Keynote III.

Advances in the Environmental Performance of Polymer Capacitors

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ABSTRACT

Aluminum and Tantalum capacitors with conductive polymer cathodes were introduced in the mid-1990s. The first applications were in consumer electronics devices like notebook computers and other portable devices. With temperature ratings of 85°C or 105°C for 1000 hours and moderate humidity resistance (60°C/90%RH), these components sufficed for these applications. As this technology matured, interest in using it in applications like automotive, data centers/telecom, and defense/aerospace increased. These applications have much more stringent requirements for reliability and lifetime under temperature, electric field, and humidity. This paper explores the degradation mechanisms of polymer capacitors under these high stress conditions and details the material science advancements that have led to new product series designed for these more demanding applications.

SCOPE

Capacitor reliability is a broad topic, as the five major types (Tantalum, Multilayer Ceramic Capacitors [MLCCs], Aluminum Electrolytic, Film, and Super Capacitor) each exhibit distinct degradation mechanisms. The focus of this paper is on the mechanisms of environmental degradation of tantalum capacitors with conductive polymer cathodes with some additional references to aluminum capacitors with similar polymer cathodes.

RELEVANCE

Conductive polymer cathode capacitors were initially introduced in the mid-1990s: first Matsushita (Panasonic) released the aluminum capacitor SP-Cap[1] followed by NEC's release of the tantalum NEOCAPACITOR[2]. The primary driver for introduction was reduced Equivalent Series Resistance (ESR) which was becoming an increasingly important loss factor as digital circuit speeds increased and voltage levels decreased. As Figure 1 illustrates, the conductivity of conductive polymers is three orders of magnitude greater than electrolytes used in aluminum electrolytic capacitors and two orders of magnitude greater than the MnO_2 used in the manganese-type solid tantalum capacitors. This increase in cathode conductivity is the primary reason for the decrease in ESR.

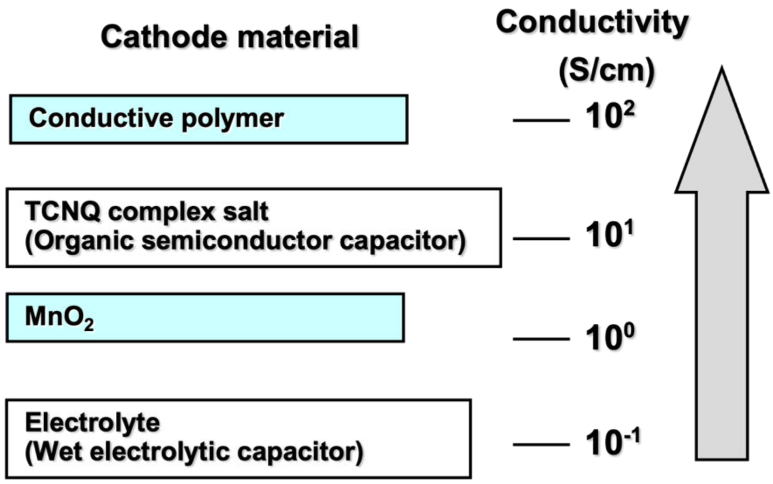


Figure 1: Conductivity of Cathode Materials

Initial stability at high temperatures were poor. For example, the original NEOCAPACITOR was only rated to 85°C (compared to 125°C for the manganese-type solid tantalum capacitor). This limited its use to consumer devices. Later a switch to a more stable conductive polymer allowed the temperature rating to be increased to 105°C[3] which allowed these components to be used in applications like notebook (laptop) computers. For these early conductive polymer-based capacitors, working voltages were generally limited to less than 16V. This restricted applications to voltage rails of 5V, 3.3V, and core voltages of microprocessors (<1.xV). Humidity ratings were limited to 60°C/90%RH which was significantly milder than the 85°C/85%RH rating generally required for applications like automotive and defense. A breakthrough in the application of conductive polymer technology by Qiu and coworkers at KEMET Electronics around 2008 allowed reliable higher voltage tantalum-polymer products to be introduced[4]. This extended to working voltage range initially to 25V and 35V, and now to 75V. This extended voltage range opened the application space beyond low voltage rails in notebook computers and consumer devices. Automotive manufacturers began to show interest in the technology as tantalum-polymer capacitors could be a solution especially as more and more digital electronics were introduced into cars. However, AEC-Q200 specifications required temperature ratings of 125°C and humidity ratings of 85°C/85%RH which tantalum-polymer capacitors had difficulty meeting because of the thermal stability of the conductive polymer and materials of construction of the packaging. Significant effort in the last 15 years has gone into developing tantalum-capacitors that can meet these AEC-Q200 requirements[5] and tantalum-polymer capacitors are now used by the major automotive Tier 1 suppliers and OEMs in their electronic modules.

Along with success with automotive, defense and aerospace manufacturers also began to show interest in tantalum-polymer capacitors[6]. Base requirements are like automotive requirements with some additional reliability guarantees needed. Initially series were introduced as Commercial Off the Shelf (COTS). However, their reliability (temperature, voltage, humidity) has now advanced to a level where MIL-SPEC series are available[7]. In addition, special hermetically sealed tantalum-polymer capacitors are offered by multiple manufacturers for the most demanding environmental conditions[8].

An emerging area for higher reliability is AI data centers. Data centers run 24/7, processors are now operating at higher power levels and higher temperatures, and failures can be costly especially for training models that take many hours and cost millions of dollars. The expectation is that components will operate 5 years (43,800 hours) at temperatures of 85-90°C and xPU suppliers are increasingly asking for proof of these lifetime commitments.

The remainder of this paper explains the physics and chemistry behind the extension of conductive polymer-based capacitors to longer lifetime and higher temperature, and humidity ratings.

TEMPERATURE AND VOLTAGE

The basic structure of a tantalum-polymer capacitor is shown in Figure 2. Fine particle size tantalum powder is sintered into a porous tantalum pellet which has a tantalum lead wire inserted or welded to it. Electrochemical anodization forms a conformal dielectric film of tantalum pentoxide (Ta_2O_5) on the tantalum pellet. Conductive polymer is then impregnated into the pores and onto the outside of the pellet to form the 2nd electrode of the capacitor. A tantalum capacitor is a polar device; consequently, the tantalum must be at a positive potential relative to the conductive polymer. Thus, the tantalum electrode is termed the anode, and the conductive polymer the cathode. A carbon-organic binder coating (usually graphitic) is deposited on the outside conductive polymer to protect the final coating of silver in an organic binder which forms a highly conductive shell on the outside of the capacitor and facilitates the connection of the cathode side of the capacitor to the final packaging.

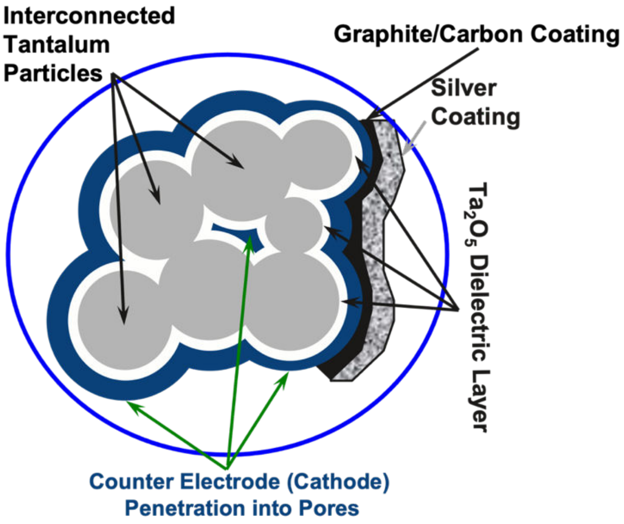


Figure 2: Internal Structure of a Tantalum Capacitor

Figure 2 represents a tantalum-polymer capacitor element, but without additional packaging, it would not be robust against the thermal and mechanical stress needed to attach it to the printed circuit board or the environmental (temperature, humidity) stress required in the end application. Figure 3 shows the most common surface mount packaging for tantalum capacitors. The lead wire on the tantalum anode side is welded to one side of a metallic lead frame and the silver coating on the conductive polymer cathode side is attached to the other side of the lead frame via a conductive silver adhesive. This assembly is then over molded with non-conductive epoxy to protect the capacitor element. The exposed lead frame is bent underneath the epoxy case, and this forms the points of attachment to the printed circuit board.

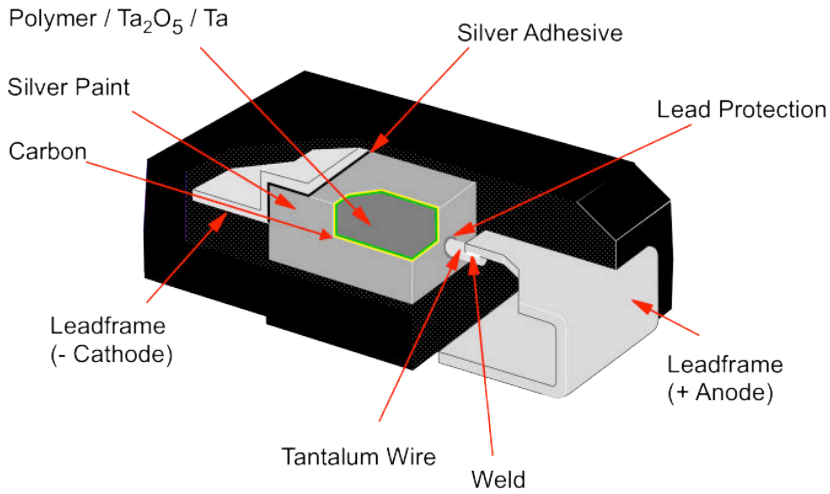


Figure 3: Surface Mount Tantalum-Polymer Capacitor

Dielectric Reliability

Life testing measures a capacitor's ability to maintain an acceptable level of the capacitors properties such as leakage current, capacitance, and ESR. In this type of testing, the capacitors are placed on test at an elevated temperature either at some voltage or unbiased. The capacitors are periodically removed from the test chamber, and the capacitor’s parameters are measured. Typical total test times are between 500 and 2000 hours although for some defense applications, testing may be done up to 10,000 hours. While useful for providing a snapshot of reliability, this test has limited predictive value for extrapolation to other voltage or temperature stress conditions, which typically reflect customer device operating environments. Accelerated life testing or time dependent dielectric breakdown testing (TDDB) tests capacitors and records failure times (by short circuit). By performing the test at different temperatures and voltages, an extrapolation model can be developed to predict time to failure under different voltage and temperature conditions.

Breakdown voltage (BDV) testing is another type of test used to assess dielectric reliability. Capacitors are tested at increasing voltages and when the leakage current rises above a certain limit, a breakdown event is recorded. This test is most often used as a measure of initial dielectric reliability.

The ability of a tantalum capacitor to withstand voltage and temperature stress without becoming a short circuit depends both on the quality of the tantalum pentoxide dielectric and the choice of cathode. Let’s first look at how a robust tantalum pentoxide dielectric is formed by electrochemical anodization and then some degradation mechanisms that can occur under voltage and temperature stress.

We can write the anodization of tantalum-to-tantalum pentoxide as:

$$Ta + 5H_20 \longrightarrow Ta_2O_5 + 5H_2 \qquad [1]$$

Commonly this reaction is carried out in dilute phosphoric acid at temperatures between room temperature an 85°C. Under these conditions, the amorphous form of tantalum pentoxide is formed (Figure 4)[9]. The stoichiometric amorphous form of the oxide forms a highly conformal coating on the underlying tantalum substrate and is a highly insulating dielectric. In phosphoric acid, some phosphate is incorporated into the outer layer of the dielectric,[10] and this does improve reliability by promoting the formation of the amorphous form of tantalum pentoxide[11]. Sometimes a thicker dielectric is formed on the outside of the pellet by utilizing a weak acid electrolyte[12]. This can improve reliability because the exterior of the anode pellet is subject to more mechanical and electrical stress than the interior.

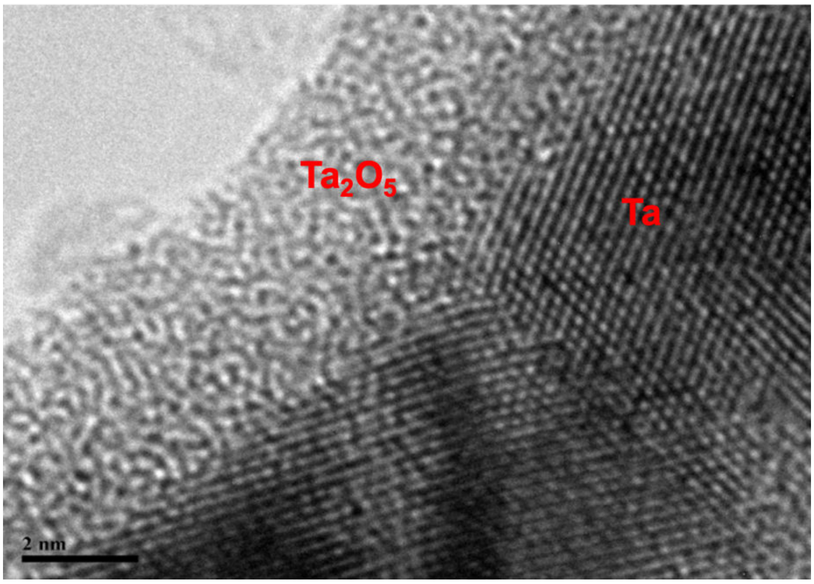


Figure 4: The Formation of an Amorphous Tantalum Pentoxide Dielectric on Crystalline Tantalum

Unfortunately, the stoichiometric amorphous form of tantalum pentoxide formed on a tantalum substrate is not thermodynamically stable. One mechanism of degradation is the migration of oxygen from the tantalum pentoxide to the tantalum substrate that can be written as:

$$Ta + Ta_2O_5 \rightarrow Ta(O)_x + Ta_2O_{5-x} + xV_o^{2+} + 2xe^- \qquad [2]$$

This reaction creates oxygen vacancies and converts the stoichiometric and highly insulating Ta_2O_5 into Ta_2O_{5-x} which is a semiconductor. As this reaction proceeds, the oxide becomes more conductive, leakage current increases, and eventually the dielectric breaks down, causing the capacitor to short circuit. Recent investigations into ReRAM memory, which uses oxygen vacancies as a “feature”, show that these vacancies probably form as conducting filaments between the anode and cathode and not uniformly throughout the dielectric[13].

Oxygen migration was recognized as a failure mechanism soon after the invention of the manganese-type solid tantalum capacitor, and Smyth, Tripp, and coworkers at Sprague Electric studied the mechanism of the reaction[14]. A scheme to slow down this reaction is shown in Figure 5. After forming the tantalum pentoxide dielectric, the pellet is heat treated to drive some of the oxygen from the tantalum pentoxide into the tantalum substrate. This forms a Ta(O) barrier layer between the oxide and the tantalum which slows down the migration of oxygen from the tantalum pentoxide to the tantalum. Since the tantalum pentoxide becomes deficient in oxygen after this step, a 2nd formation or “re-anodization” is performed to restore stoichiometry. Nitrogen atoms can also act as a barrier to oxygen migration and some powder manufacturers dope their powder with nitrogen.

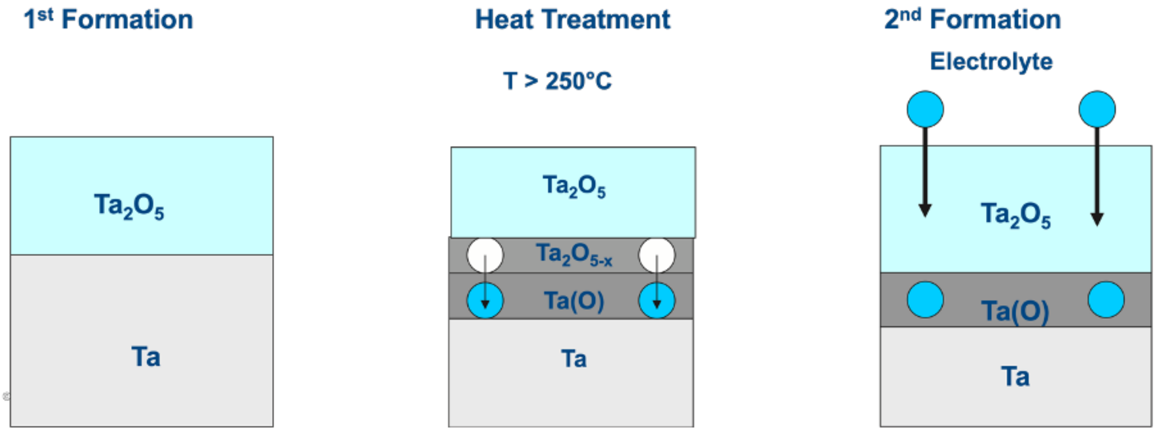


Figure 5: Stabilization of Tantalum Pentoxide Dielectric Film Against Oxygen Migration

A second mechanism for dielectric degradation is the formation of crystalline tantalum pentoxide which is more thermodynamically stable than the amorphous form. Figure 6 shows a crystal of tantalum pentoxide. Unlike the conformal amorphous form, the crystalline form grows perpendicular to the tantalum surface and has a different density than the amorphous form of the oxide. The crystalline form is a good dielectric, but forms leakage sites by the disruption of the conformal amorphous film.

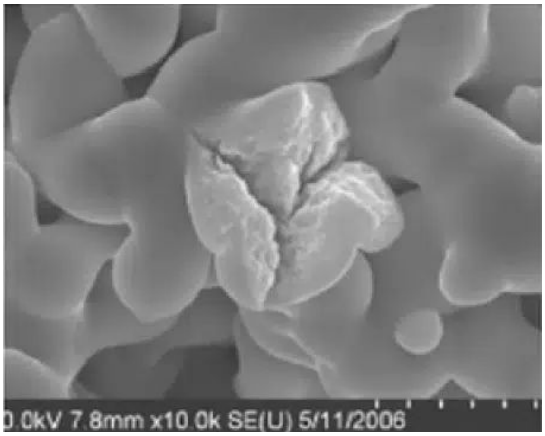


Figure 6: Crystalline Tantalum Pentoxide

Crystalline tantalum pentoxide can be formed in the thin passivating oxide layer (a few nm thick) that is present on the surface of tantalum particles, during the anodization of tantalum-to-tantalum pentoxide, and during the use of the capacitor in the electronic circuit under temperature and voltage.

Dr. Yuri Freeman and his colleagues at Tel-Aviv studied the effect of the oxygen content of tantalum anode[15]. They found that as oxygen content increased towards saturation of the lattice, a greater number of small crystals of tantalum pentoxide formed in the surface passivating film as shown in Figure 7. An amorphous dielectric could be formed over these crystals and initial performance of the capacitors were within specified limits. However, under temperature and voltage during life test, these crystals grow and eventually punch through the amorphous film, causing dielectric failure (as illustrated in Figure 8). Oxygen levels in the anode are affected by the level in the incoming powder, the sintering conditions, and how the anode is passivated after sintering. Techniques like sintering the tantalum anode pellets in the presence of a reducing agent like magnesium can significantly lower the oxygen content in the tantalum anode[16].

As discussed above, the combination of high temperatures and an electric field promotes the growth of crystalline oxide[11]. This is a major issue as anodization voltage increases. The power input to the system increases (V * I), and it is dissipated as heat. Because it is difficult to remove heat from the interior of the tantalum pellet, temperature of the pellet can rise significantly as anodization voltage increases. For anodization voltages above 100V there is almost always some crystalline tantalum pentoxide present, and anodization voltages of approximately 200V are a practical limit for anodization in phosphoric acid electrolytes. Several methods have been developed to overcome this limitation including anodization in electrolytes below room temperature[17] and modifying the anodization current-voltage profile to reduce power at higher voltages. However, these methods prolong the anodization times significantly and are only used for specialized defense and medical products.

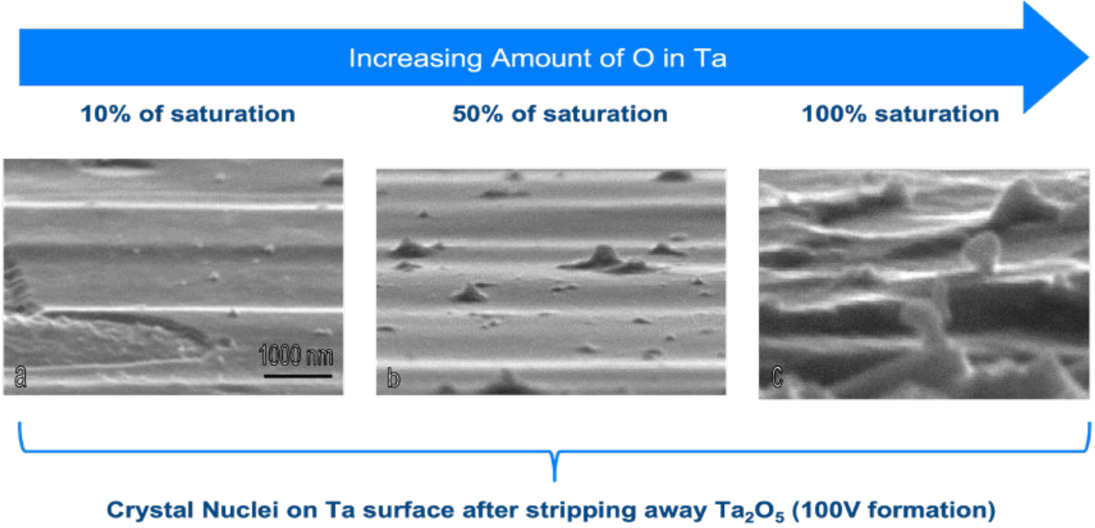


Figure 7: Crystal Nuclei on Ta at Different Oxygen Levels

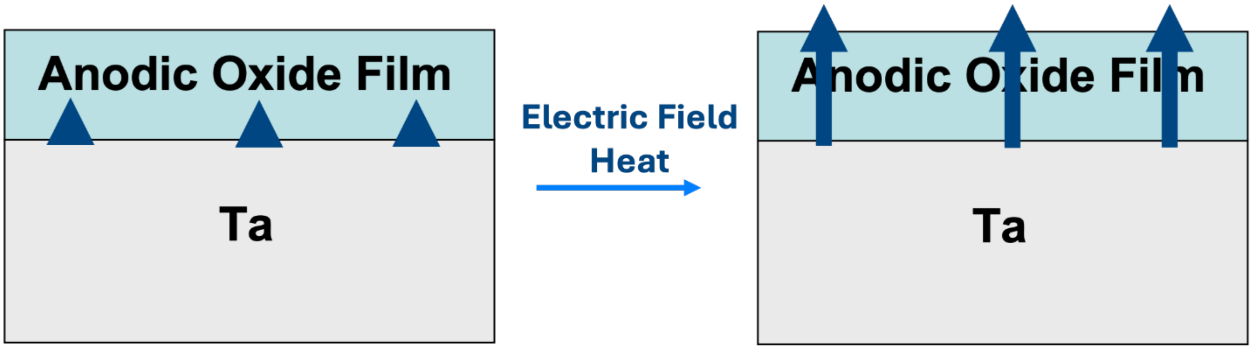
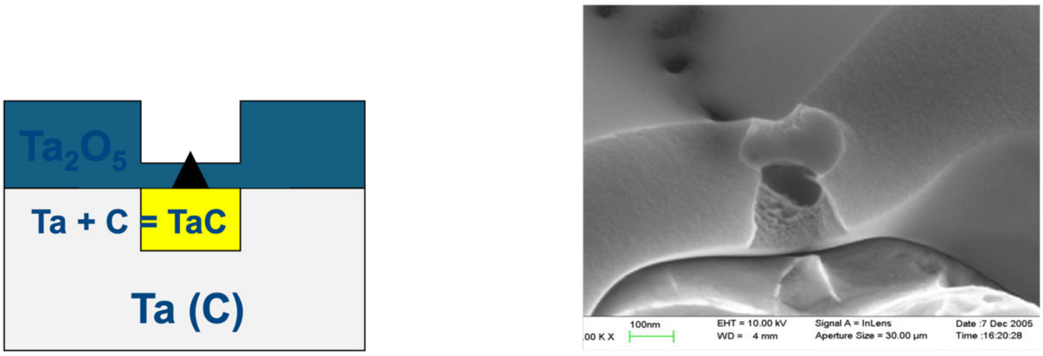


Figure 8: Growth of Crystalline Tantalum Pentoxide

Formation of a quality tantalum pentoxide dielectric is also affected by impurities in the incoming tantalum powder and residual carbon from organic binders used in the anode pellet pressing process. I've covered the effect of the most ubiquitous impurity—oxygen—above. Other important impurities include carbon, heavy metal contaminants from reactor vessels (e.g., Fe, Cr, Ni), and reducing agents and salts used in the powder production process (e.g., Na, Mg, K). Defects in the dielectric film can include areas where no dielectric forms like that show in Figure 9 for a carbon impurity[18] or mixed compounds of tantalum and the impurity which are not good dielectrics.



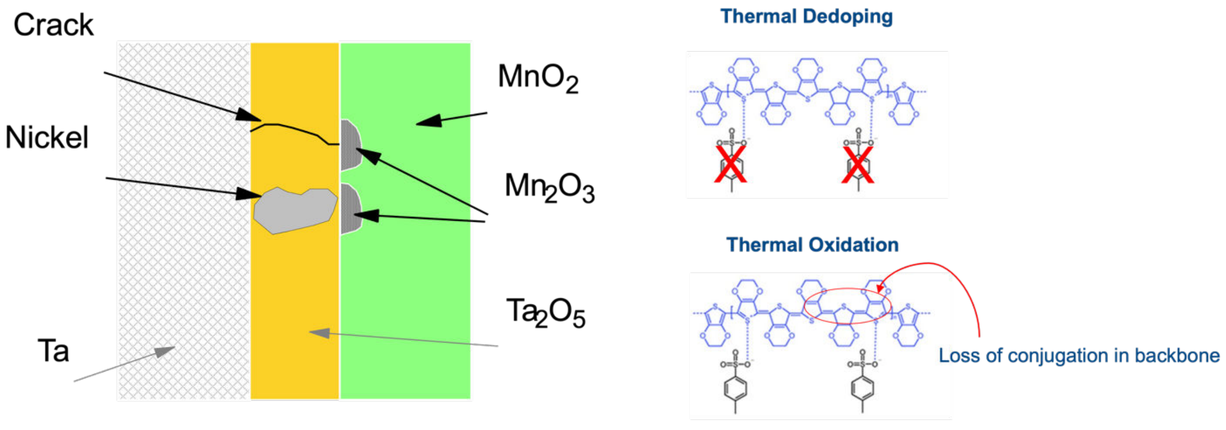
(a) Schematic illustration of Vermilyea's Defect

(b) Area of non-formation of dielectric oxide

Figure 9: Defect in Dielectric Film Due to Carbon Impurity

I covered above several mechanisms that prevent the formation of a stoichiometric amorphous tantalum pentoxide dielectric or cause it to transform into a non-stoichiometric or crystalline form. In a high surface area tantalum capacitor, it would be almost impossible to produce a completely defect-free dielectric film and even more challenging to keep it defect-free as the capacitor is subjected to mechanical, temperature, and voltage stress. Fortunately, the cathode materials chosen for solid tantalum capacitors give some help as both manganese dioxide and conductive polymers have "self-healing" ability. Self-healing occurs when the cathode material transitions from a conductive state to a non-conductive state due to joule heating at a high leakage current site. It can be detected by observing scintillations (voltage decrease spikes) during constant current injection[13].

For the manganese dioxide cathode, heat transforms the conductive MnO_2 into a non-conductive oxide in a lower valence state (probably Mn_2O_3), as shown in Figure 10(a). This reaction occurs above 500°C. Oxygen released from the MnO_2 during this reaction can also be donated to the tantalum pentoxide dielectric replacing oxygen lost by oxygen migration. However, if the leakage site is too large, the oxygen can react directly with the underlying tantalum metal and this highly exothermic reaction can cause the capacitor to "ignite" potentially damaging the circuit board and nearby components. This is one of the main drawbacks of the tantalum-manganese dioxide capacitor.



(a) (b)

Figure 10: Self-Healing of at Cathodes in Tantalum Capacitors (a)MnO$_2$ Cathode (b) Conductive Polymer Cathode

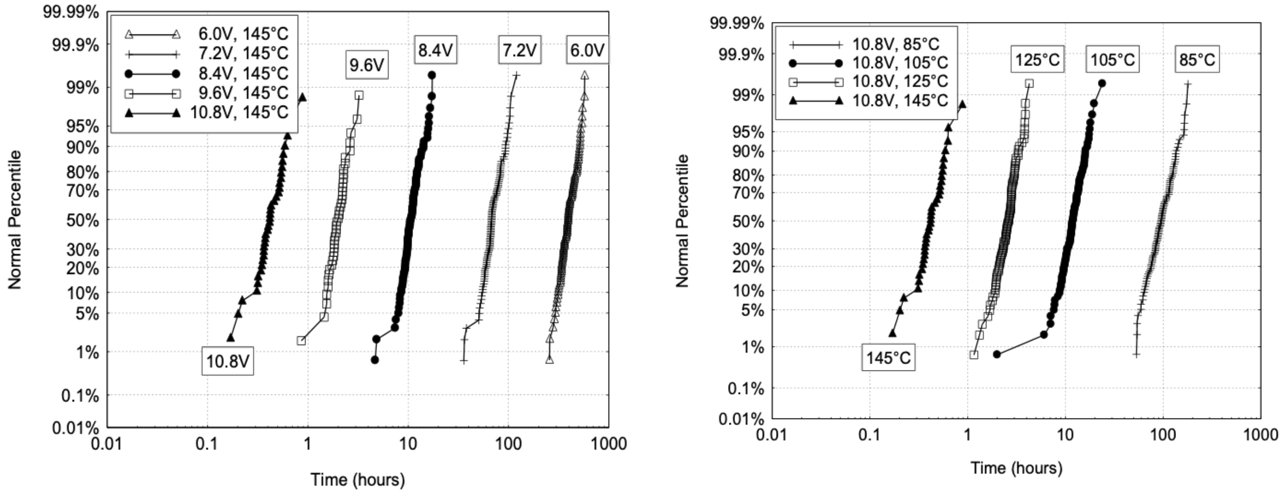
Conductive polymer cathodes become non-conductive due to thermal dedoping or thermal oxidation of the polymer backbone (Figure 10(b)). These reactions occur at much lower temperatures than the manganese dioxide transformation. The lower temperatures are an advantage in the self-healing reaction, but we'll see in the next section that they are a weakness of the conductive polymer system on high temperature exposure or long-term exposure at moderate temperatures. Unlike manganese dioxide, the polymer has no active oxygen to donate to the dielectric electric. The presence of some level of moisture in the tantalum-polymer capacitor can promote self-healing due to the generation of oxygen from water at the defect site.

The type of conductive polymer also plays an important role in the reliability of tantalum-polymer capacitors. The polymers used initially in tantalum-polymer capacitors were deposited by either *in-situ* chemical oxidation of a monomer or electrochemical oxidation. When rated voltages exceeded 16V, parts had low breakdown voltages and poor performance on long-term testing at rated voltage and temperature. The discovery that depositing some or all the conductive polymer from a pre-polymerized dispersion increased the breakdown voltage and allowed reliable higher-voltage parts to be manufactured was a significant breakthrough for tantalum-polymer capacitors[4]. The exact mechanism responsible for this is still being investigated: reduction of the surface barrier by reaction byproducts[19], damage to the dielectric by radicals during oxidative polymerization of the monomer, and difference in penetration rates through defects in the dielectric film have all been suggested.

Having covered the physical and chemical mechanisms that affect dielectric reliability, we can now examine methods to quantitatively predict the time to dielectric wear out in tantalum capacitors and provide evidence for which mechanism(s) are most import. Accelerated life testing has been used since at least the early 1960s to measure the reliability of solid tantalum capacitors with manganese dioxide cathodes and reduce failure rates by eliminating early failures from the population of capacitors from production batches that are shipped[20]. At the accelerated voltages and temperatures used to remove these early failures, no dielectric wear out was observed, so entire batches could be graded to given reliability levels without significantly affecting the failure rate of the remaining population.

The first work on dielectric reliability of tantalum-polymer capacitors was done by Reed and coworkers in the early 2000s[21]. Initial testing was done on 6.3V capacitors and this was later extended to lower voltages (2.5 and 4V) and then higher voltages (25 and 35V). The capacitors under test were in series with a fuse which blew open when the leakage current exceed a certain threshold. The time when each failure occurred was recorded. Acceleration was varied by testing at different multiples of the rated voltage and different elevated temperatures.

Figure 11 shows the results for accelerated testing on a 100µF/6.3V tantalum-polymer capacitor. The bulk of the population fails over a narrow range of times which is assumed to be dielectric wear-out. There is a much smaller secondary population of early failures. This stands in contrast to tantalum-manganese dioxide capacitors which have more early failures at even lower acceleration factors than shown in Figure 11 for the tantalum-polymer capacitors. The behavior for higher voltage (25V and greater) tantalum-polymer capacitors is a little more complex. Like their low voltage counterparts, they show a distinct wear-out region. They also have more early failures especially as acceleration voltage increases. They also have an "anti-wear-out" region at longer times which may be due to loss in capacitance. It is thought that the main mechanism of failure under rated conditions for these higher voltage tantalum-polymer capacitors is wear-out, so that region of the curve is what is fit to a model.



(a) (b)

Figure 11: Accelerated Life Testing of a 100µF/6.3V Tantalum-Polymer Capacitor (a) Voltage Acceleration (b) Temperature Acceleration

Reed and colleagues first tried to fit the wear-out portion of the curve to an equation first proposed by Prokopowicz and Vaskas[22] which has been successfully used to model the wear-out of multi-layer ceramic capacitors:

$$A = \left(\frac{V_2}{V_1}\right)^n e^{\left[\frac{E_a}{k}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)\right]} \qquad [3]$$

where A is the acceleration factor, V is the voltage, and T is the absolute temperature. The fitting parameters are n for the power law voltage exponent and E_a for the activation energy with temperature. This equation is a combination of a power law in acceleration for voltage and the Arrhenius relation for acceleration in temperature. Reed et al. were able to achieve a good fit to this equation and predict that the time to (50%) dielectric wear-out at 85°C and rated voltage to be thousands of years for tantalum-polymer capacitors. However, the voltage exponent n was different at each temperature and the activation energy E_a was different at each voltage. Clearly there was some interaction between voltage and temperature.

Based on a suggestion from Dr. Yuri Pozdeev-Freeman, Reed et al. attempted to fit the to a 'physics-based' equation based on field modified activation energy proposed by McPherson et al.[23]:

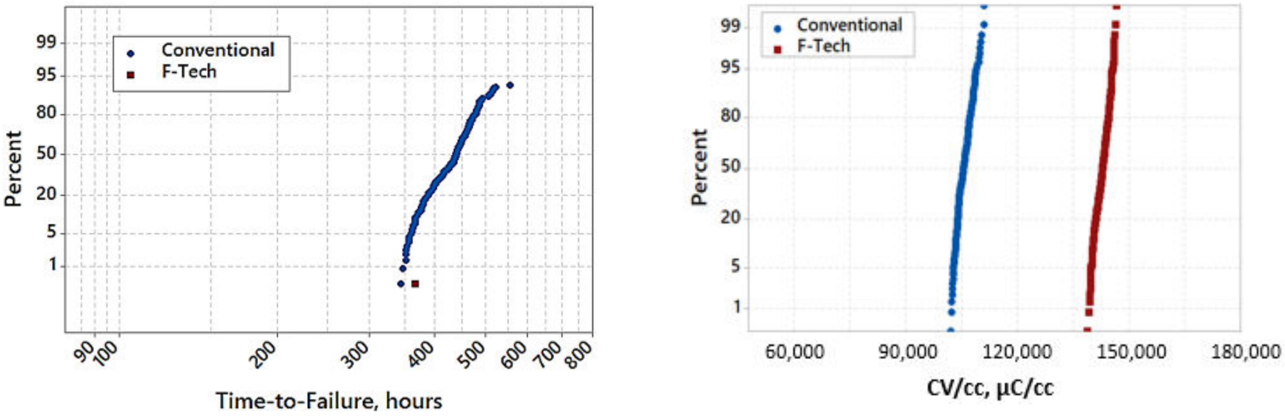
$$t = t_0 e^{\left[\frac{(W-\alpha U)}{kT}\right]} \qquad [4]$$

where t is the time to failure, t_0 is an empirically derived constant, W is the activation energy of the degradation process, and αU represents a reduction in this activation energy by the electric field in the dielectric. Reed et al. were able to get a good fit to this equation with W=1.8eV and αU=0.04eV. They concluded, based on similar results obtained for tantalum-manganese dioxide capacitors, that the dominant failure mechanism was oxygen migration. However, they also noted that the fit was not perfect and if a second degradation mechanism with the same form and W=2.5eV and αU=0.45eV was introduced, the fit was nearly perfect. They speculated that this degradation mechanism might be due to tantalum pentoxide crystallization.

More recently Teverovsky[24] and Eidelman et al.[25] have carried out similar testing to Dr. Reed's group and come to a similar set of conclusions. Both Equations 3 and 4 give good fits to the data. Equation 4 seems to be preferred as it gives a more 'conservative' (shorter time) estimate of the lifetime of tantalum-polymer capacitor wear-out. Both more recent publications give estimates for when 0.1% of the capacitors will fail by dielectric wear-out—this is a much more realistic percentage to use especially for high reliability applications. Even at the 0.1% level, predicted times are 100's to 1000's of years at 85°C and 80% of rated voltage.

Tantalum-polymer capacitors do not have the same failure signature as tantalum-manganese dioxide capacitors, and this presented a dilemma when they were first being qualified for defense/aerospace use. Normal batch grading techniques that removed early failures in tantalum-manganese dioxide capacitors could not be used for tantalum-polymer capacitors—any early failures occurred too close to wear out for tantalum-polymer capacitors and would use up a significant portion of their useful life. Reed and Caetano[26] proposed subjecting a sample of capacitor batch to accelerated life testing and using that as a measure of reliability. Cozzolino[6] discusses how this was used in one aerospace program to replace a problematic tantalum-manganese dioxide capacitor with a tantalum-polymer capacitor.

Despite the robust reliability of tantalum-polymer capacitors to dielectric breakdown, there is still a desire for further improvement, especially for critical applications in the defense and aerospace sectors. Increasing the formation to rated voltage ratio could accomplish this, but this negatively impacts the amount of capacitance obtained and could be detrimental for higher voltage parts where crystallization of the dielectric becomes a factor. A comparison of time to failure for a 220µ/16V capacitor processed using conventional pressing and sintering methods vs. that using the 'F-Tech' process invented by Dr. Yuri Freeman is shown in Figure 12(a)[27]. The F-Tech anodes were pressed using a stearic acid binder that was removed completely by aqueous washing to bring the carbon level to that of the original powder and sintered in a magnesium atmosphere and carefully passivated after sintering to bring the oxygen to a low level. The Figure 12(a) shows that the conventional capacitors fail by dielectric wear out at 350 to 550 hours, but only 1 out of 200 capacitors with F-Tech anodes have failed at this point. Remarkably, the CV/cc is higher for the F-Tech parts than the control (Figure 12(b)) so improved reliability has been achieved with increased capacitance (or decreased size).



(a)

(b)

Figure 12: Conventional Processed Anode vs. F-Tech for D Case 220μF/16V (a) Parts Tested at 105°C and 1.3x Rated Voltage (b) CV/cc Comparison

Moisture plays an important role in the self-healing mechanism of tantalum-polymer capacitors. In conventional surface mount parts with an epoxy casing, it is difficult to control the moisture level because moisture can enter and leave through the epoxy case or the interface between the epoxy case and lead frame. However, in hermetically sealed parts, moisture can be introduced and retained in the part during use[28]. Freeman et al.[29] demonstrated increased BDV and much smaller leakage current shift on life test for 60 and 75V hermetically sealed tantalum-polymer parts that contained a controlled level of moisture vs. those that were packaged in a dry state.

Degradation of Conductive Polymer Cathodes

The manganese dioxide cathode does not begin to thermally degrade until several hundred degrees Celsius. Therefore, loss of capacitance or increase of ESR at typical rated temperatures for these capacitors of 125°C is not an issue[30]. The situation for conductive polymer cathodes is quite different, as these organic compounds can exhibit significant thermal degradation in air. This can cause loss of capacitance and increase of ESR. This loss of capacitance and increase of ESR can become the primary failure mechanism for these devices and occur on a shorter time scale than failure by dielectric wear out. Under vacuum conditions, such as space applications, the degradation is much slower due to the absence of air so thermal degradation of the conductive polymer is less of a concern[30].

Intrinsically conductive polymers were discovered in the late 1970s and the Nobel Prize in Chemistry was awarded in 2000 to MacDiarmid, Shirakawa, and Heeger for the discovery[31]. The polymer they discovered, polyacetylene (see Figure 13) was very conductive, but unfortunately had limited stability in air which made its industrial use impractical. This is due to its aliphatic backbone. Soon after, conductive polymers with aromatic backbones like polypyrrole (PPy) were discovered and these turned out to be more stable in air. The first capacitors with conductive polymer cathodes used PPy—deposited by electrochemical oxidation for the Panasonic SP-Cap and by chemical polymerization for the NEC NEOCAPACITOR. The original NEOCAPACITOR could only be used to 85°C because of the thermal instability of chemically polymerized pyrrole. The electrochemically deposited PPy was somewhat more stable probably due to the denser nature of the deposited material. Note that conductive polymers are much more stable in an inert atmosphere like nitrogen where oxidation and loss of conjugation in the backbone does not occur. In an inert atmosphere, conductivity degradation is by thermal dedoping which occurs at higher temperatures than backbone oxidation.

The conductive polymer poly 3,4-ethylenedioxythiophene or PEDOT was discovered in the 1980s at Bayer AG by Dr. Fredrich Jonas and his colleagues, who patented its use as a cathode for capacitors[32]. The ether bridge on the ring protects it from oxidation and PEDOT is more stable in air than PPy (Figure 14[33]).

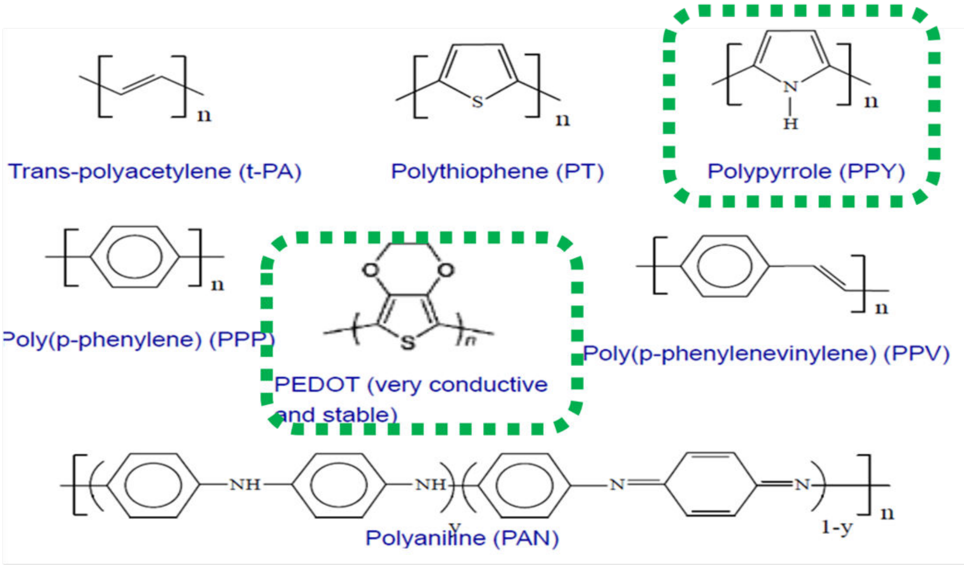


Figure 13: Intrinsically Conducting Polymers

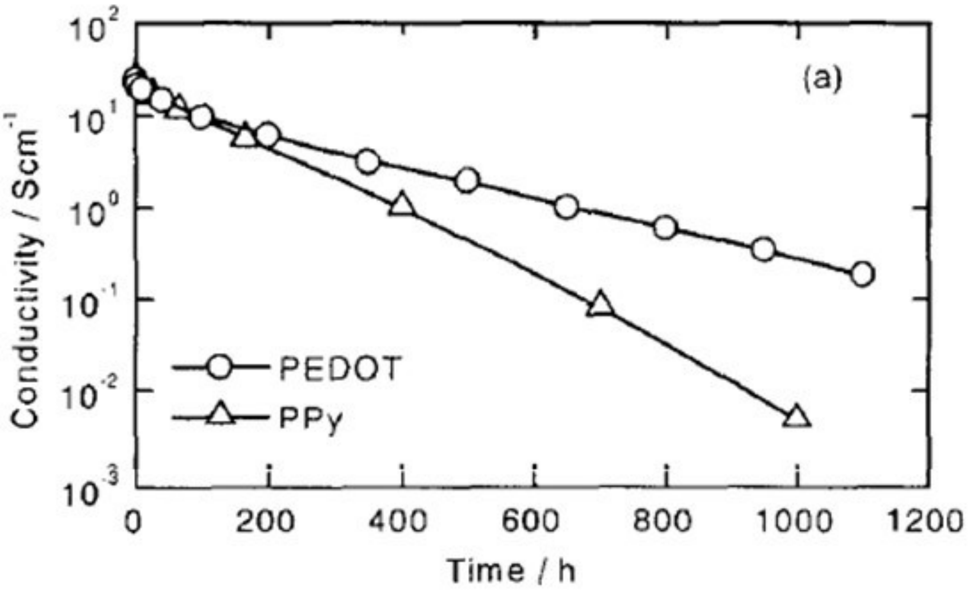
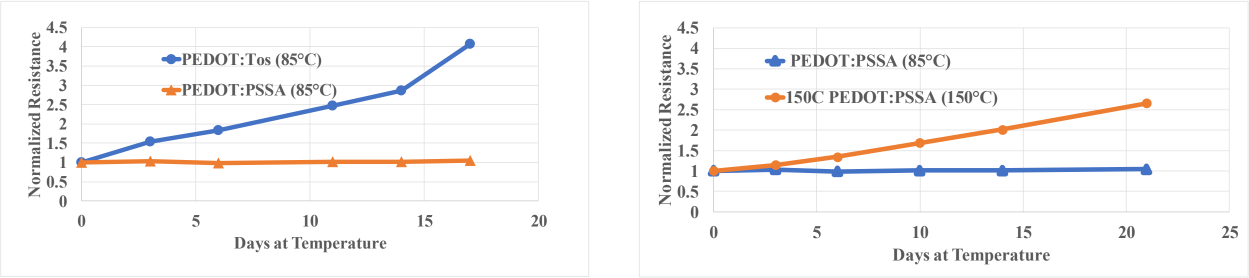


Figure 14: Change in Conductivity of PEDOT and PPy as a Function of Time in 125°C Air

Originally PEDOT was developed as an *in-situ* chemically polymerized conductive polymer—iron tosylate oxidizer/dopant was reacted with the EDOT monomer to synthesize PEDOT doped with tosylate ions. Bayer later developed a “pre-polymerized” suspension of this polymer in water where the PEDOT was doped with polystyrene sulfonic acid (PSSA) and excess PSSA formed a shell around the polymer allowing small particles of it to be suspended in water[34]. This was the version of the polymer that provided the breakthrough that allowed reliable higher voltage tantalum-polymer parts to be produced. It also proved to be more thermally stable to conductivity degradation than the in-situ version (Figure 15[35]). Jin et al.[36] hypothesized that this is due to high molecular weight PSSA shell that surrounds and protects the conductive polymer from oxidation.



(a)

(b)

Figure 15: Increase in Resistance Due to Thermal Degradation (a) Comparison of In-Situ (PEDOT:Tos) and Pre-Polymerized (PEDOT:PSSA) at 85°C in air (b) PEDOT:PSSA at 85 and 105°C in air.

Despite these advances in the intrinsic stability of conductive polymers, Figure 15 shows that the polymer will exhibit long-term degradation in air in the temperature range of interest for tantalum-polymer capacitors. Manufacturers of conductive polymers, such as Heraeus have introduced antioxidants that can improve the performance[37] shown in Figure 15. Research on improving the intrinsic stability of the conductive polymers continues. We need to rely on the packaging material external to the pellet in Figure 3 to protect the conductive polymer from the external air atmosphere. While developing automotive-grade tantalum-polymer series with 150°C capability, Chacko et al.[35] identified the following pathways to oxygen ingress to the conductive polymer:

- Primary Pathways
    - Through the mold epoxy
    - Through defects in the mold epoxy (i.e. pinholes, show-throughs)
    - Through the lead frame-mold epoxy interface
- Secondary Pathways
    - Through the cathode layers
    - Through delaminations in cathode layers
    - Through cracks/defects in cathode layers
    - Through exposed conductive polymer (at the top of the part where carbon and silver coatings are absent)

Several candidate improvements were identified. These included:

- Choosing an epoxy material with better adhesion to the lead frame.
- Using a lead frame plating like Ni/Pd/Au that does not melt when the part is reflowed (like a Sn plating).
- Roughening the lead frame to increase adhesion between the lead frame and epoxy case.
- Process and material control and final visual (or AOC) inspection procedures to reduce pinholes and show-throughs.
- Improving the adhesion between the cathode layers[38].

Teverovsky evaluated several general purpose and automotive grade tantalum-polymer capacitors[30]. Cross sections of parts exposed to high temperatures showed air ingress at the positive and negative lead frame-epoxy interfaces. Failed capacitors also exhibited delamination between cathode layers. This validated some of the mechanisms hypothesized by Chacko et al. Teverovsky also found much more stable ESR performance on temperature exposure of the automotive grade capacitors providing independent validation of the results reported by Young and Qazi, Ye et al.[5], and Chacko.

Modeling of the degradation of capacitance and ESR of tantalum-polymer capacitors is at a much earlier stage than the modeling of the dielectric wear-out. Teverovsky studied the capacitance, DF, and ESR degradation of general purpose, COTS, and automotive-grade tantalum-polymer capacitors from three different manufacturers over the temperature range of 100-175°C[39]. ESR increased faster than (120Hz) capacitance decreased. A Weibull-Arrhenius model was used to fit the results using 3 times the initial ESR as the failure criteria. There was considerable variation in the results, but the general conclusion was that time to 1% failure at 55°C ranged from a few years to about 88 years. Contrast this to the dielectric wear out results where hundreds to thousands of years of lifetime are predicted at 85°C and 0.8x rated voltage. Clearly oxidation of the polymer leading to ESR increase is a much more limiting degradation mechanism with temperature exposure than dielectric wear out in tantalum-polymer capacitors.

Automotive grade tantalum-polymer capacitors meeting AEC-Q200 specifications are now available from multiple component manufacturers[40]. Panasonic has released aluminum-polymer SP-Cap series with an enhanced temperature performance of 125°C 3000h and 5000h (targeted at AI data center applications)[41] and YAGEO(KEMET) also has a 125°C 3000h rated series[42]. In addition, aluminum-polymer capacitors are available in the “V-Chip” configuration where an aluminum can is used to encapsulate the capacitor. While not hermetic, this configuration generally has less pathways for air to diffuse in and degrade the conductive polymer. Various ratings like 105°C/5000h[43] and 125°C/4000h[44] are available. The trade-off is that these capacitors are larger (both height and footprint) than tantalum-polymer capacitors of the same capacitance and voltage.

PERFORMACE IN HUMID ENVIROMEMTS

Performance in humid environments encompasses many different properties including initial change in parametric values (e.g., capacitance) on exposure to moisture, short term degradation due to moisture in the case during board reflow (MSL), and long-term changes due to extended moisture exposure. This section focuses on mechanisms related to long-term exposure. In the tantalum capacitor, the tantalum pentoxide dielectric is very stable against chemical attack and does not degrade in the presence of moisture in contrast to the aluminum oxide dielectric in aluminum capacitors which can undergo significant hydration. Therefore, the mechanisms of degradation on long-term exposure are related to the anode and cathode metals and polymers.

Leakage Current Increase Due to Corrosion

As noted in the section on dielectric reliability, moisture can have a positive effect on tantalum-polymer capacitors by donating oxygen to vacancy sites in the dielectric. On humidity testing of tantalum-polymer capacitors, we often observe an initial leakage current decrease due to this mechanism. At longer exposure times, leakage current can begin to increase.

There are two mechanisms of leakage current increase (eventually leading to short circuits). One mechanism, occurring in the absence of bias, is the diffusion of silver from the silver coatings on the exterior of the capacitor element to the dielectric. Unlike conductive polymers or MnO_2, silver has no self-healing mechanism and contact with the dielectric at a leakage site will eventually lead to a short in the capacitor. The other mechanism occurs under bias and is corrosion of copper on the positive side of the lead frame which leads to copper dendrite growth from the anode side to the cathode side of the capacitor and leakage current increases and shorts. I’ll now discuss the chemical basis behind these mechanisms and some actions that have been taken to minimize or eliminate these failure modes.

The most common reagent for the in-situ oxidation of EDOT monomer to conducting PEDOT polymer is iron(III) para-tosylate. The reaction is carried out in the presence of excess p-toluene sulfonic acid. After the reaction, there is some excess iron(III) tosylate as well as the reduced iron(II) form of the salt, various oligomers of EDOT, and excess free p-toluene sulfonic acid. Manufacturers do their best to remove the excess reactants and byproducts, but complete removal is not possible. When moisture penetrates to the capacitor element, these ionic species form an electrolyte solution. Ag+ ions can be formed from the small amount of AgO in the silver coating or by oxidation of Ag by iron(III)[45]. Since silver tosylate is soluble, these silver ions can dissolve in the electrolyte solution.

With no positive bias on the anode, the Ag+ is free to diffuse to the interior of the capacitor pellet through the carbon coating and the conductive polymer. PEDOT can reduce Ag+ back to metallic silver[46]:

$$\text{PEDOT} + \text{Ag}^+ \rightarrow \text{Ag} + \text{PEDOT(ox)} \qquad [5]$$

If this happens adjacent to the dielectric, silver metal will contact the dielectric. Figure 16 shows the breakdown voltage (BDV) is very low for the $Ta/Ta_2O_5/Ag$ systems. There is a high probability that silver contact with the dielectric will lead to a short circuit once voltage is applied to the capacitor.

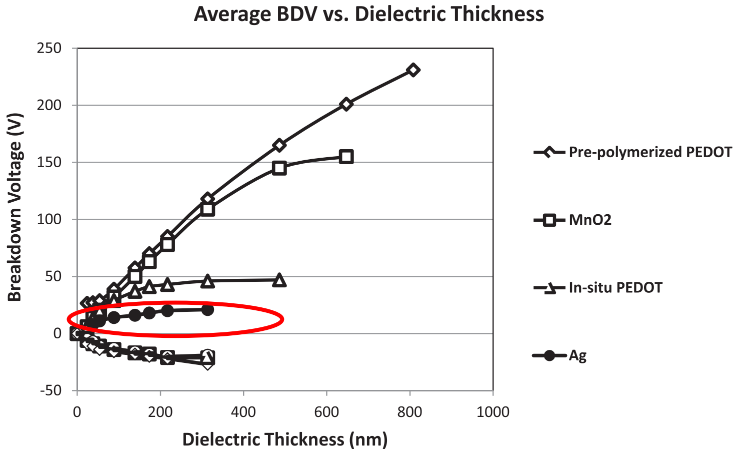
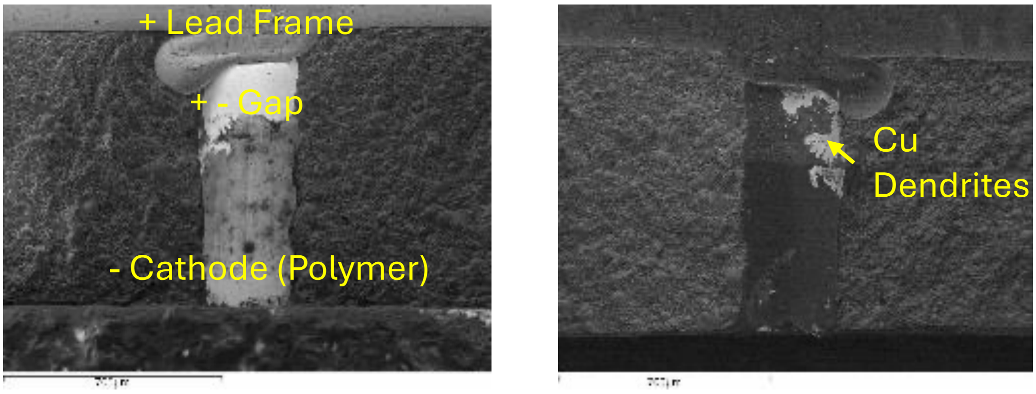


Figure 16: Breakdown Voltage vs. Dielectric Thickness for Different Cathode Materials on Ta/Ta₂O₅

When the capacitor is biased with voltage, the predominant corrosion reaction is the oxidation of copper near the tantalum riser wire weld area in the positive lead frame. Figure 17 shows a close-up of the positive lead frame area in a tantalum-polymer capacitor. The tantalum riser wire is welded to the lead frame. The cathode polymer coats part of the riser wire and there is a gap with no polymer that separates the positive and negative and prevents a short circuit. Figure 17(b) shows the situation after exposure to humidity under bias—Cu dendrites have bridged the gap between the positive and negative connection.



(a)

(b)

Figure 17: Corrosion of Copper Lead frame (a) Before Exposure to Humidity and Bias (b) After Exposure

As discussed above, ionic impurities left over from the polymerization process can dissolve in the moisture inside the part to form an electrolyte solution. Under bias, copper at the positive lead frame can corrode to Cu^{2+} by:

$$Cu \rightarrow Cu^{2+} + 2e^- \qquad [6a]$$

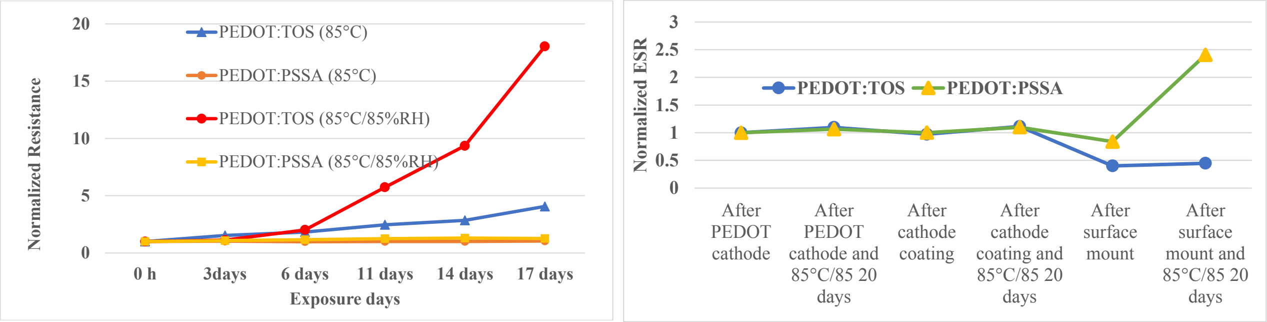
with possibly hydrogen evolution at the cathode

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \qquad [6b]$$

After the Cu dissolution, Cu^{2+} can migrate to the cathode and, similarly to Ag^+, react with the PEDOT polymer to form dendritic metal. When the copper bridges between and the positive and negative electrodes, the capacitor will be a short circuit.

ESR Increases

ESR can also increase when tantalum-polymer capacitors are exposed to humidity. Chacko et al. studied the mechanisms driving this increase[47]. When films of the conductive polymer PEDOT are exposed to humidity, the stability of films fabricated from the pre-polymerized polymer (PEDOT:PSSA) is greater than that of those fabricated from the in-situ polymer (PEDOT:ToS), as shown in Figure 18(a). This is hypothesized to be due to the same mechanism as the greater thermal stability of PEDOT:PSSA—the excess PSSA that surrounds the polymer forms a protective shell. However, Figure 18(b) shows that the opposite behavior is observed on polymer cathodes in the tantalum-polymer capacitor. Here the parts fabricated with PEDOT:Tos are more stable than those with PEDOT:PSSA.

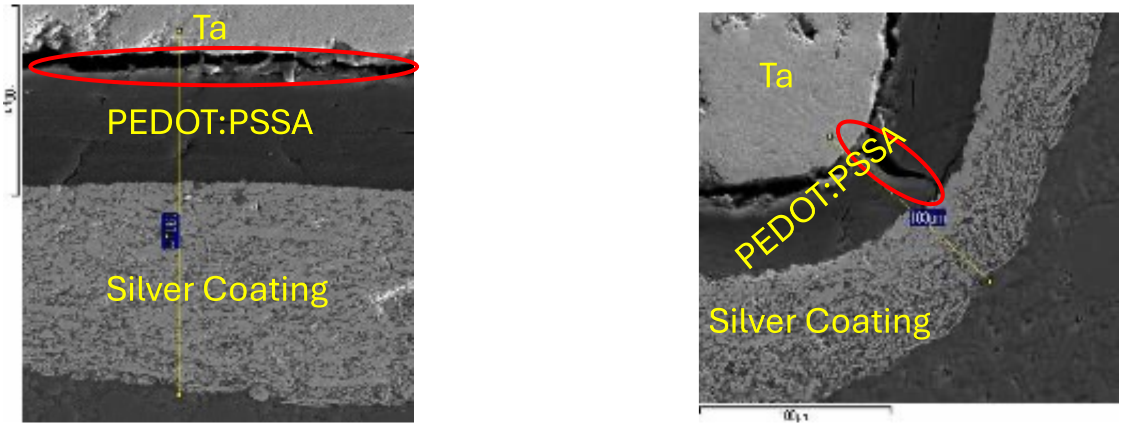


(a)

(b)

Figure 18: Resistance/ESR Changes of PEDOT Polymers on Exposure to Humidity (a) Polymer Fims (b) Polymer Cathodes in Ta Capacitors

Examination of SEM micrographs of failed capacitors reveals the reason for this behavior. There were two types of defects observed in PEDOT:PSSA cathodes after exposure to humidity. One type was delamination as shown in Figure 19(a). Here the delamination occurs at the Ta/Ta_2O_5/PEDOT:PSSA interface, but delamination has also been observed between the PEDOT:PSSA layers and between the PEDOT:PSSA and the C/Ag. The other type of defect was cracking within the PEDOT:PSSA layer as shown in Figure 19(b). Both types of defects lead to ESR increase in the capacitor.



(a)

(b)

Figure 19: High ESR Ta-Polymer Parts (a) Delamination between Cathode and Ta Anode (b) Crack in Cathode

Chacko et al.[47] hypothesized that the thermomechanical stresses of mounting the capacitor on the printed circuit board caused interfaces between layers to weaken, and then moisture sorption into the polymer caused further stress. The PEDOT:PSSA polymer absorbs more water than the PEDOT:ToS polymer due to the significant excess PSSA surrounding the conductive polymer core. Somewhat higher ESR shifts were observed on biased humidity testing. This was explained by voltage induced stresses in the polymer film combined with dedoping of the polymer after delamination.

Improvements

Improvements in humidity performance are complicated by there being three potential mechanisms—corrosion of the silver coating, corrosion of the copper lead frame, and delamination of the conductive polymer. There is no "one solution," and manufacturers solutions combine improvements at the packaging level (epoxy, lead frame) and the conductive polymer itself.

As with protection against oxidation of the polymer, the epoxy case plays a key role in protecting the interior capacitance against moisture attack. The amount of moisture absorbed by the epoxy case is dependent on humidity level and time. Different epoxy formulations can have significantly different moisture absorption as shown in Table 1. Selection of a low moisture absorbing epoxy can significantly slow down degradation in a humid environment. Choosing the epoxy encapsulation material involves balancing manufacturability and final material properties; moisture absorption is just one of several factors to consider.

Table 1: Moisture Absorption of Epoxies after 72h at 85°C/85%RH

Product	Absorption (%)
Epoxy A	0.3
Epoxy B	0.3
Epoxy C	0.15
Epoxy D	0.25
Epoxy E	0.5

The choice of lead frame material is critical is reducing high leakage or shorts on biased humidity testing. The properties of some common lead frame materials are shown in Table 2. Because of its low electrical resistivity, Alloy 194 was the lead frame of choice for most tantalum-polymer capacitors. It also has a very high thermal conductivity which contributes to good heat dissipation and higher ripple current ratings. Its 97.5% copper content contributes to its susceptibility to corrosion. Alloy 752 is a copper-nickel-zinc alloy and has been used in the past in tantalum capacitors. It has a coefficient of thermal expansion close to Alloy 194, making the mold tooling compatible when changing the lead frame. However, its electrical resistivity is about 15x that of Alloy 194 so there is an ESR penalty. Alloy 42 or one the stainless-steel alloys can eliminate copper completely. The resistivity of these alloys is twice that of Alloy 752 giving an even larger ESR penalty, but corrosion due to copper migration can be eliminated.

Table 2: Properties of Common Lead Frame Materials

Property	Units	Alloy 194	Alloy 752	Alloy 42	316SS
Electrical Resistivity	Ω-cm x 10^{-6}	1.98	28.70	61.00	74.00
Thermal Conductivity	W/m-K	259	33	10.5	16.3
CTE	µm/m-°C	17.6	16.2	5.3	16
Composition		Cu 97.5% Fe 2.35% P 0.03% Zn 0.12%	Cu 65% Ni 18% Zn 17%	Fe 55% Ni 42%	Fe 65% Cr 17% Ni 12% Mo 2.5%

The plating layer on the lead frame also plays a role. Better stability of both the plating and the plating/lead frame interface (which is also a potential source of moisture ingress) is obtained with Ni/Pd/Au plating vs. Sn or Sn/Pb plating.

Another approach to reducing corrosion of the lead frame is to apply a protective coating especially near the tantalum wire-lead frame weld area. Such coatings have been suggested by Liu et al.[48] and applied by at least one manufacturer. A challenge is that some of these coatings contain fluorine groups, due to the excellent hydrophobicity of these types of polymers. Draft regulations in Europe and other regions propose to ban these "PFAS" types of coatings, and manufacturers are now aggressively seeking substitutes.

The moisture uptake of the conductive polymer plays a significant role in the humidity behavior of the capacitor. As discussed above, moisture uptake by PEDOT:PSSA can promote delamination and cracking. The primary issue is the PSSA content of these polymers as PSSA is very hydrophilic. Buhna et al.[49] have replaced some of the PSSA with other polyanions and shown significant improvement in ESR performance in humidity testing[47].

Like degradation on temperature exposure, degradation on humidity exposure can be accelerated by delamination between the cathode layers (conductive polymer, carbon, silver). Interlayer adhesion promoting agents that are used to improve temperature performance can also improve humidity performance[38].

Corrosion only happens in the presence of ionic species that form an electrolyte. In the case of *in-situ* polymer, these species are left over reactants from the polymerization process that are not removed by washing, and in the case of pre-polymerized material they are excess PSSA. Removal of as much of these materials as possible can reduce the corrosion rates.

SUMMARY AND OPPORTUNITIES FOR FURTHER WORK

Tantalum capacitors with conductive polymer cathodes continue to grow in market share at the expense of tantalum capacitors with manganese dioxide cathodes. Figure 20 shows that the market share (by value) of tantalum-polymer capacitors surpassed that of tantalum-MnO_2 capacitors in 2019 and continues to grow. To continue this growth path, tantalum-polymer capacitors must continue to expand to applications that have demanding reliability and environmental requirements like automotive, AI data centers, and defense/aerospace.

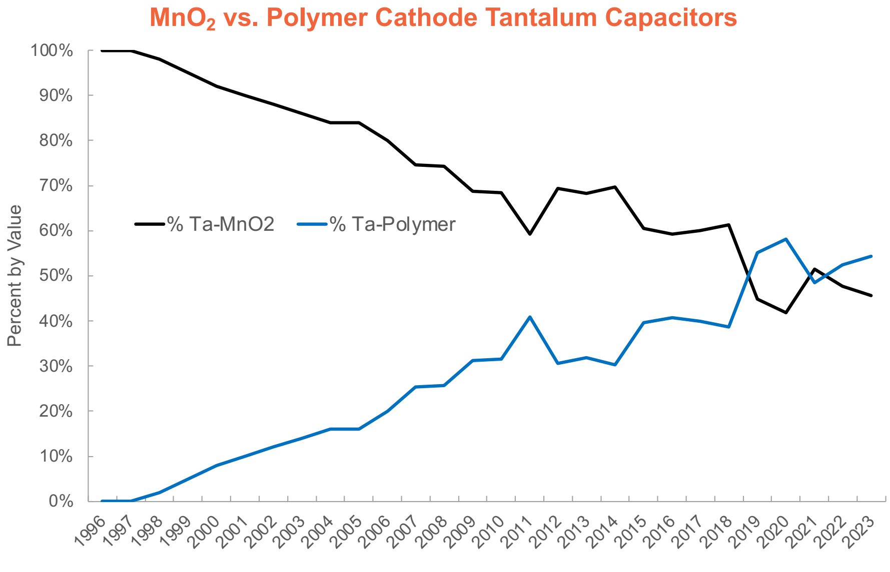


Figure 20: Market Share of Tantalum-Polymer and Tantalum-MnO_2 Capacitors

High dielectric reliability has already been achieved for these capacitors by applying lessons learned on dielectric formation during the development of tantalum-manganese dioxide capacitors and choice of the right type of polymer. Expected times to dielectric failure range from hundreds to thousands of years at 85°C and 0.8-1x rated voltage which should be sufficient for most applications. Special techniques are available, if needed, to produce even higher reliability parts. COTS and MIL-SPEC tantalum-polymer parts are now available and reliability estimation methods are in place to assure that these parts meet the reliabilities required by these specifications.

ESR increase and capacitance loss on prolonged temperature exposure remain a concern for tantalum-polymer capacitors. AI datacenters are asking for 5 year (~44,000 hours) lifetime at 85-90°C for components used on motherboards and solid-state drives. Automotive electronic systems manufacturers are also seeking longer lifetime as electric vehicles are expected to last longer than internal combustion vehicles and autonomous electric vehicles might operate near a 24/7 duty cycle. The expectation is moving from 10,000 hours lifetime to greater than 100,000 hours of lifetime. Several performance improvements were covered, and series have been introduced that meet the 125°C AEC-Q200 requirement and even are capable of 150°C operation. Some models are available to predict lifetimes at other operating conditions, but more work is needed to develop robust models.

The major mechanisms of degradation in humidity are now known for tantalum-polymer parts, and parts are now available that meet the 85°C/85%RH specification in AEC-Q200. No robust models are currently available for humidity exposure; these are needed to predict lifetime at other conditions of temperature and humidity. This remains an opportunity for future work.

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