Kinetics of Moisture Sorption and Reverse Bias Degradation in Chip Tantalum Capacitors

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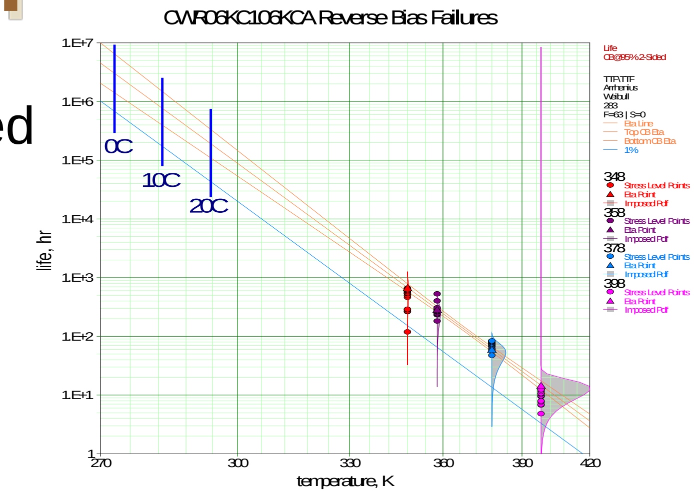
Introduction



- In previous tests RB degradation was considered depending on *T* and *V* only.
  The rate of degradation was simulated using a general Weibull log-linear model

$$F(R) = 1 - \exp\left[-\left(\frac{R}{R_c}\right)^{\beta}\right] \qquad R_c = A \times \exp\left(\frac{E_a}{kT}\right) \times V^n$$

- Calculations yielded E_a =0.95 eV, n = 6.5, and β = 1.63. This allowed for estimations of the probability of failure at different operating conditions.
- Later, it was shown that moisture has a strong effect on the degradation process and behavior of capacitors in vacuum and in air is different.

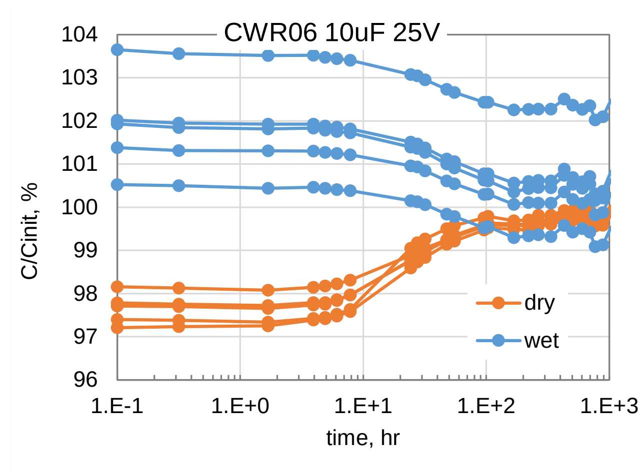
✓ To analyze the effect of moisture, one need first an assessment of timing of moisture sorption and desorption processes.

✓ In this study (i) kinetics of moisture sorption has been analyzed and (ii) an attempt to understand the mechanism of moisture has been made.

Outline

- Experiment.
- Kinetics of moisture sorption and desorption.
- Simulation of moisture variations in the slug.
- Reverse bias degradation of leakage currents at different environmental conditions.
- Physical models.
- Conclusion.

Experiment



- ❑ Two types of conformal coated (CC) and one types of molded case (MC) 10 μF 25 V tantalum MnO_2 capacitors.
- ❑ Kinetics of moisture sorption and desorption was monitored by variations of capacitance.
- ❑ Reverse leakage currents were monitored with time at different environments, temperatures and voltages.
- ❑ Each group of capacitors had 7 to 14 samples.

- ✓ Slugs can be used as moisture sensors.
- ✓ *C(t)* variations are reproducible and can be characterized by two parameters: induction period, t_D, and characteristic time, τ.

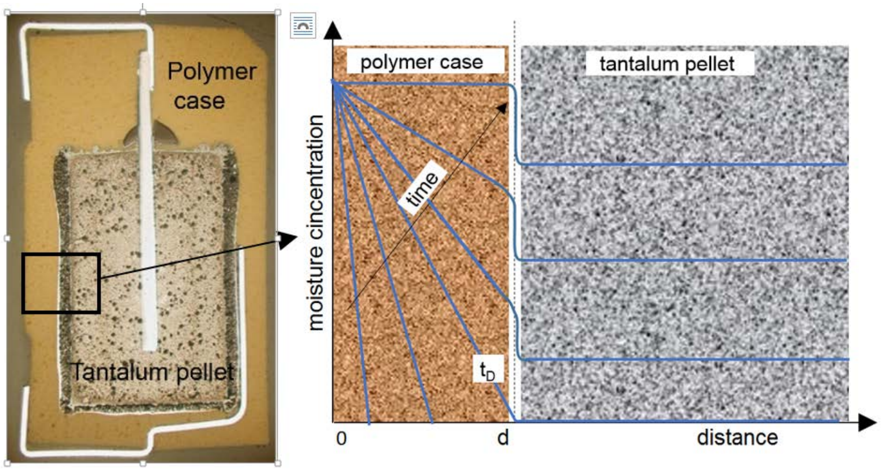
Simulation of Moisture Sorption

Induction period corresponds to a diffusion delay:

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

Moisture flow into the slug at $t > t_D$:

$$\frac{\Delta m(t)}{\Delta t} = \tilde{p}\,\frac{S}{d}\left[P_o - P_i(t)\right]$$



C and $P_i \sim \Delta m$: $\Delta C(t) = \alpha \times \Delta m(t)$, and $P_i(t) = \gamma \times \Delta m(t) = (\gamma/\alpha) \times \Delta C(t)$

Solution for moisture sorption:

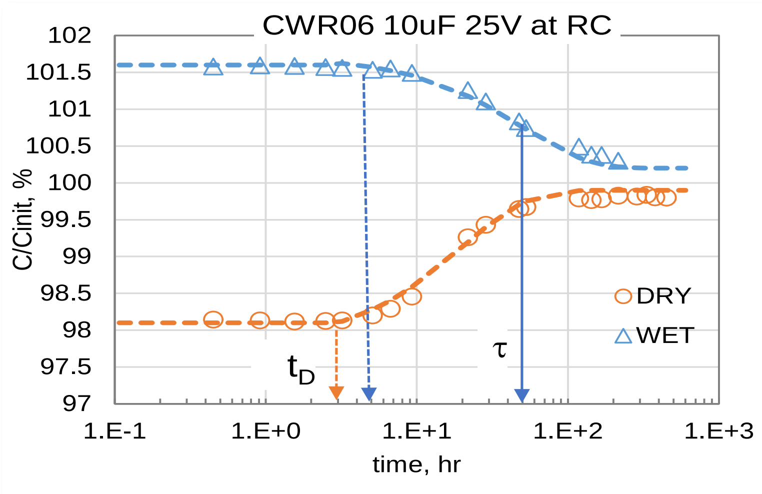
$C(t) = C_{min}$ .... at $t \le t_D$

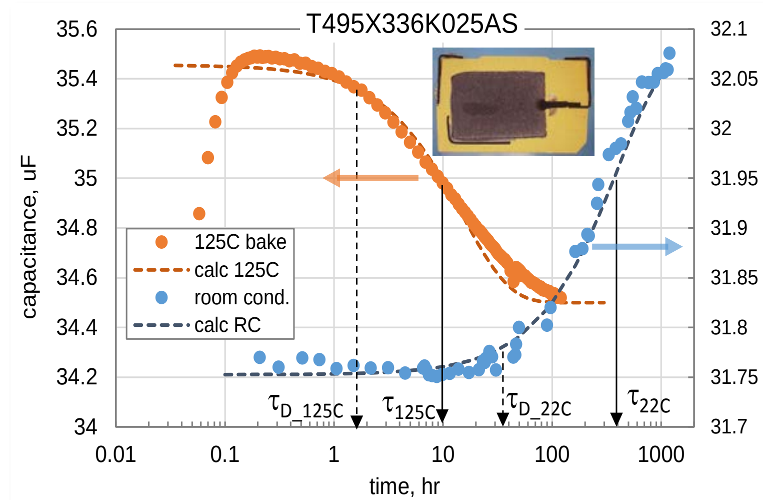
$$C(t) = C_{\min} + \left(C_{\max} - C_{\min}\right) \times \left[1 - \exp\left(-\frac{(t - t_D)}{\tau}\right)\right]$$ at $t > t_D$

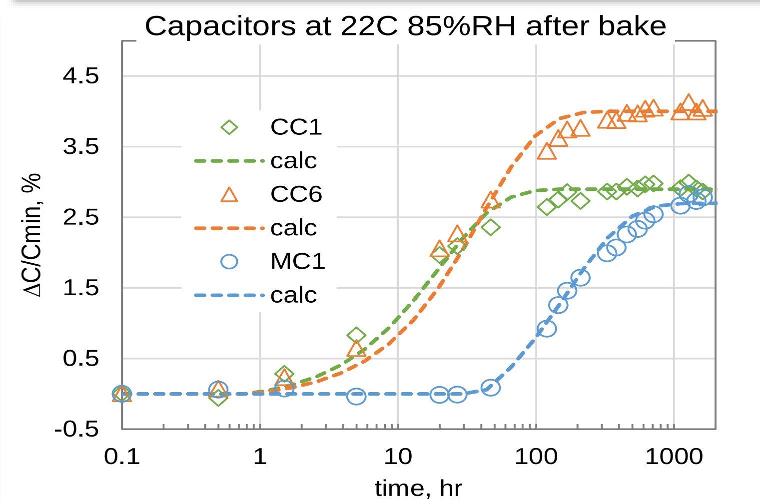
$$\tau = \frac{d}{\gamma \times \tilde{p} \times S}$$

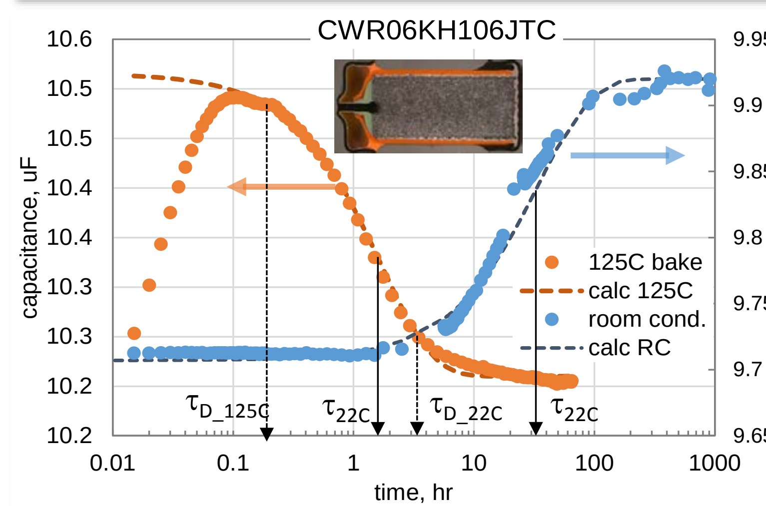
✓ Values of t_D and τ can be estimated based on characteristics of encapsulating polymers and slugs.

Examples of Capacitance Variations





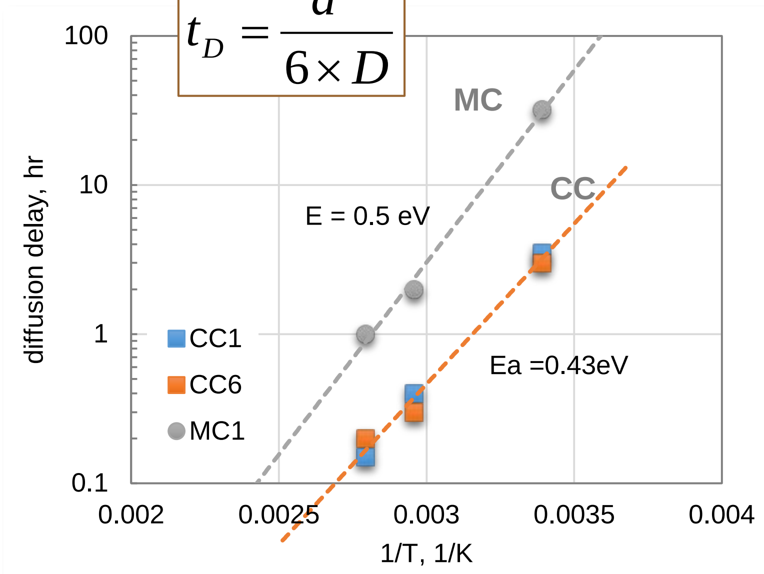




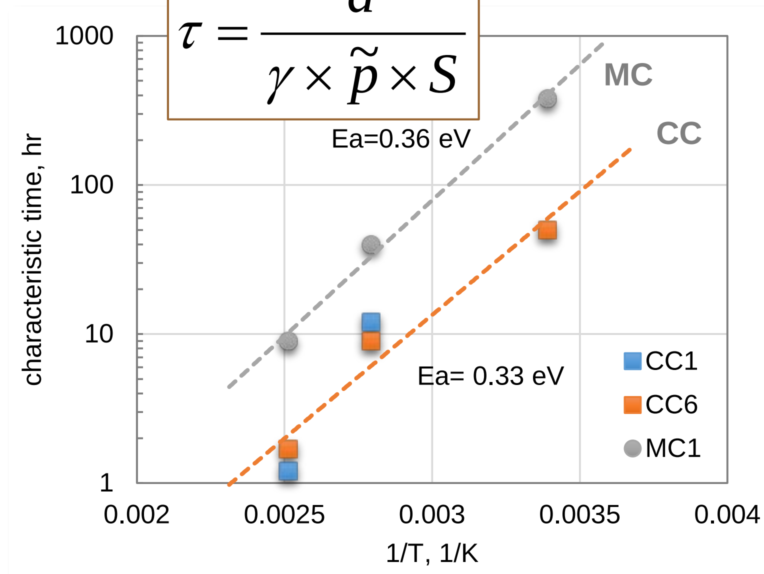
Dashed lines are calculations based on the model.

Temperature Dependencies of Characteristic Times

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



$$\tau = \frac{d}{\gamma \times \tilde{p} \times S}$$



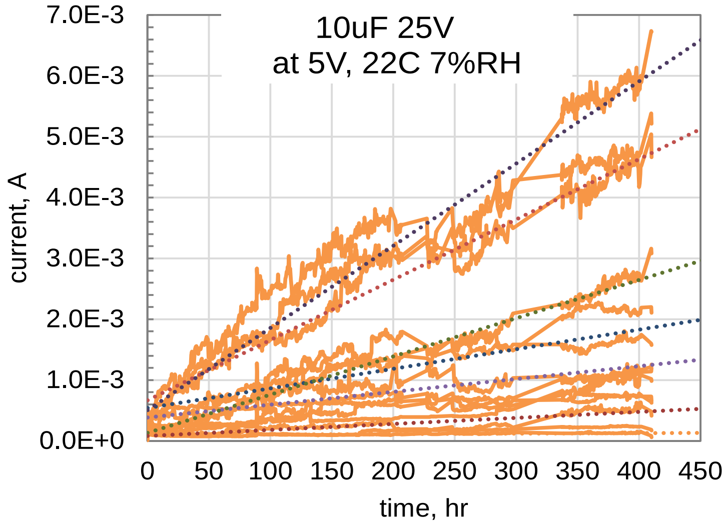
$$D = D_o \exp(-U / kT)$$

$$\tilde{p} = \sigma \times D$$

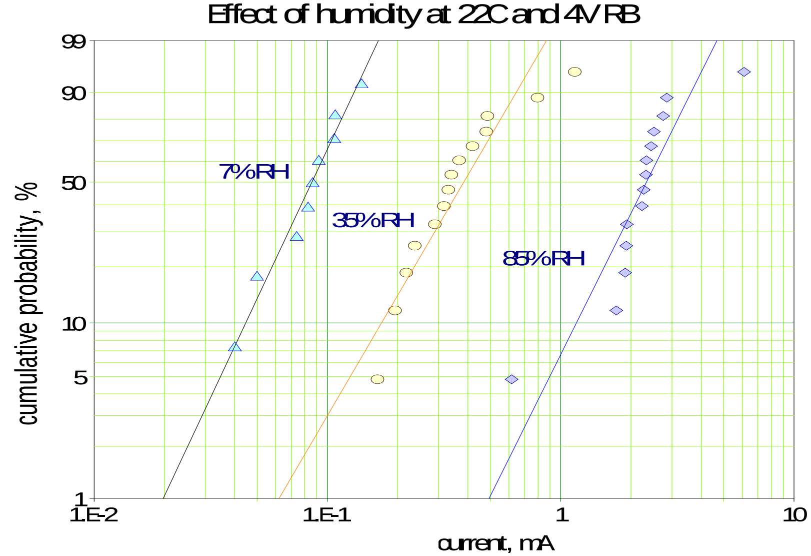
- ✓ For MC: $D_o = 3.6\times10^{-6}$ m^2/sec and $U = 0.42$ eV; for epoxy coatings: $D_o = 4.8\times10^{-6}$ m^2/sec and $U = 0.4$ eV, which is close to t_D data.
- ✓ Coefficient of sorption has a poor dependence on temperature, which corresponds to E_a values for τ.

Effect of Moisture

Example of RB degradation



Distributions of leakage currents (100hr) at different RH

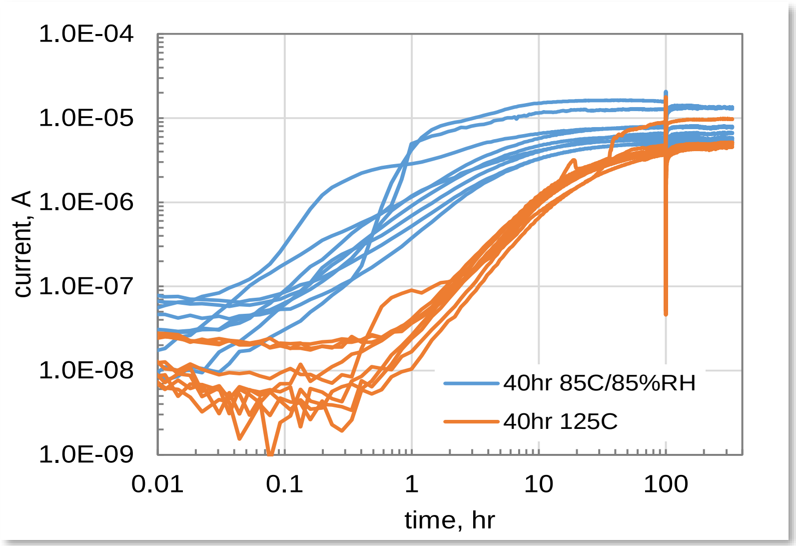


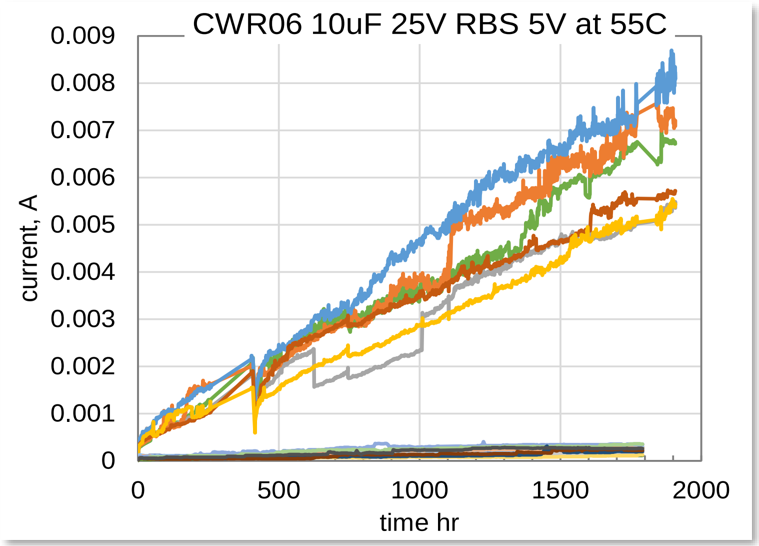
- ✓ Degradation can be approximated with linear functions, R ≈ const.
- ✓ Increasing RH from 7% to 35% increases the rate of degradation ~ 3 times. At 85% RH the rate increases ~ 20 times.

Effect of Moisture, Cont'd

Testing at 2V, room conditions.
Preconditioning: (i) bake at 125 °C and (ii) soaking in moisture at 85 °C 85% RH.

Testing at 5V in air and in vacuum.
Preconditioning in air: 125 °C for 100 hr; in vacuum ~3×10^{-6} torr: 75 °C for 100 hr.

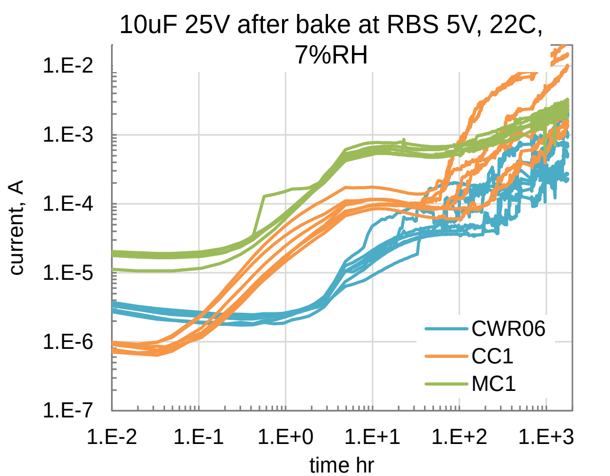


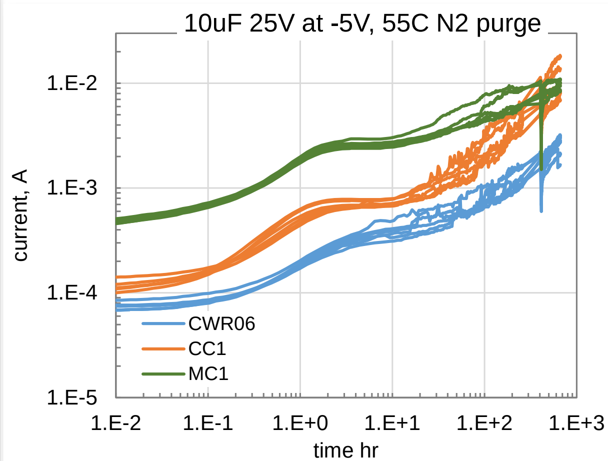


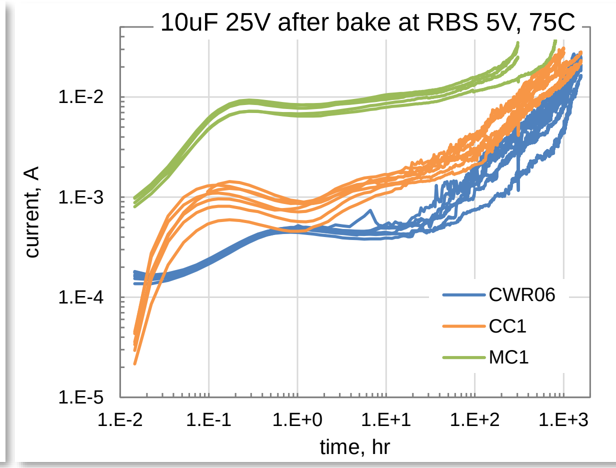
- ✓ Preconditioning affects the rate of degradation and the level of the steady-state currents.
- ✓ There is a substantial difference in RB behavior between dry air and deep vacuum conditions.

Effect of Temperature at Dry Conditions

RB degradation for 3 part types at 22 ^oC, 55 ^oC, and 75 ^oC

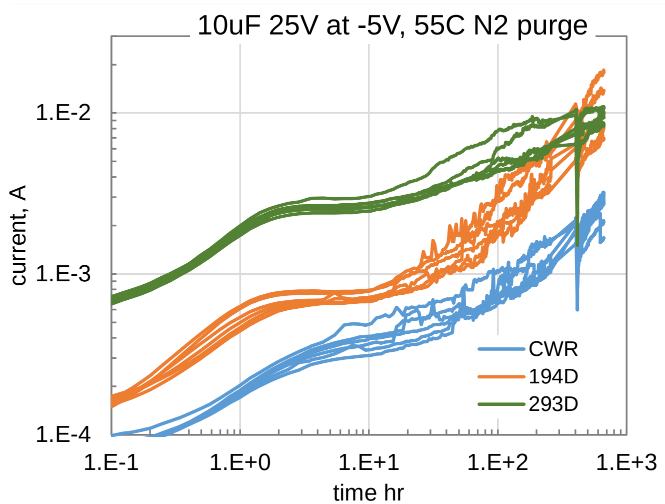


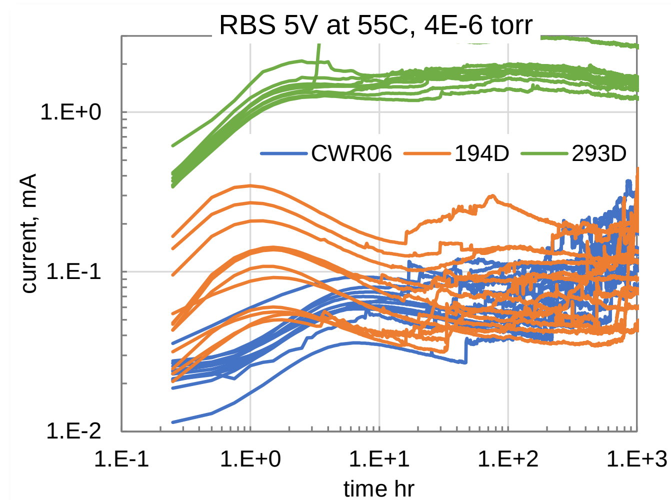




- ✓ A two-stage degradation process in all part types.
- ✓ The level of degradation can vary ~100X depending on type of capacitors.
- ✓ Time to the first maximum decreases with T; E_a ~0.63 eV.
- ✓ The rate of long-term degradation has E_a ~1 eV.

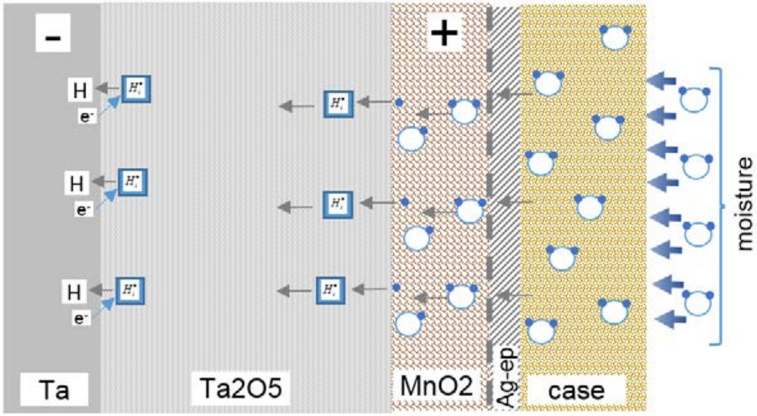
RB Degradation in Vacuum and in Dry Air at 55ºC





- ✓ Initial humps are similar in air and in vacuum.
- ✓ In dry air degradation continues after ~ 10 hrs, while there is a trend to stabilization in vacuum.
- ✓ Currents in air after 1000 hrs are >10X greater than in vacuum.

Ionic Currents



- Protons are injected from MnO2 and are discharging at the cathode. Hydrogen diffuses into tantalum.
- According to this mechanism conduction depends on the moisture flow through the case:

$$\left.\frac{\Delta m(t)}{\Delta t}\right|_{max} = \tilde{p}\frac{S}{d}P_0$$

- Assuming that all water molecules will dissociate forming protons, the maximum ionic current is:

$$I_{i\_max} = \frac{\Delta m(t)}{\Delta t}\frac{qN_A}{M} = \frac{qN_A}{M}\tilde{p}\frac{S}{d}P_0$$

- Estimations for RC show I_{i_max} ~ 6 μA, which is ~1000X less than experimental data.
- Also, ionic conduction should stabilize after the diffusion delay time, t_D, which is a few hours at room temperature.

✓ Ionic conduction can not explain excessive reverse currents in the presence of moisture.

Degradation in Vacuum

Oxygen vacancies (OV) in Ta2O5

- Built-in OV are formed at the Ta/Ta2O5 interface by absorption of oxygen in tantalum.

$$O_O^x \Leftrightarrow V_O^{\bullet\bullet} + 2e^- + 1/2O_2$$

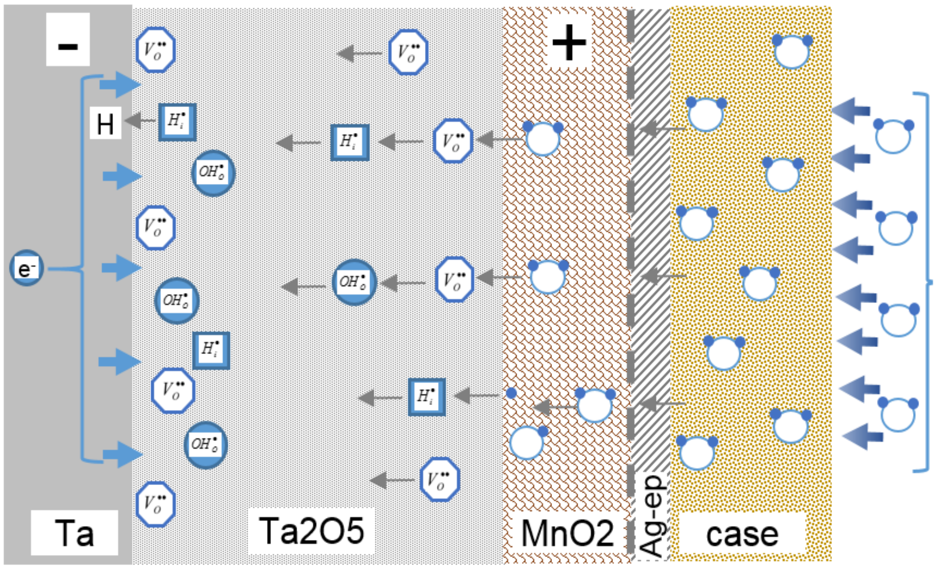
- Generation and recombination of OV.
- Concentration of OV depends on temperature exponentially with E_a ~ 1 to 1.5 eV.
- Migration of V_O^{++} to Ta/Ta2O5 interface during RBS builds up a charge that reduces Schottky barrier and increases injection of electrons.
- Charge accumulation stabilizes with time resulting in stabilization of currents.
- Erratic behavior might be due formation of conductive filaments.

✓ Degradation is due to sweeping of remnant protonic species and generated V_O^{++} in Ta2O5 towards Ta.

✓ The level of degradation is controlled by processes of migration, diffusion, generation and neutralization of OVs.

Degradation in Humid Environments

- Protons can migrate as “free” particles or by transport vehicle mechanism.



- Formation of hydronium ions:

$$H^{+} + H_2O \rightarrow H_3{}^{+}O$$

- Injected protons bond with oxygen:

$$H_i^{\bullet} + O_O^{x} \longrightarrow 2OH_O^{\bullet}$$

- Reaction of OV with water:

$$H_2O + V_O^{\bullet\bullet} \longrightarrow 2H_i^{\bullet} + O_O^{x}$$

- Formation of partially filled OV:

$$H_2O + V_O^{\bullet\bullet} + O_O^{x} \longrightarrow 2OH_O^{\bullet}$$

- The time to the first maximum is:

$$\tau_1 = \frac{d^2}{\mu \times V}$$

- ✓ At RT τ_1 ~ 30 hr -> μ_1 ~ 4×10^{-16} $cm^2/(V\times sec)$, which is close to literature data for OV.
- ✓ Various protonic species can be formed by reactions with OVs.
- ✓ The species act similar to V_o^{++} reducing the barrier at the Ta/Ta2O5 interface and increasing electronic currents.

Conclusion

- Slugs in Ta capacitors can be used as moisture sensors.
- A model that describes *C-t* variations using moisture characteristics and sizes of plastic packages and tantalum slugs has been developed.
- RB degradation depends strongly on the presence of moisture in capacitors and is due to protonic complexes formed by reactions of water molecules with oxygen vacancies.
- Mechanisms of degradation of leakage currents under RB and FB conditions are similar and are due to migration of positively charged ionic species. However, only RB degradation is accelerated by the presence of moisture even at room conditions.