

Research Article

Abnormal Capacitance Increasing at Elevated Temperature in Tantalum Capacitors with PEDOT:PSS Electrodes

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Received 7 July 2018; Revised 26 August 2018; Accepted 12 September 2018; Published 1 October 2018

Academic Editor: Gerard Ghibaudo

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Due to the importance of capacitance temperature stability in precise analog circuit applications, capacitance instability at elevated temperature of 125°C was investigated in tantalum capacitors with PEDOT:PSS counter electrodes. Capacitance-voltage measurement supposed that residual ions in the PEDOT:PSS dispersion caused an accumulation of charges at the dielectric-cathode interface which contributed to an increase in the dielectric constant and resulted in the capacitance increasing at high temperature. Based on the hypothesis, water wash process was applied and capacitance dropped significantly at high temperature. This study shows that an additional water wash process is necessary to improve the capacitance temperature stability after each dispersion dip step.

1. Introduction

Due to much lower equivalent series resistance (ESR) and more benign failure mode than the incumbent MnO₂-cathode technology, conductive polymer tantalum capacitors are expanding their market share in both the commercial world and military world. The first tantalum and aluminum polymer capacitors were introduced into the markets in early 1990s [1, 2]. At that time, tantalum capacitor with conductive polypyrroles cathode outperformed polyanilines and polythiophenes [3]. Because the processing of 3,4-ethylenedioxythiophene (EDOT) is much simpler than other conducting polymers and it is not classified as toxic chemical like pyrrole, Poly(3,4-ethylenedioxythiophene) (PEDOT) becomes the material of first choice for solid electrolytic capacitors.

Tantalum polymer capacitors are not without faults. It was found that the dominant failure mechanism after high temperature life testing may be capacitance loss and ESR increasing rather than dielectric breakdown [4]. At elevated temperature, the thermal stability of PEDOT is a major argument to substitute the much more stable MnO₂ in tantalum electrolytic capacitors. The first generation of conductive polymer tantalum capacitors was limited to using

temperatures of 105°C because it was found that some percentage of the devices would suffer steadily increasing ESR at higher temperature [5].

During the last decades, researchers from tantalum capacitor manufacturers had been dedicated to improve the thermal stability of tantalum polymer capacitors. It was learned that principle mechanism of ESR increasing after high temperature lifetime operation is oxidation of the conductive polymer [5]. As the deterioration mechanism of ESR shift was well understood, new 125°C and 85°C/85%RH capable of tantalum capacitors were introduced by leading tantalum capacitor manufacturers [5–7].

Besides ESR increasing and capacitance loss after long-term operating at high temperature, tantalum polymer capacitors also suffer electrical parameter deviation at elevated temperature, such as capacitance instability and DC leakage current increasing. The capacitance of tantalum polymer capacitors can shift dramatically with the change of temperature and dc or ac bias. For example, the capacitance shift of polymer technology at 125°C is up to the range of +30% to +50%, while the predecessor MnO₂ remains within +15%. For electrical parameter instability of tantalum polymer capacitors does not cause catastrophic failure in field applications, it draws less attention from researchers.

However, applications such as VCOs, PLLS, RF PAs, and low-level analog signal chains are very sensitive to noise partially contributed by capacitance shift of decoupling capacitors on the power supply rail [8]. Thus, it is important to investigate the phenomenon of capacitance shift with the change of temperature, especially at elevated temperature.

2. PEDOT:PSS Dispersion

Deposition methods for PEDOT cathode used in electrolytic tantalum capacitors include chemical oxidative polymerization or in situ polymerization, electrochemical oxidative polymerization, and conducting polymer dispersions.

In the in situ polymerization, a monomeric precursor of the conducting polymer is polymerized by an oxidizer. Iron salt like Fe(III) toluenesulfonate is commonly used as oxidizer in in situ polymerization. The monomer and oxidizer can be brought either sequentially or as premixed reactive solution. There are several major disadvantages in in situ polymerization process. First, the processing time is long because for every cycle two more dips are necessary. Moreover, residuals of the oxidizer and monomer involved in the polymerization reaction can cause surface charge at the Ta₂O₅/PEDOT interface, affecting the barrier and resulting in high dc leakage and low breakdown voltage [9].

In electrochemical polymerization process, a monomeric precursor of the conductive polymer is polymerized at an electrode. During the polymerization, ionic dopants from the electrolyte are incorporated into the polymer. For capacitor application, first, an auxiliary electrode layer has to be deposited on the surface of the insulating dielectric. The auxiliary electrode is contacted with an external electrode. Because of the large inner surface and the high aspect ratio of the small pores, polymer built up in the porous anode body by electrochemical polymerization is quite difficult. Another disadvantage of the electrochemical process is the more sophisticated technical setup.

In order to overcome disadvantages of electrochemical or in situ polymerization and to further simplify the manufacturing process, a nanoscale conducting polymer PEDOT:PSS dispersions for the formation of the cathode layer within the porous structure of electrolytic capacitors was developed. The new technology allows for the direct deposition of the cathode layer by simple coating steps without any polymerization. Since no chemical polymerization takes place during the deposition of the conductive polymer, there are no side products like iron salts, which have to be washed out or could deteriorate the performance in the finished product [5]. The leakage current and break-down voltage of the dielectric is not deteriorated, thus leading to the introduction of a new line of high-voltage tantalum polymer capacitors with long-term reliability [10–12].

3. Experimental

3.1. Fabrication of Tantalum Capacitors. Tantalum powder with specific charge per volume from 15,000 μ C/g to 23,000 μ C/g was pressed with tantalum wires into rectangular pellets, with a 5.8g/cm³ green density. The pellets were then sintered

in vacuum around 1450°C for 30 min. The tantalum anodes were anodized in a dilute aqueous solution of 0.01 mol % phosphoric at 65°C and then were annealed at 400°C for 30 min. The formation voltage was 124 volts for 50V47 μ F and 153 volts for 63V33 μ F, respectively. After annealing, a reformation process was performed at the formation voltage for 60 min. In this study, Clevios P with PEDOT:PSS ratio (w/w) of 1:2.5 was applied by dipping the Ta/Ta₂O₅ pellets into a waterborne dispersion and subsequent drying in air and at room temperature and then at 130°C. The particle size d_{50} of PEDOT particles in the dispersion is less than 30 nm. Before dipping into the dispersion, porous pellets were first vacuum-pumped. The purpose of pumping process is to evacuate air that filled in small pores in porous tantalum anodes and enable the dispersion to penetrate into the pellets more easily. In the prepolymerized process, 4–6 cycles were applied to provide a maximum coverage of the tantalum pentoxide dielectric with the PEDOT particles inside and outside the porous tantalum pellets. After the coating process of PEDOT:PSS, a graphite layer was coated on the pellets and then pasted with a thin silver layer and assembly to lead frame. The capacitors were finally encapsulated with epoxy before measurement.

3.2. Measurement. Prior to starting to test, capacitors were dried at +125°C \pm 5°C for 30 min and then restored to room temperature. Capacitance of 13 samples was measured at 25°C \pm 3°C and 125°C \pm 5°C, respectively. Capacitors were brought to thermal stability at each temperature. Capacitance measurements were performed with Agilent E4980A Precision LCR Meter. Test frequency was 120 Hz \pm 5 Hz. The magnitude of the ac voltage was 1.0 volt root mean square (rms) and the dc bias voltage was 2.2 volts. Capacitance-voltage measurement technique was used to further investigate the abnormal increasing in capacitance. Capacitance of the samples was measured at 2.2V, 10V, 15V, 20V, 25V, and 30V bias conditions, respectively.

4. Results and Discussion

In this study, abnormal capacitance increasing at elevated temperature of 125°C was observed for polymer tantalum capacitors without water wash process as shown in Figure 1. Compared with the initial value at 25°C, capacitance change at 125°C is in the range of 71% to 77% for 63V33 μ F with 15,000 μ C/g anodes 153V formation and even as high as over 102% to 122% for 50V47 μ F with 23,000 μ C/g anodes 124V formation. The capacitance change is reversible upon the temperature range from 25°C to 125°C and there is no hysteresis observed.

In Figure 2, capacitance-voltage measurement shows that the average capacitance change of all samples for 50V47 μ F decreases dramatically with the bias voltage increasing. At low bias condition (2.2V), the capacitance change at high temperature was about 110%. Interestingly, as the bias voltage increased to 30V, capacitance shift rolled off to the level of 20%. The effects of bias voltage on capacitance were also found to be similar in 63V33 μ F and other type capacitors with PEDOT:PSS electrodes.

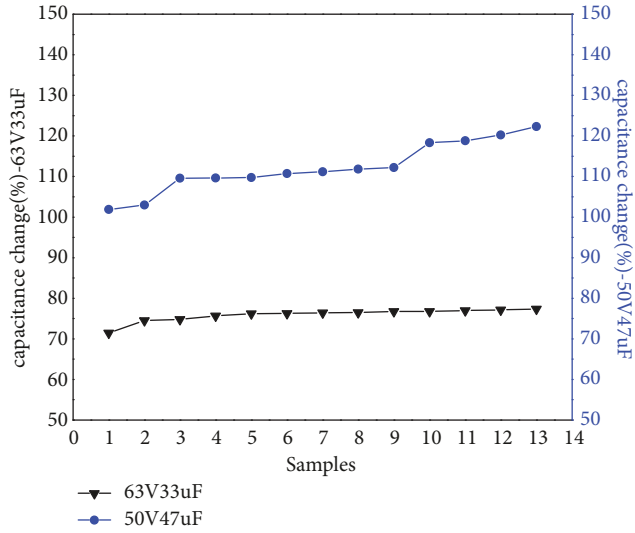


FIGURE 1: Capacitance change in percentage at 125°C without water wash process for polymer tantalum capacitors with 15,000 μ C/g anodes 153V formation for 63V33 μ F and 23,000 μ C/g anodes 124V formation for 50V47 μ F.

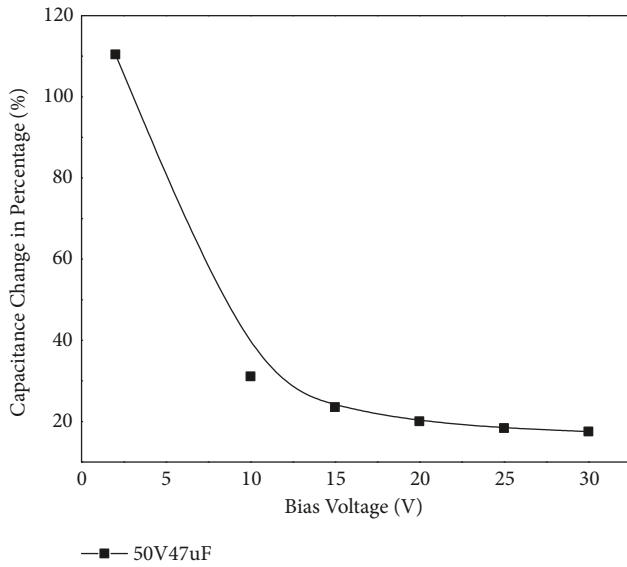


FIGURE 2: Capacitance-voltage characteristic of 50V47 μ F tantalum capacitors at 125°C.

In Figure 3, the capacitance change of all samples with water wash process for 50V47 μ F decreases compared to samples without water wash steps measured at 2.2V of standard bias condition. The effects of water wash process on capacitance stability were also found to be similar in 63V33 μ F and other type capacitors with PEDOT:PSS counter electrode. In this study, the introduction of an additional water wash process after each dispersion dip step is to wash out residual ions with the PEDOT:PSS film.

According to capacitor theory, capacitance is determined by the following formula:

$$C = \frac{\epsilon_0 \cdot \epsilon \cdot A}{d} \quad (1)$$

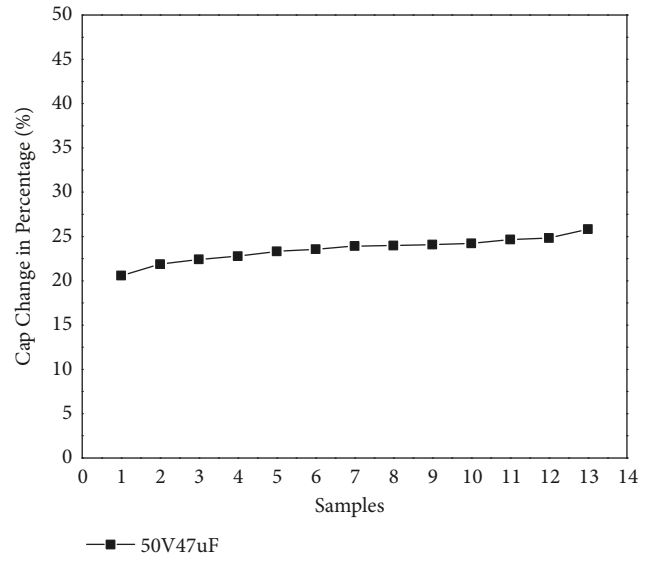


FIGURE 3: Capacitance change of 50V47 μ F at 125°C with water wash steps.

where ϵ_0 is the dielectric constant for free space (8.855×10^{-12} Farads / m), ϵ is the dielectric constant for tantalum pentoxide (about 27), A is the surface area in m^2 , and d is the dielectric thickness in m. In these parameters, ϵ_0 is a constant and does not vary with temperature and the surface area A is predetermined by the tantalum powder used and the anode dimension which depends less on temperature. Furthermore, the thickness d of the anodic oxide tantalum film is directly proportional to the formation voltage with the coefficient in the range of 1.6 nm/V to 2.0 nm/V [13]. For the coefficient of temperature expansion (CTE) of tantalum pentoxide is in the order of $10^{-5}/K$, the thickness of the dielectric film will only change in the same order [14]. Thus, thickness of tantalum pentoxide is not the main cause for the increase in capacitance. Furthermore, the inherent variation of the dielectric constant for tantalum pentoxide with temperature is considerably stable within 10% at 150°C and would not cause abnormal capacitance increase [15]. These conclusions are verified by tantalum capacitors with manganese oxide electrode whose capacitance shift at 125°C is generally less than 15%.

Based on experiment, Freeman, et al. introduced a model that explained the mechanism of capacitance dependency with temperature [15]. According to the model, the PEDOT layer can shrink upon cooling and expand upon heating and resulted in the changes of the effective surface area which contribute to the overall device capacitance. However, the abnormal capacitance increase observed in this study cannot be explained by the surface area model. First, the capacitance measured at 125°C was as high as 1.7 to 2 times compared to the value at room temperature and exceeded the wet capacitance (1.1 times the capacitance of the finished device at room temperature) measured after the dielectric formation. Practically, surface area change would not cause such a large relative change in capacitance. More importantly, strong capacitance dependency on voltage was observed at elevated

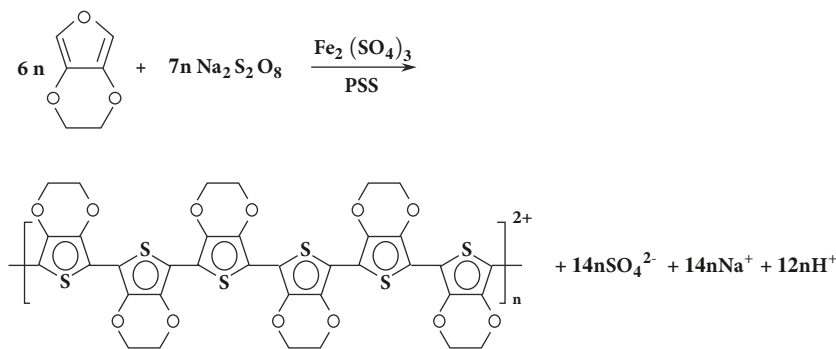


FIGURE 4: Reaction scheme for the PEDOT synthesis using Sodium peroxodisulfate as an oxidant.

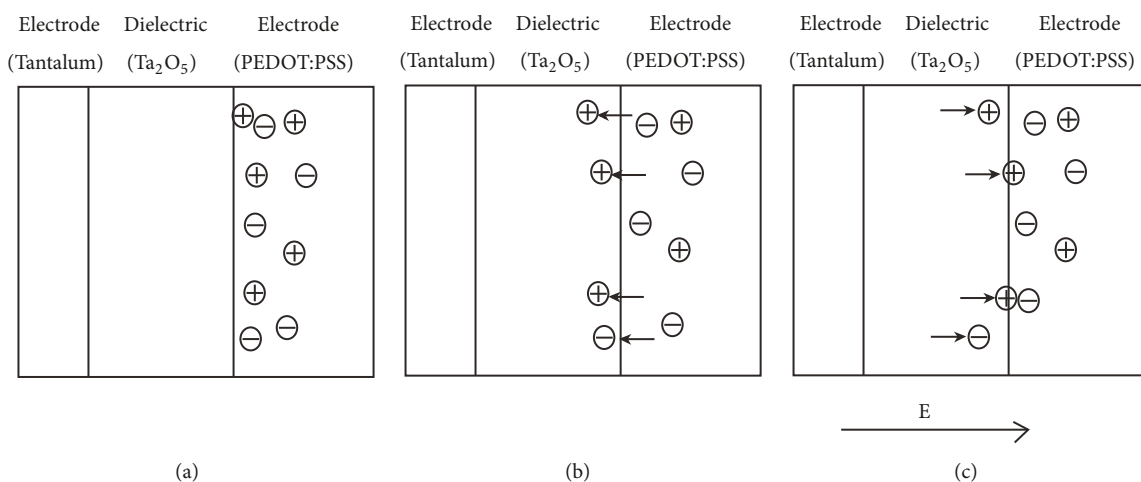


FIGURE 5: Interfacial polarization of tantalum capacitors with PEDOT:PSS electrode.

temperature. As seen in Figure 2, the capacitance decreased dramatically as the biased voltage increased. Obviously, the effective surface area theory cannot explain the capacitance-voltage relationship. It is believed that there are other mechanisms that may contribute to the abnormal capacitance changes.

Fundamentally, dielectric constant is a measure of dielectric polarization under an electric field. There are electronic, ionic, orientational and interfacial polarizations [16]. For tantalum pentoxide, ionic polarization is the main polarization mechanism [16]. Based on dielectric theory, both electronic and ionic polarizations are less dependent on temperature, and orientational polarization is inversely proportional to the temperature. Thus, it is supposed that the abnormal increase in capacitance may be caused by interfacial polarization due to the introduction of conductive polymer PEDOT:PSS.

The PEDOT:PSS complex was synthesized by mixing the polystyrene sulfonic acid with PEDOT. For Clevis P dispersion, the molar ratio of thiophene groups to sulfonic acid groups is 1:1.19, which corresponds to a weight ratio of 1:2.5. During the oxidative polymerization of EDT monomer in the presence of PSS, sodium peroxodisulfate is used in combination with an Fe(III) salt as a catalyst. As shown in Figure 4, the reaction mixture turns more acidic as the reaction progresses, since each mol of EDT releases

two moles of protons [3]. Theoretically, there are residuals such as protons, sodium, sulfate, Fe(III), and other species in the PEDOT:PSS complex after the completion of the synthesis.

At elevated temperature, impurities such as H⁺, Na⁺, and Fe³⁺ ions diffuse toward the interface between PEDOT:PSS cathode and tantalum pentoxide dielectrics to form an accumulation of charges; thus interfacial polarization occurs as depicted in Figure 5. Dielectric materials, although perfect, contain crystal defects, holes, and surface imperfections. As depicted in Figure 5(a), residuals in PEDOT:PSS have an equal number of positive ions and negative ions, but the positive ions are assumed to be far more mobile because they are relatively small. In the absence of electric field or at lower bias condition, positive ions may diffuse into the dielectrics of tantalum pentoxide under high temperature as shown in Figure 5(b). These positive charges accumulate at the interface and attract more electrons to the negative electrode. These additional charges on the negative electrode, of course, appear as an increase in the dielectric constant. Figure 5(c) shows that, at higher bias condition, the diffused positive ions on the dielectric side may drift back to the cathode or combination with electrons and the effect of interfacial polarization is reduced; thus, the capacitance dropped under higher bias condition as shown in Figure 2.

TABLE 1: Characteristics of Clevios P dispersion.

Characteristics	min.	max.	Measured value	Unit
Solid Content	1.2	1.4	1.32	%
pH	1.5	2.5	1.9	
Sodium		500	233	ppm
Sulfate		80	ND	ppm
Iron	/	/	0.64	ppm

In order to verify the main sources that contributed to the capacitance variation, further analysis was done. For Clevios P dispersion used in this study, the main physical and chemical characteristics are shown in Table 1. Although Fe(III) salt was used as catalyst, it can be easily washed out and the residual of Fe ions is almost negligible and not specified in the specification. The main residual species given are sodium and sulfate, and the maximum contamination levels are 500 ppm and 80 ppm, respectively. In order to further analyze residual species, contents of sodium and iron were measured through leaching analysis. The contents of sodium and iron were 233 ppm and 0.64 ppm, respectively, as shown in Table 1. As seen from the characteristics table, the specified value of pH for the dispersion is in the range of 1.5 to 2.5, and the measured value is 1.9, which indicated that the hydrogen ion concentration is high.

From the analysis and measurement, residuals in the PEDOT:PSS complex contributing to the abnormal capacitance increase at high temperature are mainly H^+ and Na^+ ions in tantalum capacitors with PEDOT:PSS electrodes.

Based on the above hypothesis, it can be assumed that an additional water wash process can reduce the content of impurity ions which resulted in the improvement of capacitance temperature stability. As shown in Figure 3, the capacitance change at high temperature decreased dramatically compared to samples without washing steps during PEDOT:PSS dispersion dipping process.

However, though an additional water wash process can improve the capacitance stability, capacitance changes at high temperature in conductive tantalum capacitors with PEDOT:PSS electrode are still higher than the conventional ones with manganese dioxide electrodes. The reasons for this larger capacitance change have already been well explained by the surface area model developed by Freeman et al. [15]. For mechanisms of capacitance dependency with temperature in PEDOT cathode system are complicated, the pore structure of the anode, preparation methods of the dielectrics of Ta_2O_5 , the material of PEDOT used, deposition methods of PEDOT, and so forth can contribute to the capacitance variation. For the new generation tantalum capacitor technology, more efforts may be needed to further improve the capacitance-temperature stability.

5. Conclusions

The abnormal capacitance increase in tantalum capacitors with PEDOT:PSS electrodes at elevated temperature of 125°C was investigated by capacitance-voltage measurement. It was supposed that residuals such as hydrogen and sodium ions

in the PEDOT:PSS dispersion caused an accumulation of charges at the dielectric-cathode interface, which appeared as an increase in the dielectric constant and resulted in the capacitance increase at high temperature. This study shows that an additional water wash process is necessary to improve the capacitance temperature stability after each dispersion dip step.

Data Availability

The data used to support the findings of this study are included within the article and can be accessed without any restrictions.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

Acknowledgments

The authors would like to acknowledge the support of Xinyun Electronics Components Corporation for providing capacitor samples, testing facilities, and financial funding.

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