced either by increased $E$, as in case of thinning of the dielectric, or by increased $\mu$, as in case of cracks.

- Catastrophic failures occur when $\Phi_B$ decreases to $\Phi_{Bcr}$. For capacitors having small, micrometer-size defects $\Phi_{Bcr}$ is low so catastrophic failures are unlikely.

- In the range of typical HALT conditions voltage increases the probability of catastrophic failures to a greater degree compared to temperature. This might result in errors in AFs.
Effect of Cracking on Degradation of MLCCs at HT

Stretched exponential dependence of $\Phi_B$ with time.
In bulk: $\tau_V = 200 \text{ hr, } (\mu_V \sim 5 \times 10^{-15} \text{ cm}^2/\text{Vs})$
Along the crack: $\tau_c \sim 10 \text{ hr, } (\mu_V \sim 10^{-13} \text{ cm}^2/\text{Vs})$.

$\Phi_B(t) = \Delta \Phi_B \times \left[ 1 - \exp \left( -\left( \frac{t}{\tau_V} \right)^\gamma \right) \right]$

$\tau_V = \frac{0.78 \times d^2}{\mu_V \times V}$

$\Delta \Phi_{B_{cr}} = 0.54 \text{ eV}$

✓ Model: accelerated migration of $V_O^{++}$ along the cracks.
✓ Simulations are in reasonable agreement with experimental data.
Future Work on Ceramic Capacitors

- Evaluation of IDC capacitors used for FPGAs.
- Comparative analysis of performance and reliability of BME and PME capacitors.
  - Breakdown voltages.
  - Analysis of failures in BME capacitors with defects.
  - Express testing to determine reliability acceleration factors for BME capacitors.
  - Guidelines for selecting “auto” MLCCs for different project levels.