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## Life model for tantalum electrolytic capacitors with conductive polymers

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#### ABSTRACT

Tantalum electrolytic capacitors have been on the market for more than half a century, in a range of applications. However, the most common design uses  $MnO_2$  as the electrolyte, which can be thermodynamically unstable and, upon failure, can damage the circuit. To mitigate this risk, an alternative to the  $MnO_2$  electrolyte was developed using conductive polymers. Compared to  $MnO_2$ , polymer Ta capacitors are more resilient to surge current, have a lower equivalent series resistance, and are ignition-free. However, polymer electrolytes are susceptible to degradation at high temperature and humidity. This paper presents an experimental study of polymer Ta capacitors from two different manufacturers, tested under six different environmental conditions, and characterized electrically at intervals during those tests. A time-to-failure model was developed to predict the degradation as a function of temperature and humidity.

#### 1. Introduction

Tantalum electrolytic capacitors are a type of passive component commonly found in electronic circuits. They consist of a pellet of Ta metal as an anode covered by an insulating oxide layer that forms the dielectric and surrounded by a solid electrolyte as a cathode. Ta capacitors are considered to be volumetrically efficient since they can achieve high capacitances with a relatively low volume. Ta capacitors are an alternative for miniaturized electronic components and are used in computers, cellphones, aerospace applications, military applications, and the health industry.

In the 1950s, Taylor and Haring [1] from Bell Laboratories invented a Ta capacitor that used, for the first time, a solid electrolyte. They built a porous Ta/Ta<sub>2</sub>O<sub>5</sub>MnO<sub>2</sub> capacitor that achieved higher capacitances per unit volume compared to other technologies. Their capacitor replaced the liquid electrolyte with MnO<sub>2</sub>, an electronically conducting semiconductor. Ta powder was sintered to form a porous slug and then was coated with a dielectric of Ta<sub>2</sub>O<sub>5</sub> over the entire surface. A layer of MnO<sub>2</sub> was deposited on top of the oxidized film.

The main parts of a Ta capacitor are the Ta wire partially covered by a dielectric (typically  ${\rm Ta_2O_5}$ ) and the electrolyte, a carbon layer, silver paint, and silver adhesive to increase the conductivity of the capacitor (see Fig. 1). The Ta wire is welded to the anode of the capacitor, and the cathode lead is soldered to the silvered anode. However, there are some capacitors in which the Ta wire is not welded but embedded into the

tantalum slug. Some Ta capacitors have a washer that prevents the electrolyte from passing up the wire and causing short circuits during manufacture [2].

When capacitors are subjected to electrical stresses, they can exhibit dielectric breakdown, a common failure mechanism. Dielectric breakdown is the failure that occurs when the dielectric  $({\rm Ta}_2{\rm O}_5)$  is not capable to withstand a certain electric field (from voltage stresses) causing it to break, allowing the current to flow from the anode to the cathode. This current that "leaks" is referred to as leakage current [3]. If the current is higher than a certain threshold the capacitor fails. Even though dielectric breakdown occurs in capacitors, some of them are able to recover or self-heal.

The leakage current flows and concentrates around the defect areas from the dielectric breakdown. This concentrated current causes the temperature within this very small region to rise significantly. As the  $MnO_2$  heats up past 380 °C, it begins to release oxygen, changing the material structure from  $MnO_2$  to a reduced state such as  $Mn_2O_3$ . Since this material has a higher resistivity than the original, the current that flows around the defect area is reduced. This process is referred to as "self-heating" [3].

Even though self-healing can be beneficial to Ta capacitors, those that use  $MnO_2$  can still present exothermic failures. The temperature rise during the healing process produces a high amount of heat in the failure site and thus a substantial release of oxygen can occur. The released oxygen can combine chemically with the Ta substrate in an

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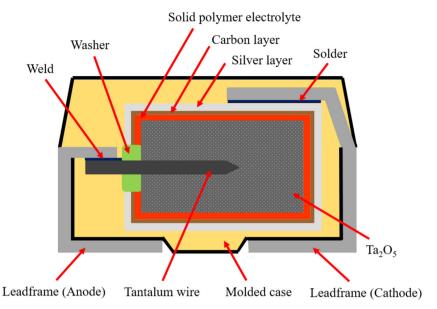


Fig. 1. Schematic of a polymer Ta capacitor.

uncontrolled exothermic reaction that causes a catastrophic ignition of the MnO<sub>2</sub>-based Ta capacitor [4]. To overcome this issue, conductive polymers were considered as an alternative to replace conventional MnO<sub>2</sub>. The ignition mechanism does not occur in Ta capacitors with conductive polymers because there is not enough oxygen in the surroundings of the dielectric. These polymers are also 20 to 100 times more conductive than MnO2-based Ta capacitors, and their equivalent series resistance (ESR) is considerably lower. However, Ta capacitors with conductive polymers tend to be more expensive and to fail from a short circuit due to an increase in leakage current [5]. The most common types of polymer electrolytes are tetracyano-quinodimethane (TCNQ) salts, polyaniline (PANI), polypyrrole (PPY), and polyethylene dioxythiophene (PEDOT) [4]. There are other polymers available, but they do not exhibit stable properties for capacitor technologies. From all the conductive polymers available, PEDOT has been found to exhibit the highest conductivity and stability [6-8].

Dielectric breakdown is directly related with an increase in leakage current of the capacitor since it causes destruction in the insulators across the electrodes usually by melting and evaporation. The dielectric breakdown occurs in different manners for polymer Ta capacitors than MnO<sub>2</sub>s. Vasina et al. [9] studied the dielectric phenomena in Ta capacitors and compared the performance between MnO<sub>2</sub>s and polymerbased electrolytes. The results observed were that the dielectric breakdown for MnO<sub>2</sub>-based Ta capacitors occurred approx. at three times the rated voltage whereas polymer-based capacitors exhibited it at one to two times the rated voltage. Even though conductive polymers are more conductive than MnO<sub>2</sub>, the authors then concluded that MnO<sub>2</sub>-based Ta capacitors were more capable of self-healing than their counterpart polymer Ta capacitors. The reduction in self-healing capabilities represents a higher risk of high leakage current failure mechanism.

Even though conductive polymers, such as PEDOT, represent a solution for the ignition issue in MnO<sub>2</sub>-based Ta capacitors, they also have one major drawback. In the presence of high temperature and humidity, conductive polymers tend to degrade and thus lose their conductive properties [10,11]. Jin et al. [12] showed that when heated in air, PEDOT deteriorates by decreasing its conductivity. The failure mechanism for this phenomenon is related to oxidation by oxygen. X-ray photoelectron spectroscopy (XPS) and Fourier-transform infrared (FTIR) spectroscopy revealed that PEDOT's poor stability in air was attributed to the decrease of doping level and molecular chain breaking. The polymer degradation due to elevated humidity conditions also

occur in polymer aluminum electrolytic capacitors were ESR and leakage current failures have been reported [13].

One of the reliability issues with polymer Ta capacitors is their susceptibility to degradation under humidity exposure by increasing their dissipation factor and leakage current [14]. Furthermore, the acidic reaction of PEDOT:PSS in humid environments was found to lead failures related to corrosion and metal migration from the lead frames in the capacitor [15]. Teverovsky [16] studied the effect of elevated humidity and moisture absorption in Ta capacitors with conductive polymers and with MnO<sub>2</sub>. He evaluated the impact of moisture by testing at dry condition (5% RH) and 85% RH. A pre-conditioning at 125 °C to remove the initial moisture was conducted. In his results, the author found that the time required to remove all the moisture from a saturation level was between 10 and 15 h at 125 °C for commercial polymer Ta capacitors. Lower temperatures can be also used but the baking time would be longer. The bake-out conditions were necessary to avoid pop-corning failures during soldering. After conducting the environmental tests, he concluded that the capacitance after exposure to 85% RH was approx. 27% larger than in dry conditions for polymer Ta capacitors and 10 times for MnO2 capacitors. On the contrary, the author did not find changes in the dissipation factor for both tests but speculated that this might not be similar for interim moisture levels.

Young and Qazi [17] found that temperatures in excess of 85  $^{\circ}$ C have an impact on the dissipation factor (DF) and ESR of polymer Ta capacitors over time. Likewise, 85  $^{\circ}$ C/85% RH condition represents the testing limit used to assess the corrosive characteristics of the product over a long period of exposure time to temperature and humidity. This condition has often being compared with the degradation observed at 125  $^{\circ}$ C. Based on this, the automotive industry has accepted the fact that if a device can pass the 85  $^{\circ}$ C/85% RH condition for 1000 h, the device will be able to withstand the environmental conditions in the field for a period of 5 to 10 years at more 'realistic' temperatures and humidity conditions.

Dehbi et al. [18] conducted a study to assess the performance of Ta capacitors under elevated temperature conditions and bias to simulate automobile applications. In their investigation they found that the ambient temperature had the largest effect in the life of Ta capacitors when compared to voltage bias. The authors concluded that for temperatures  $> 100\,^{\circ}\text{C}$  and bias stress the primary failure modes were increase in leakage current and impedance. Furthermore, the authors found that the lifetime of these capacitors could be roughly estimated using the product of a power law of the voltage and an exponential of

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