

Development of High Temperature Tantalum Polymer Capacitors

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Abstract

This paper focuses on the development of new 150°C capable surface mount polymer tantalum capacitors and the enabling technologies. The conductivity stability of the conducting polymers at high temperatures as well as the equivalent series resistance (ESR) stability of the polymer tantalum capacitors at these temperatures were investigated in this study. Analysis of the oxygen permeation paths causing polymer oxidation and materials solutions for preventing oxygen permeation and polymer oxidation are described. The development of new cathode and protective coating material technology is presented. Their effectiveness in providing high temperature ESR stability is demonstrated by high temperature life test at 150°C of polymer capacitors.

Key words

Tantalum Capacitors, Polymer Capacitor, Conducting Polymers, High Temperature, PEDOT

I. Introduction

Tantalum polymer capacitors are increasingly being used for applications demanding high reliability in automotive, medical, military and space systems. Application of intrinsically conducting polymer materials as the cathode for tantalum capacitors results in significantly lower equivalent series resistance (ESR) when compared to MnO₂ cathode systems [1], [2]. Higher performance and superior quality of polymer capacitors achieved over the last few years made these capacitors the preferred components for many applications. One concern of polymer capacitors has been the poor reliability in high humidity and high temperature environment. KEMET has recently developed a number of technologies to solve this problem and we were successful in developing polymer capacitors for high humidity and high temperature applications. Young et al [3] reported improved polymer capacitors with high reliability in 85°C/85%RH and 125°C environment. Ye et al [4] reported recently the successful introduction of polymer capacitors for automotive high humidity high temperature (85°C/85%RH and 125°C) applications. Chacko et al [5] recently reported a detailed investigation of the mechanisms of the conductivity stability of these polymers and ESR stability of polymer capacitors in 85°C/85%RH environment. These studies showed that the interfacial resistance stability is more predominant in influencing the reliability of the capacitors than the intrinsic stability of the conducting polymer.

Conducting polymers such as Poly(3,4-ethylenedioxythiophene) (PEDOT) are known to lose

conductivity in a high temperature environment due to oxidation and loss of conjugation of the polymer component [6]. Reed et al [7] demonstrated that extended exposure of polymer capacitors to air (primarily oxygen) at elevated temperature resulted in oxidation of the polymer thus increasing the dissipation factor (DF) and ESR of the component. In the absence of oxygen, exposure to 125°C alone (under inert atmosphere) does not have a significant effect on the polymer and hence provides a way for producing 125°C capable components. Young et al [3] demonstrated enhancements to the component's construction to slow the rate of polymer oxidation and allow for more stabilized performance through the 1000 hours test duration. Their enhancements primarily focus on improved packaging that slows or prevents hot air from reaching the polymer layers. By slowing or preventing the hot air from reaching the polymer, oxidation of the polymer is reduced or eliminated throughout the 1000 hours of test time thus meeting the requirements of the test. These technological advances enabled 125°C capable polymer capacitors which could meet the AEC Q-200 requirements and has been successfully introduced to the Automotive industry in the past few years [3], [4].

In recent years there has been significant increase of electronics content and passive components in automotive systems due to real time sensing and automation. Some of these automotive applications requires polymer capacitors with temperature capability at or above 150°C. Applications such as down-hole oil and gas exploration, geothermal,

military, and aerospace applications demand higher temperature capable polymer capacitors. Polymer capacitors are desirable for several of these applications due to their low ESR, lower derating, and benign failure mode compared to MnO₂ capacitors.

II. Experimental

A. PEDOT Film Fabrication

In-situ oxidative polymerization of PEDOT was performed by polymerization of 3,4-ethylenedioxythiophene (EDOT) in the presence of iron (III) toluenesulfonate (oxidizer) with a monomer/dopant ratio of 3:1. The in-situ film was fabricated as follows: A glass substrate was immersed in oxidizer solution, then taken out and dried for 30 minutes in ambient conditions. This was followed by dipping in monomer. Polymerization was completed by drying for one hour. The obtained film is in a doped state with tosylate ion (TOS) as counter-ion. The film from the pre-polymerized polymer (PEDOT: PSSA and additives) was prepared by casting the dispersion on a glass substrate and subsequent drying at 130 °C for 30 min

B. Capacitor Fabrication with PEDOT Cathode.

Tantalum powder was pressed into rectangular pellets of 2.5 mm × 2.5 mm × 4 mm width and 6.5 g/cm³ density. The pellets were sintered in vacuum at 1350 °C for 20 min. Tantalum anodes were anodized in an aqueous solution of 0.1% of phosphoric acid at 80 °C. In-situ PEDOT (PEDOT: TOS) cathodes were prepared by oxidative polymerization of PEDOT on the anode by polymerization of the monomer EDOT in the presence of the oxidizer iron (III) toluenesulfonate. Pre-polymerized (PEDOT: PSSA) cathode were fabricated by dipping the anodes in the prepolymer dispersion. Conductive carbon particle filled layer and conductive silver particle layers were applied over the PEDOT layer followed by assembling onto lead frame using conductive adhesive. These assembled capacitors were molded and were mounted to the PC board using a lead-free solder reflow process (260 °C peak temperature).

C. Film Characterization.

The sheet resistance of the films was measured by a four-point probe with a Keithley 2400 source meter.

D. Capacitor Characterization.

ESR of the capacitors were measured at 100 kHz using Agilent E4980A Precision LCR Meter.

III. Discussions

A. High Temperature Stability of Conducting Polymers

High temperature stability of the polymer capacitors requires higher temperature cathode materials capable of withstanding the high temperature environment. Thermal and conductivity stability of the conducting polymers depends on the dopants or counter ions used in these materials. Dopants can be monomeric (low molecular weight) anions or polymeric (high molecular weight) anions. The chemical structure of the two types of conducting polymers commonly used in capacitors are shown in Fig. 1.

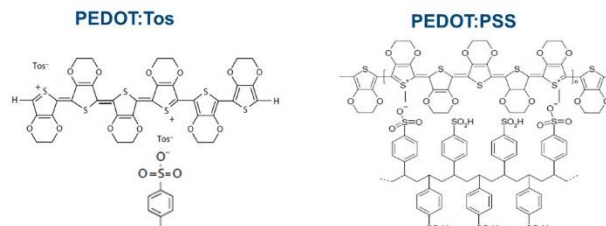


Fig. 1. Chemical Structure of PEDOT: TOS and PEDOT: PSSA

PEDOT polymers with polymeric dopants such as high molecular weight polystyrene sulphonic acid (PSSA) has shown significantly increased temperature stability compared to conducting polymers with low molecular weight dopants such as tosylate (Tos) anions.

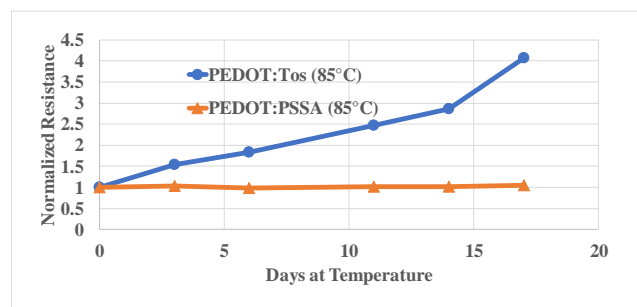


Fig. 2. Normalized resistance of PEDOT films on exposure to 85 °C

Fig. 2 shows a comparison of the thermal stability of the in-situ (PEDOT: TOS) films compared to slurry (PEDOT: PSSA) films. X-ray Photoelectron Spectroscopy studies showed loss of dopants for the PEDOT: TSA insitu films on exposure to 85°C environment[5]. Enhanced thermal stability of PEDOT: PSSA slurry film is attributed to the protective effect of PSSA shell around PEDOT. However, PEDOT: PSS based polymer films showed conductivity decrease under extended exposure at 150°C (Fig. 3). The protective effect of the polymeric shell PSSA decreases as the environment temperature approaches the glass transition

temperature (140-152°C) of the PSSA. XPS studies of PEDOT: PSS on thermal treatment suggest decreases in the surface PSSA concentration on heating [8]. Decrease in protective effect and enhanced oxidation rate of polymer at higher temperature contributes to this decrease in conductivity.

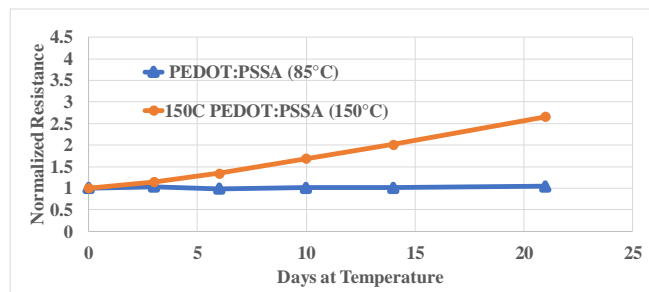


Fig. 3. Normalized resistance of PEDOT films on exposure to 85 °C and 150°C

B. Development of 150°C Capable Polymer Capacitors

As discussed in the previous session, polymer oxidation is the fundamental failure mode for conductivity degradation of conducting polymers. This conductivity degradation leads to ESR increase in polymer capacitors in high temperature environment. Advances in PEDOT materials and advances in packaging enabled 125°C capability but more technological innovation were needed for enabling 150°C capability. Polymer oxidizes when oxygen permeate into the conducting polymer interfaces and to the bulk of the conducting polymer. We started our developmental studies by analyzing pathways for oxygen into the conducting polymer layers in the capacitor.

C. Polymer Oxidation and Oxygen Pathways in Polymer Capacitors

Polymer oxidation occurs when oxygen enters the capacitors and find its way into the conducting polymer through mold epoxy and conducting layers such as carbon and silver. Oxygen permeates into the conducting polymer at different rates in each capacitor depending on the processing history and variations. High temperature ESR shift variation in a typical sample of the capacitors is due to these differences in oxygen permeation rate. There are several pathways for oxygen permeation into the capacitor and into the conducting polymer. Primary pathways are the pathways through which oxygen from environment enters the capacitor through mold epoxy. Secondary pathways are the pathways through which oxygen in the encapsulant or mold epoxy find its way into the conducting polymer.

Primary pathways. There are three primary pathways for oxygen permeation into the package. The first one is the gap

between lead frame egress and the mold epoxy. The second pathway is through the defects such as pin holes, show throughs, and cracks in mold epoxy. The third primary pathway is the oxygen diffusion through the bulk of the mold epoxy. Fig. 4 illustrates these three primary pathways. As the Fig. 4 illustrates, oxygen permeation is at a faster rate through the first two primary pathways. There is a longer pathway for oxygen permeation through the bulk of the epoxy due to the filler particles. The filler particles in mold epoxy provide a tortuous path for oxygen diffusion and thus decrease the rate of oxygen permeation. Filler concentration and filler aspect ratio influence the tortuous path provided by the bulk of the mold epoxy. The glass transition temperature of the mold epoxy also influences the oxygen permeation rate through the bulk of the epoxy at high temperature. Oxygen permeation through the egress and through defects is at a higher rate than through the bulk of the epoxy since oxygen encounters no tortuous path. Depending on the adhesion of the mold epoxy to the lead frame, these egresses can be larger or smaller. Molding conditions and any residual volatiles in the cathode layers influence the defects size and concentration.

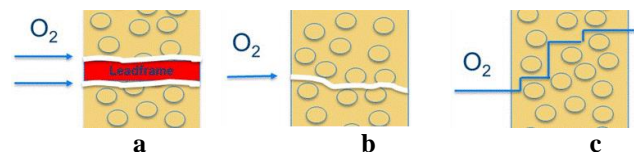


Fig. 4. Primary pathways for oxygen permeation. a. Through LF/mold epoxy egress b. Through defects in mold epoxy c. Through bulk of the epoxy

Secondary pathways. There are several secondary pathways for oxygen permeation into the package (Fig.5). Once the oxygen enters the package through the primary pathways, oxygen can find its way to the conducting polymer through several secondary pathways.

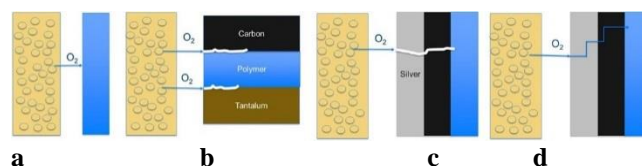


Fig.5. Secondary pathways for oxygen permeation. a. Through exposed conducting polymer areas (not covered by carbon and silver -wire side) b. Through delamination between polymer interfaces c. Through cracks in cathode layers d. Through the bulk of the silver and carbon layers.

One such pathway for oxygen to conducting polymer is the polymer surfaces which are not covered by carbon and silver coatings. Wire side anode top surfaces are typically not covered by carbon and silver and oxygen can directly enters

to conducting polymer through these surfaces. In some cases, corners of the anodes are not covered by carbon and silver and these polymer surfaces can get oxidized faster. Residual volatiles in the capacitors can diffuse into cathode layers or diffuse out of cathode layers and these diffusion under thermomechanical stresses can cause cracks in the cathode layers. Oxygen permeation through the bulk of the silver and carbon layers is influenced by the conductive filler concentration, filler aspect ratio, and glass transition temperature of the binder system. Conducting polymers has relatively higher coefficient of thermal expansion (CTE) than the tantalum or carbon filled coating and so these interfaces are prone to delamination due to CTE mismatch induced thermomechanical stresses. These interfaces can delaminate if the adhesion force between the layers is lower than the induced stresses. Permeation of oxygen through this delaminated interface can reach the conducting polymer at a faster rate and can cause oxidation at a faster rate.

D. High ESR failures in 150°C Life test

Fig. 6 shows the 150°C life ESR test results from some of the developmental experiments. SEM cross section of one of the high ESR part was examined and is shown in Fig. 6b. Oxygen permeation through the cracks in the cathode layers and subsequent polymer oxidation is responsible for the high ESR shift in this part.

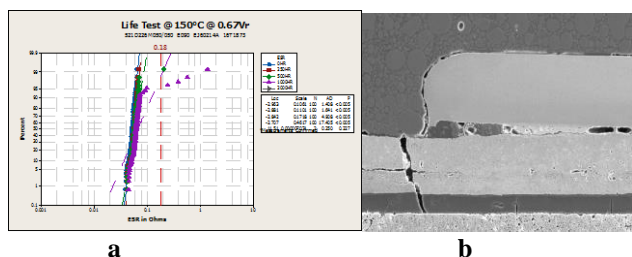


Fig. 6: a. ESR distribution of 150°C Life test at 0hour, 250-hour, 500-hour, 1000 hour. b. SEM cross section of one of the high ESR capacitor

E. Development of New Cathode Materials

Interlayer Crosslinking. KEMET's patented new cathode material system involves cathode and protective coating materials which significantly enhance interlayer crosslinking of cathode layers, lead frame, and mold epoxy [9], [10]. These interlayer crosslinking results in decreases in oxygen permeation through several of the primary and secondary oxygen permeation pathways. Crosslinks formed by the covalent bond between polymer chains provide a tortuous path for oxygen permeation. As illustrated in Fig. 7, oxygen tortuosity increases as the crosslink density increases.

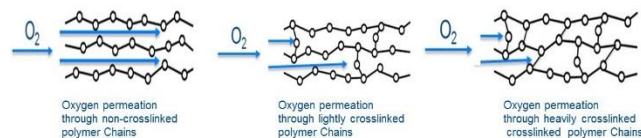


Fig. 7. Oxygen permeation through non- crosslinked polymer chains and crosslinked polymer chains

Cathode Coatings. Oxygen permeation through cathode interfaces are high due to the gap between the interfaces. These gaps are generated by poor interfacial adhesion between the cathode layers or through delamination caused during reflow. Our analysis of the oxygen permeation pathways suggests that improvements in cathode layer material and interfaces can inhibit oxygen permeation through secondary pathways. The new cathode materials improve interlayer adhesion through interlayer crosslinking [9]. By providing reactive functional groups which are available for reacting with each of the cathode layers, interlayer adhesion is significantly enhanced. Interlayer crosslinking is the crosslinking between a reactive group in one of the cathode layers and a reactive group in adjacent layer (see Fig. 8, 9). This interlayer crosslinks improve adhesion between these layers and prevent delamination between these layers during reflow. The reduced interfacial gap and higher crosslink density between the cathode layers significantly reduces the oxygen permeation rate.



Fig. 8. Oxygen permeation through non-crosslinked cathode layer interfaces and interlayer crosslinked cathode interfaces.

Protective Coating. We have developed and patented protective coating materials to address some of the primary oxygen permeation pathways [10]. As Fig. 9 illustrates, these novel protective coating materials on the lead frame provide reactive functional groups to form interlayer crosslinking between the mold epoxy and the lead frame. This interlayer crosslinks improve adhesion between the lead frame and mold epoxy. The reduced interfacial gap and higher crosslink density between these layers significantly reduces the oxygen permeation rate. This reduced oxygen permeation rate is reflected in the excellent ESR stability (Fig.10) of the new polymer capacitors.



Fig. 9. Interlayer crosslinking between mold epoxy layers and lead frame with hydroxy and epoxy functional groups

Fig. 10 shows the storage and life test performance of these improved capacitors prepared with new cathode and protective material technology. The results suggest that this new technology provides excellent ESR stability for these capacitors and enabled 150°C 2000-hour storage (unbias) and life (bias) test capability

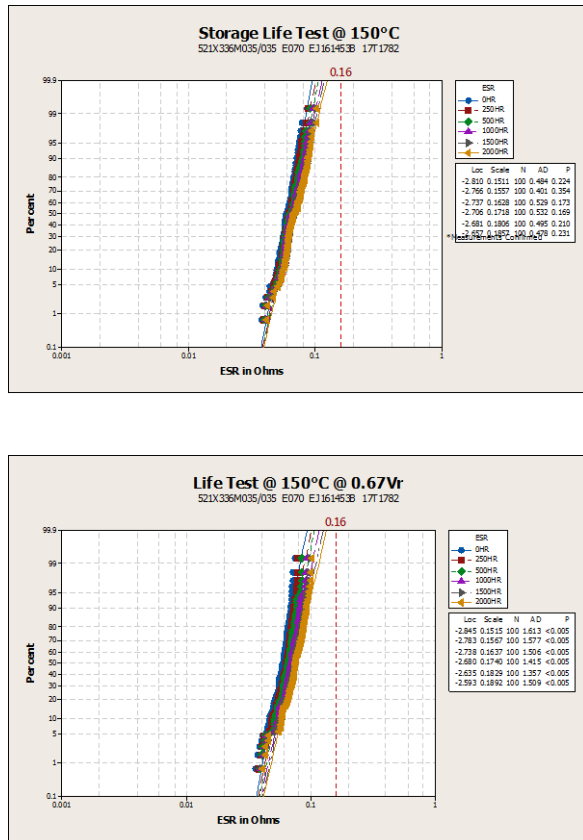


Fig. 10. Storage and life test ESR results of new capacitor at 150°C.

V. Conclusions

Oxygen permeation into the conducting polymers through several primary and secondary pathways causes polymer oxidation leading to ESR failures in high temperature life

tests. We have developed new cathode and protective coating material technology which provide interlayer crosslinking and interlayer adhesion between cathode layers and between mold epoxy and lead frame. This interlayer crosslinking decreased oxygen permeation by increasing tortuosity for oxygen path leading to significantly decreased oxygen permeation and thus polymer oxidation. This technology enabled 2000 hour 150°C capable polymer capacitors.

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