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CAPACITANCE STABILITY OF POLYMER TANTALUM CAPACITORS UNDER
DIFFERENT ENVIRONMENTAL CONDITIONS

A Thesis
Presented to
the Graduate School of
Clemson University

In Partial Fulfillment
of the Requirements for the Degree
Master of Science
Electrical Engineering

by
Eyob Negussie Tarekegn
December 2020

Accepted by:
Dr. William R. Harrell, Committee Chair
Dr. Goutam Koley
Dr. Igor Luzinov

ABSTRACT

Polymer Hermetic Sealed (PHS) Tantalum capacitors with pre-polymerized PEDOT cathodes and different dielectric thicknesses were used to study the stability of Polymer Tantalum capacitors under different environmental conditions. In particular, capacitance dependence on temperature, frequency, and dc bias voltage were studied in humid and dry capacitors with varying dielectric thicknesses. Capacitance and ESR measurements were performed to characterize the capacitors.

Humid capacitors were observed to have higher capacitance than dry capacitors for all dielectric thicknesses. The capacitance for all dielectric thicknesses was observed to increase with temperature in both humid and dry capacitors. Humid capacitors showed a stronger temperature dependence at lower temperatures while dry capacitors showed a stronger temperature dependence at higher temperatures. These temperature effects were more pronounced in thinner dielectric capacitors, and the results were explained by the integrity of the dielectric-polymer interface. The capacitance for all dielectric thicknesses was also observed to decrease with an increase in frequency, both in humid and dry capacitors. The frequency effect was more pronounced in humid capacitors with thinner dielectrics. These results were explained by the RC ladder effect, secondary transitions of the polar segments of the polymer cathode, and lower reactance and lower self-resonance frequency of the thinner dielectric capacitors.

DEDICATION

I would like to dedicate this thesis to my parents, Negussie Tarekegn and Hamelmal Yigzaw, and my brother, Rediet N. Tarekegn, for always supporting and encouraging me to be a better person.

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CHAPTER 1

INTRODUCTION

1.1 Electrolytic Capacitors

The discovery of Electrolytic capacitors started with the discovery of valve metals. Valve metals are anodes that when inserted in an electrolyte solution form a surface oxide layer, which increases resistance of the metal and blocks the current flow [1]. This behavior of metal was first discovered by Eugene Ducretet in 1875, which then led to the discovery of the Electrolytic capacitor. Electrolytic capacitors that were made of aluminum metal were used in AC motors in the 1890s, but none of them were stable. The first stable Electrolytic capacitors were developed by Charles Pollak, which he received the patent for in 1896 [2].

Electrolytic capacitors have metals as an anode, metallic oxide grown on top of the metal as a dielectric, and a conductive electrolyte as a cathode. The conductive electrolyte could be a liquid solution or a solid. Capacitors with a liquid electrolyte solution are called Wet Electrolytic Capacitors, and capacitors with a solid electrolyte are called Solid (or Dry) Electrolytic Capacitors. The dielectric thickness of an Electrolytic capacitor is very thin compared to capacitors with a plastic dielectric, and this capability of Electrolytic capacitors allows for making a capacitor that has a high capacitance in a small volume. In Figure 1.1 a photograph of an Electrolytic capacitor from 1914 is shown, which was much smaller than any other type of capacitor at the time.

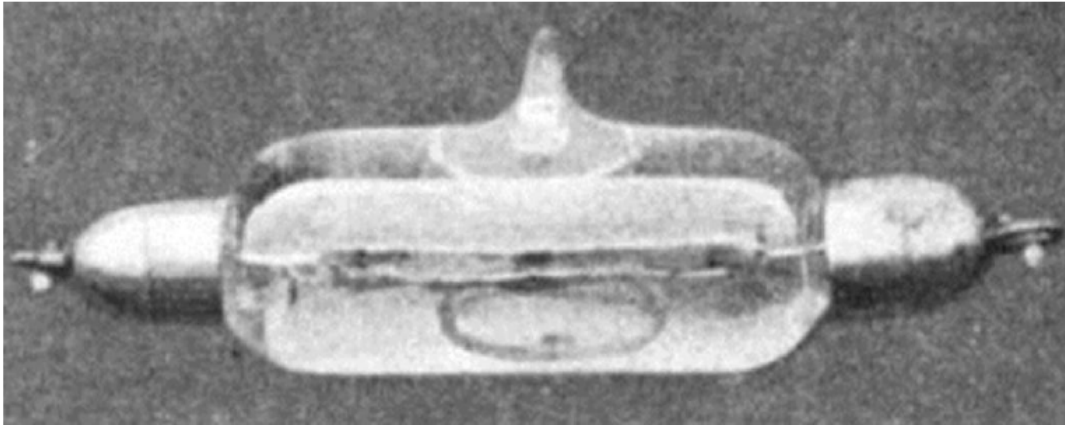


Figure 1.1. Electrolytic capacitor from 1914 (oldest known photograph of an Electrolytic capacitor), about 5cm in length and 1.5 cm in diameter with a capacitance of approximately $2 \mu\text{F}$ [1].

Different metals have been used as the anode for Electrolytic capacitors, but the most common ones are Aluminum and Tantalum. Another metal that is often used is Niobium. In Figure 1.2 the various metals and electrolytes used in Electrolytic capacitors are shown.

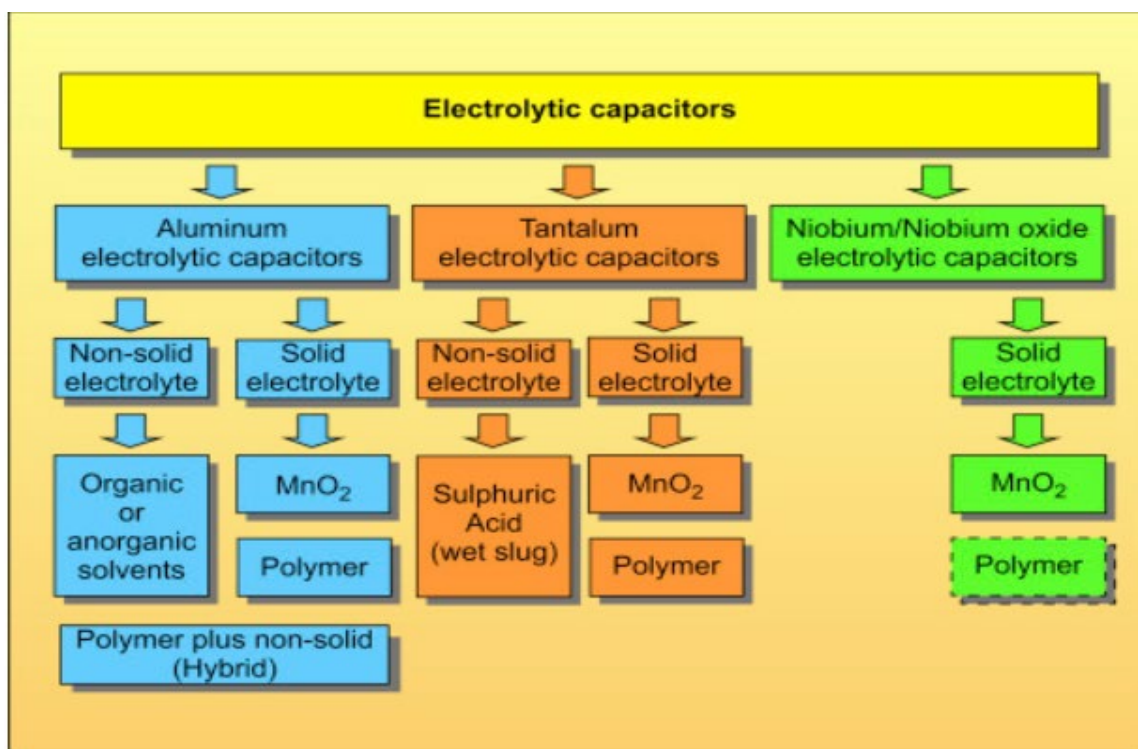


Figure 1.2. Various types of Electrolytic capacitors [3]

The basic structure of an Electrolytic capacitor is similar to a parallel plate capacitor. For this reason, the capacitance of an Electrolytic capacitor can be modeled as a parallel plate capacitor, where the capacitance is given by:

$$C = \frac{\epsilon_0 \epsilon_r A}{d} \quad 1.1$$

where ϵ_0 is the permittivity of free space, ϵ_r is the relative permittivity of the dielectric, A is the area of the capacitor, and d is the dielectric thickness. As shown in Equation 1.1, the

capacitance of a capacitor can be increased by using a dielectric material with high dielectric constant, large surface area and small thickness.

1.2 Wet Electrolytic Capacitors

Wet Electrolytic capacitors are a type of capacitor where a conductive liquid electrolyte solution is used as a cathode. The dielectric of a Wet Electrolytic capacitor is formed by inserting the anode metal into an electrolyte bath, applying voltage and passing current through it to form an oxide layer. This electrochemical process of forming the oxide layer is known as anodization. In Figure 1.3 the anodization process is illustrated. The thickness of the oxide layer is controlled by the applied voltage, also known as the formation voltage, which is applied between the anode metal and the electrolyte bath. This ability of forming a thin oxide layer allows us make capacitors that have a large capacitance. However, the oxide growth rate is different from metal to metal. For example, for Tantalum capacitors the oxide growth rate is 1.7 nm/V [4], whereas for Aluminum it is 1.36 nm/V [5]. There is also a limit to the voltage applied across the electrodes to form the oxide layer. If the voltage goes above this limit, the impurities in the anode and the temperature of the electrolyte bath will cause the dielectric oxide to break down. Aluminum has a limit of 1100 V for a maximum thickness of 1.5 μm , and Tantalum has a limit of 700 V for a thickness of 1.1 μm [5].

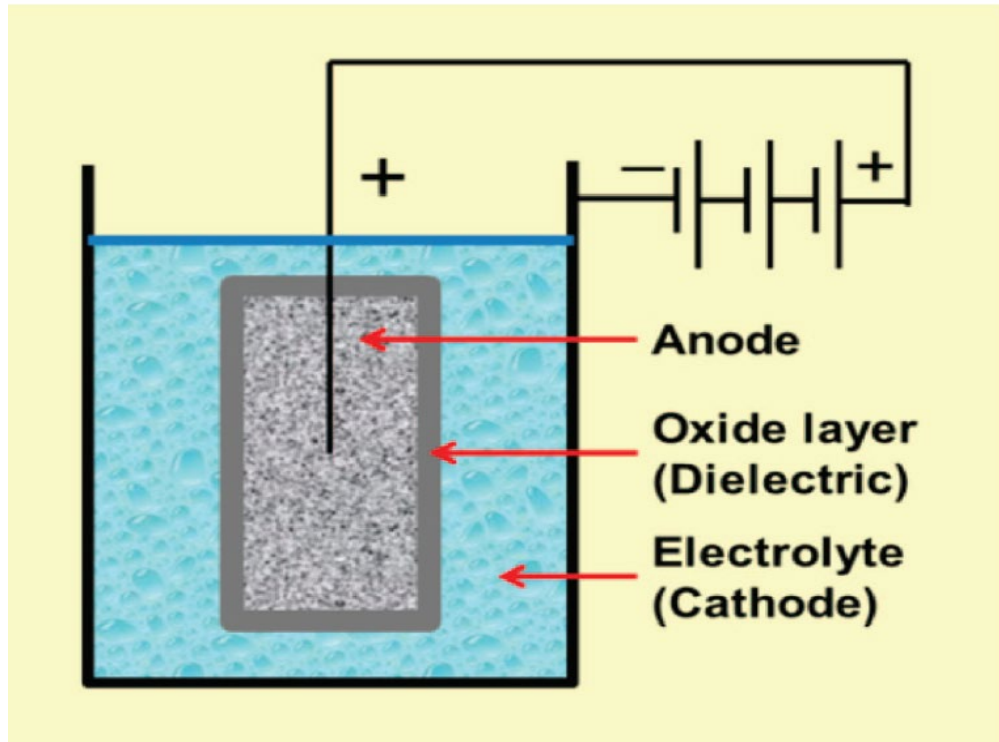


Figure 1.3. Principle of anodic oxidation [1]

There is a two-fold advantage for using Wet Electrolytic capacitors. First, since the cathode is a liquid electrolyte it conforms to the dielectric surface, giving it a large surface area and thus, a large capacitance. Second, the ability to reform the dielectric at the fault (or defect) site during capacitor operation. Impurities on the anode metal or in the electrolyte solution used for dielectric formation, create a fault site within the dielectric layer. These faults can reside as inclusions of a conductive element in the dielectric and lead to the breakdown of the dielectric at lower voltages [4]. In Wet Electrolytic capacitors, however, the dielectric layer can be reformed at the fault sites. Since an electrolyte is used as a cathode, the anodization process that is used to form the dielectric layer can be used to reform the dielectric layer at the fault sites.

1.3 Polar and Non-Polar Capacitors

Based on their polarities and connection to the circuit, capacitors are classified as polar or non-polar capacitors. Non-polar capacitors, also known as bipolar capacitors, can be connected either way in a circuit, and do not have a distinct polarity. Also, they have less leakage current, but they are bigger in size than polar capacitors of the same capacitance. Common examples of non-polar capacitors are Ceramic and Mica. On the other hand, Polar capacitors are polarity dependent and must be connected in a circuit taking their polarity into consideration. Their polarity is labeled on the capacitor case. The positive terminal is always connected to the anode and negative terminal to the cathode. If they are connected in a circuit in “reverse” polarity, the capacitor, and perhaps the whole circuit, can be damaged permanently. Most Electrolytic capacitors are polar capacitors. The polarity used in Electrolytic capacitors for circuit connection must be the same as the polarity used for the formation of the oxide layer. Reversing the polarities might dissolve the oxide layer in the electrolyte and short the capacitor, or in extreme cases the electrolyte can heat up and explode [6]. Thus, it is very essential that Electrolytic capacitors are connected according to their polarities.

1.4 Summary of Chapters

In Chapter 2, the electrical model and some parameters of Electrolytic capacitors are discussed. Terms such as dc leakage (DCL), breakdown voltage (BDV), working voltage (WV), equivalent series resistance (ESR), and equivalent series inductance (ESL), are defined in detail.

In Chapter 3, the history of the Tantalum Electrolytic capacitor is reviewed in detail. The first Tantalum Electrolytic capacitor was a Wet Tantalum capacitor, which was manufactured in the 1940s. Subsequently the Solid Tantalum capacitor was developed in the 1950s by Bell Labs, using MnO_2 as a solid electrolyte cathode. Fabrication of both Wet and Solid Electrolytic Tantalum capacitors are discussed in detail. The instability of Tantalum- MnO_2 capacitors at high frequency operations is also discussed, where its instability is explained using the Resistance-Capacitance (RC) Ladder effect. Furthermore, the self-healing property and failure modes of Tantalum- MnO_2 capacitors are discussed.

In Chapter 4, the Polymer Tantalum capacitor is discussed with some historical perspective. Some of the benefits of Polymer Tantalum capacitors in comparison to Tantalum- MnO_2 capacitors are discussed. Fabrication of Polymer Tantalum capacitors, especially the two different methods of depositing PEDOT onto the dielectric oxide, is discussed. The advantages of using Polymer Hermetic Sealed (PHS) capacitors are also discussed. Finally, some new technologies, including Flawless Dielectric Technology (F-Tech) and Simulated Breakdown Screening (SBDS), are presented.

In Chapter 5, the fabrication process of the PHS capacitors that are used in this research are presented. The electrical measurements employed to characterize the capacitors are also presented in this chapter.

In Chapter 6, the results of the electrical measurements are presented and discussed. Capacitance dependence on temperature ($C(T)$), capacitance dependence on frequency ($C(f)$), and capacitance dependence on dc bias voltage ($C(V)$) for different dielectric thicknesses of the Polymer Tantalum capacitors are investigated under dry and humid

conditions. The results are explained using models that are consistent with the known theories.

In Chapter 8, the final chapter, the results from previous chapters are summarized. Ideas for future work that would improve the capacitance stability of Polymer Tantalum capacitors are also presented.

CHAPTER 2

ELECTRICAL MODEL AND PARAMETERS OF ELECTROLYTIC CAPACITORS

The dielectric that is grown between the anode and the cathode electrode has a very high resistance, and its main purpose is to keep the anode and the cathode at a certain distance and prevent any flow of current between the anode and the cathode. However, capacitors usually experience a relatively small current through the dielectric. This small current through the dielectric is known as dc leakage (DCL), or leakage current. The leakage current can occur when there are impurities on the electrodes of the capacitor. The dielectrics formed over these impurities does not form a strong bond. When a very high dc voltage is applied across the capacitor, these bonds can break down and lead to the leakage current. The leakage current is proportional to the applied voltage; as the dc voltage applied across the capacitor increases, the insulation of the dielectric becomes weaker and the leakage current through the dielectric increases. In addition to the electrodes, the leakage current is also affected by the strength and thickness of the dielectric. The voltage that results in this leakage current in the capacitor is called the Breakdown Voltage (BDV). To avoid the leakage current, capacitors are usually manufactured to operate at below half of their breakdown voltage. It is dangerous to operate capacitors at their breakdown voltage. A high voltage might overheat the capacitor, which results failure in the capacitor and sometimes this failure could be an explosion which affects other components that are in close proximity to the capacitor. The maximum voltage at which the capacitor operates

safely and reliably is called the Working Voltage (WV). The working voltage is determined by the manufacturer based on reliability and life tests on a large number of capacitors.

Another important parameter of Electrolytic capacitors is the maximum reverse voltage. The maximum reverse voltage, as the name implies, is the maximum voltage that can be applied at a reverse polarity without any damage to the capacitor. This is typically a very small voltage for Electrolytic capacitors due to their polar nature. Electrolytic capacitors are polar capacitors and applying a high reverse voltage dissolves the oxide layer in the capacitor and shorts the capacitor [6]. That is why some capacitor manufacturers advise not to use Electrolytic capacitors in a circuit where a reverse voltage could be applied across the capacitor. But if a reverse voltage must be applied, manufacturers give general guidelines on the maximum reverse voltage that can be applied on the Electrolytic capacitors. For example, the most common guidelines for Tantalum Electrolytic capacitors are: 10% of the working voltage to a maximum of 1 V at 25°C, 3% of the working voltage to a maximum of 0.5 V at 85°C, and 1% of the working voltage to a maximum 0.1 V at 125°C [7]. Applying a reverse voltage that is bigger than these maximum reverse voltages, results in failure in the capacitor, and in an extreme case it might even lead to an explosion of the capacitor. Therefore, it is crucial not to exceed the maximum reverse voltage of Electrolytic capacitors.

Practically, capacitors are not ideal, they always have some parasitic components that affects their performance and reliability. Some of these parasitic components are illustrated in the circuit model of a capacitor that is shown in Figure 2.1. The Effective Series Resistance (ESR), also denoted as R_S in Figure 2.1, is a frequency dependent

parasitic element. The parameters that contribute to the ESR are the lead wire resistance, the electrode resistance, and the dielectric loss. The dielectric loss is the energy loss that goes into heating the dielectric material when AC voltage is applied. It is essential for the ESR to be as low as possible, because high ESR dissipates heat in the capacitor and affects the capacitor operation and reduce the expected lifetime of the capacitor, especially for those capacitors used in power supply and high frequency applications. The Effective Series Inductance (ESL), also denoted as L_S in Figure 2.1, is a restriction of current through a defined path. The current into and out of the plates of the capacitor must follow a restricted path defined by the dimensional properties of the capacitor's plate [8]. The longer is the restricted path, the higher is the ESL. Therefore, ESL determines the speed at which the stored energy of a capacitor is transferred to a load. The speed of this energy transfer increases as ESL decreases. This is critical for digital circuit applications, such as, microprocessors, and therefore, it is essential for ESL to be as low as possible. R_P is the insulation resistance or the leakage resistance of the capacitor. It determines the ability of the dielectric to resist the dc leakage current. C_D is the inherent dielectric absorption. Dielectric absorption is the measure of the reluctance of the dielectric to give up its electrons, which in other words is the incomplete discharge of the capacitor. This is an intrinsic property of the material and increases with the dielectric constant [9]. Finally, R_D is the dielectric loss due to dielectric absorption and molecular polarization [10], and it need to be kept as low as possible. Thus, to increase a capacitor's performance and reliability, the values of parasitic elements, such as ESR, ESL, R_D and C_D , must be as low as possible, and R_P must be as high as possible.

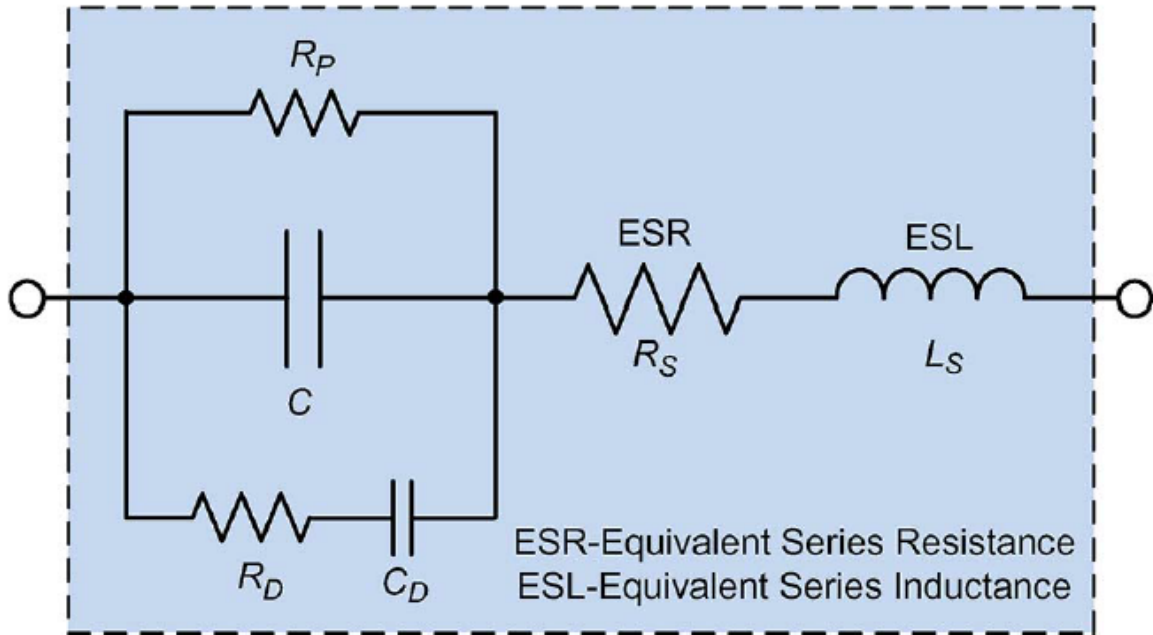


Figure 2.1. Simplified circuit model of a capacitor [10]

Electrolytic capacitors have higher capacitance per unit volume than any other capacitors, which results high volumetric efficiency. Volumetric efficiency is the amount of charge that can be held within a given volume. Since charge is the product of capacitance and voltage ($Q = C \cdot V$), volumetric efficiency is measured using the product of capacitance and voltage per unit volume or gram, which is expressed as:

$$Volumetric\ Efficiency = \frac{C \cdot V}{cc} \quad 2.1$$

where C is the capacitance, V is the voltage, and cc is the volume in cubic centimeters. There are two main reasons for having high volumetric efficiency in Electrolytic capacitors, the first one is the large surface area of the dielectric/electrode interface and the second one is the small dielectric thickness. This high volumetric efficiency of Electrolytic capacitors allows capacitors to be miniaturized, which makes them attractive for military, space, and medical applications.

When fabricating Electrolytic capacitors all the above discussed parameters and parasitic components must be taken into consideration. In order to avoid leakage current and operate capacitors safely, the applied voltage across the capacitors must be under the maximum working voltage of the capacitor, which is usually half of the breakdown voltage, and the capacitors should not be connected in a reverse bias polarity (- on the anode side and + on the cathode side); however, if they are connected in a reverse bias polarity, the voltage must be below the maximum reverse voltage. Moreover, to manufacture Electrolytic capacitors that have small power loss, high speed of energy transfer to the load, stable with frequency, long lifetime, and high reliability, the values of ESR, ESL, R_D and C_D , must be as low as possible, while keeping the leakage resistance (R_P) as high as possible.

CHAPTER 3

HISTORY OF TANTALUM CAPACITORS

3.1 Introduction

Even though Tantalum is a more expensive metal than Aluminum, Tantalum capacitors are used extensively throughout the world. That is because of some of the benefits Tantalum has over Aluminum metal. Tantalum's anodic oxide, Ta_2O_5 , has higher dielectric constant than Aluminum's anodic oxide, Al_2O_3 , which allows manufacturers to miniaturize the capacitor's size. The oxide of Tantalum is thermally [11] and chemically [12] more stable than that of Aluminum, making Tantalum capacitors preferable for high reliability applications. Tantalum capacitor's high volumetric efficiency and longer shelf-life are also additional advantages Tantalum has over Aluminum [13]. Some comparisons of the more important physical characteristics between Tantalum and Aluminum are shown in Table 3.1. As shown in Table 3.1, tantalum oxide has a dielectric constant that is more than twice of that of aluminum oxide, which contributes to the capacitance and miniaturization of Tantalum capacitors. The oxide growth rate of tantalum oxide is also higher than that of aluminum oxide, meaning for a given voltage Tantalum gives a thicker oxide than Aluminum. There are also some drawbacks of Tantalum metal in comparison to Aluminum. Tantalum metal is denser than Aluminum, which makes Tantalum capacitors a bit heavier than Aluminum capacitors. The other drawback is that Tantalum is less conductive than Aluminum. In general, however, Tantalum capacitors are more advantageous than Aluminum capacitors.

Table 3.1. Comparison of Physical and Electrical Properties of Tantalum and Aluminum.

Metal	Density(g/cm ³)	Resistivity (ohm-cm)	Anodic Oxide	Dielectric Constant of Oxide	Oxide Growth Rate (nm/V)
Aluminum	2.7	2.65 x 10 ⁻⁶	Al ₂ O ₃	8	1.36
Tantalum	16.6	12.5 x 10 ⁻⁶	Ta ₂ O ₅	27.6	1.7

3.2 Fabrication of Tantalum Capacitors

Tantalum anodes are fabricated from a pure tantalum metal powder. The particle size of the powder is determined based on what type of capacitor one wants to build. Large particle sizes are used for high voltage capacitors, whereas fine powders are used for small voltage capacitors. This is because during the anodization process, the dielectric grows out of the surface of the tantalum particles by about one third of its thickness and into the particles by about two thirds [14]. Therefore, if fine powders were used for high voltage capacitors, each particle would be consumed and isolated. The surface area is also affected by the tantalum powder's particle size, which determines the volumetric efficiency of the capacitor. This volumetric efficiency is measured in charge per unit gram, $C \cdot V/g$. The finer the powder is the larger the total surface area of the tantalum anode, which in turn means larger capacitance. Tantalum powder has gone through a transformation in terms of

the powder's particle size. In the 1960s, the volumetric efficiency of tantalum was about 1000 CV/g. Since then tantalum powder volumetric efficiency increased steadily until 1981, the year tantalum ore price was at its peak [15]. After 1981 tantalum powder CV/g has increased enormously to 150,000 CV/g in the 2000s, and above 250,000 CV/g currently. The finest tantalum powders are produced by sodium reduction of potassium tantalum fluoride or direct magnesium reduction of tantalum pentoxide [16]. In Figure 3.1 the evolution of tantalum powder along with photographs of 330 μ F Tantalum capacitors with a working voltage of 6.3 V, made with coarse, medium, and small size tantalum powders, are shown. The sizes of the dots in Figure 3.1 are proportional to the average sizes of the tantalum powder particles. As shown in Figure 3.1, the particle sizes of tantalum powders have decreased tremendously throughout the years, which led to an enormous increase in volumetric efficiency of Tantalum capacitors and, thereby, miniaturization of Tantalum capacitors.

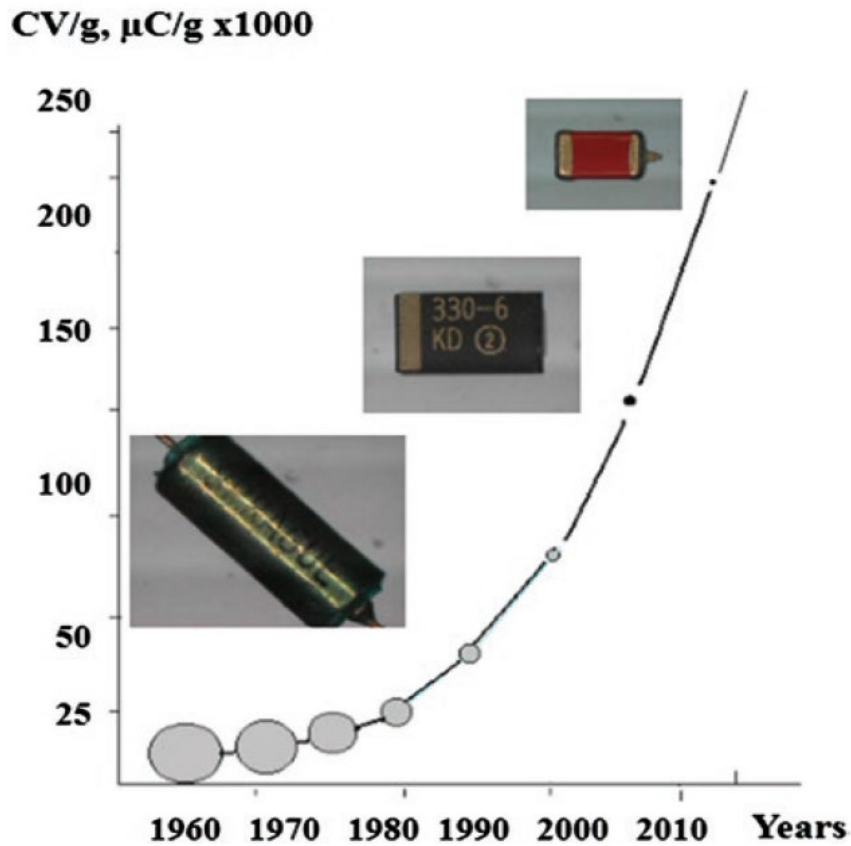


Figure 3.1. Evolution of tantalum powder [16].

To fabricate Tantalum capacitors, the tantalum powder is first placed in a cavity with a small tantalum wire in the middle of the powder. A lubricant is mixed with the powder to help the particles adhere to each other when pressed. The powder is then compressed at high pressure to form a tantalum slug, while allowing for the wire to stick out of the pressed slug.

The tantalum powder particles in the pressed slug are in contact with each other and with the tantalum wire, but not good enough contact. Therefore, the slug is sintered to create an even better contact between the particles and with the wire. In Figure 3.2 tantalum

powder particles in a die cavity before and after pressing and sintering are illustrated. The sintering process occurs in a vacuum oven at 1350°C for 10 minutes, to create a strong contact between the particles in the pressed slug. The lubricant used for adhesion between the particles is removed during the sintering process.

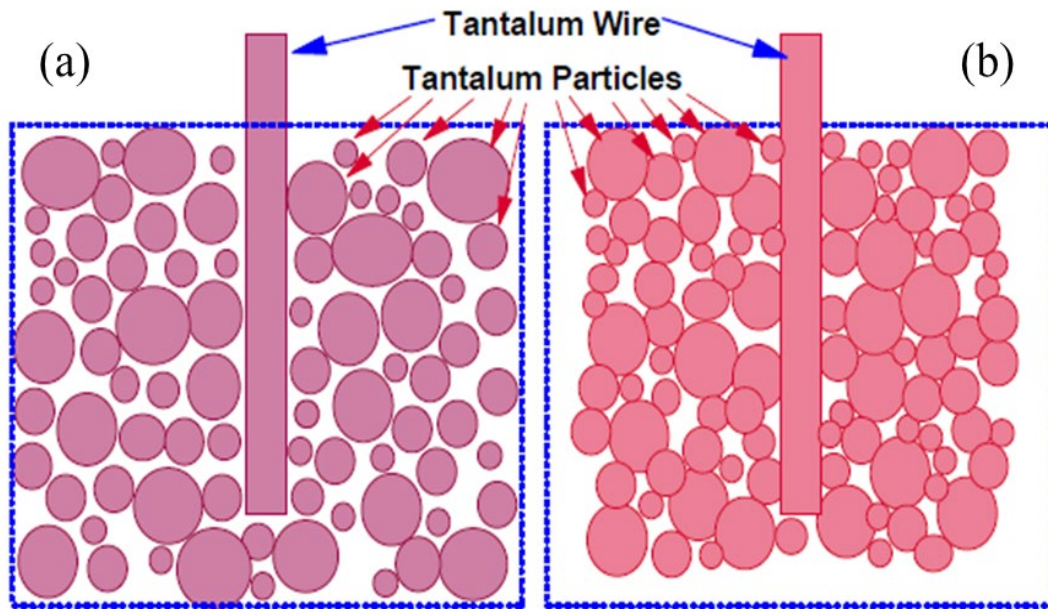
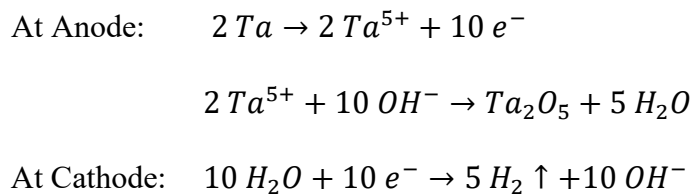


Figure 3.2. Tantalum pellet before (a) and after (b) pressing and sintering [4]

At this point the tantalum slug is as pure as it can get. The point of contact between the particles have increased enormously; however, there are still voids in the slug. That is why tantalum slug is referred to as a sponge-like structure. The voids in the slug, however, turn out to be an advantage for Tantalum capacitors, as they increase the surface area of the anode where the dielectric can potentially grow, and thus increase the volumetric efficiency of the capacitor.

After sintering, an anodic tantalum oxide, Ta_2O_5 , is grown on the exposed surface of the tantalum slug using an electrochemical process. The tantalum slug is immersed in an acidic electrolyte solution, such as phosphoric acid, at elevated temperature, typically $85^\circ C$. The electrolyte solution is biased with a voltage to oxidize the exposed tantalum surface, and the thickness of the oxide layer is controlled by the voltage applied during the oxidation process. The voltage applied is increased linearly until the desired voltage is reached while keeping the current constant. The voltage is then kept at the desired level while the current decays, to ensure all of the exposed tantalum surfaces are oxidized and acquire the same dielectric thickness. The chemical equations that describe this process are:



In these chemical reactions, the Tantalum ion, Ta^{5+} , from the anode and hydroxide, OH^- , from the electrolyte solution react with each other and form tantalum oxide, Ta_2O_5 , and water, H_2O , as a by-product. The H_2O is then removed from the solution by evaporation of hydrogen gas, H_2 . The surface area of the capacitor can be calculated using the very first equation given in Chapter 1, Equation 1.1. The equation is rewritten here for convenience, but this time in terms of the surface area:

$$A = \frac{Cd}{\epsilon_0 \epsilon_d}$$

The thickness of the dielectric oxide can be calculated using the following equation:

$$d = aV_f \tag{3.1}$$

where a is a proportionality coefficient, which is 1.7 nm/V at room temperature and 2 nm/V at 80°C for tantalum, and V_f is the formation voltage. The formation voltage is the maximum voltage applied to grow the oxide during the electrochemical process.

At this point essentially two thirds of the principal layers of the capacitor have been fabricated and the final primary layer is the cathode. Based on the type of cathodes we use, Tantalum capacitors can be divided into two types: Wet and Solid. As discussed in Chapter 1, Wet Electrolytic capacitors have a conducting liquid electrolyte solution as a cathode, such as sulfuric acid. Wet Tantalum capacitors were the very first Tantalum capacitors manufactured in the 1940s [17]. Wet Tantalum capacitors have the advantage of a cathode consisting of a liquid electrolyte that conforms to the dielectric surface, penetrates through the voids, and reforms the dielectric at the fault sites during operation. Wet Tantalum capacitors are also preferable for application that require high working voltages. They can work reliably up to 150 V.

As much as having a liquid electrolyte as a cathode has the aforementioned advantages, there are also some disadvantages to it. Wet Tantalum capacitors are not operational at low temperature, because at low temperatures (below 0°C, or below 10°C

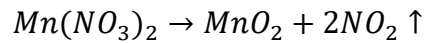
for sulfuric acid) the electrolyte freezes. Wet Tantalum Electrolytic capacitors also have high equivalent series resistance, which is due to the poor conductivity of the electrolyte cathode. Furthermore, they require a hermetically sealed package since the electrolyte has an acidic nature. Leakage of the electrolyte, or a caustic gas that might be generated from the electrolyte at high temperature would be dangerous. To combat these disadvantages of having a liquid electrolyte as a cathode and the need for even smaller size capacitors, a Solid Tantalum capacitor was developed, where a solid electrolyte is used as a cathode.

3.3 Solid Tantalum Capacitors

The first Solid Tantalum capacitor was developed by Bell labs in the 1950s [18]. The solid electrolyte that was used for this purpose was manganese dioxide, MnO_2 . MnO_2 is a semiconductor with a resistivity of 2 to 6 ohm-cm [4]. Since it is a solid electrolyte, there would not be any danger of leakage of an electrolyte. Compared to Wet Tantalum capacitors, the Manganese capacitors had better stability for thermal cycles that were required during the surface mount assembly process, and it was also smaller in size and had a longer shelf life. However, the maximum working voltage was decreased from that of the Wet Tantalum capacitor (150 V) to approximately 50 V. Even though this lower maximum working voltage prohibits Solid Tantalum capacitors from high voltage applications, the development of low-power electronics makes this problem less significant.

In order to deposit MnO_2 , the tantalum slug with a dielectric oxide layer on the surface is dipped into an aqueous solution of $\text{Mn}(\text{NO}_3)_2$ and then heated in an oven at

approximately 250°C [14] to produce MnO₂. This impregnation process continues with different concentrations of Mn(NO₃)₂ until the MnO₂ penetrates through the voids and a desired thickness of the cathode is reached. The chemical equation that describes this process is:



As shown in the chemical equation, at high temperature, typically at 250°C, manganese nitrate decomposes into manganese dioxide and nitrogen dioxide.

Once the deposition of MnO₂ is completed, we have a complete capacitor in theory; however, we need packaging for the capacitor to be used in a circuit. First, a thin layer of carbon (or graphite) is coated onto the tantalum slug with an outside layer of MnO₂. Then silver is coated on top of the carbon. The purpose of the carbon is to lower the interfacial resistance between MnO₂ and silver [19]. In Figure 3.3, each layer of the capacitor, including the carbon and silver layers, is shown.

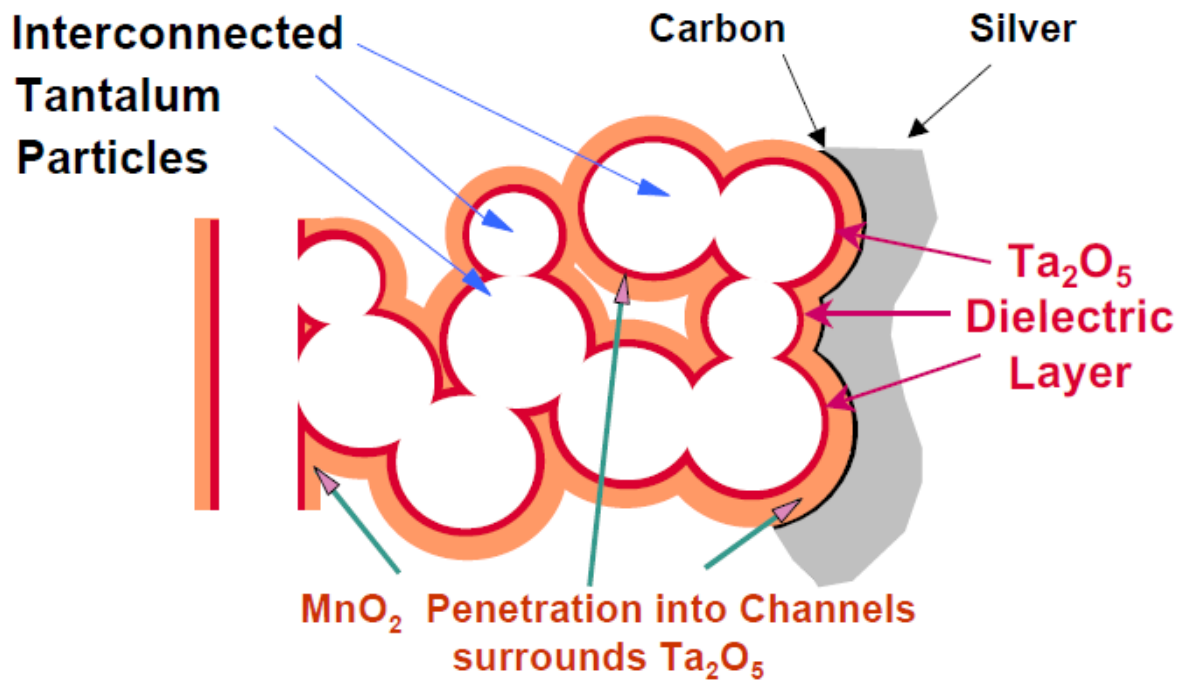


Figure 3.3. Structure of Tantalum - MnO₂ capacitor [19]

To make an external anode and cathode connection for the capacitor, a leadframe plate is welded to the tantalum wire and another leadframe plate is connected to the outer layer of the slug (the silver layer) [19]. The whole structure is then inserted into a molded epoxy case, with the leadframes bent down and sticking out in order to make an external connection. A finished surface mountable capacitor, manufactured by KEMET Electronics Corporation, is shown in Figure 3.4.

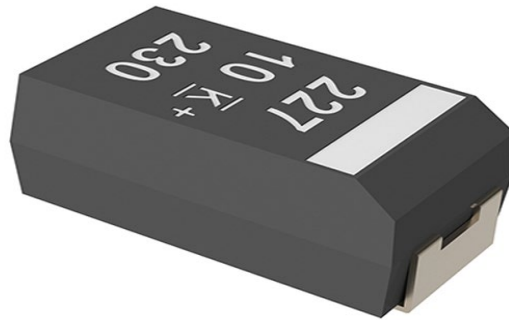


Figure 3.4. KEMET's Surface mount Tantalum-MnO₂ capacitor [20]

3.4 Resistance-Capacitance (RC) Ladder Effect

The capacitance of Electrolytic capacitors decreases as frequency increases. The same goes for a Solid Electrolytic capacitor; the capacitance stability of Tantalum-MnO₂ capacitors is affected at high frequency operations. This effect of frequency can be modeled by the Resistance-Capacitance (RC) ladder effect. In Figure 3.5 the RC-ladder model with a distributed capacitive element network in a Tantalum-MnO₂ capacitor is illustrated. Tantalum powder particles that are covered by Ta₂O₅ and MnO₂, are shown in Figure 3.5, forming an individual capacitor element that contributes to the capacitance of the main capacitor. Each of these individual capacitor elements are electrically connected to the terminals of the main capacitor since the tantalum powder particles are physically connected to each other. If we neglect to consider the resistivity of tantalum ($\rho = 12.5 \times 10^{-6}$ ohm-cm), which is extremely small compare to the resistivity of MnO₂ ($\rho = 2-6$ ohm-cm), we can simplify the physical structure of the RC-ladder model that is shown in Figure 3.5 into the circuit model that is shown in Figure 3.6. This circuit model, that is shown in Figure 3.6, considers only the resistance that is created from the resistivity of the cathode,

MnO₂. For a capacitor element C₁, which is located close to the cathode in Figure 3.6, the time constant can be expressed as:

$$\tau_1 = C_1 \cdot R_1 \quad 3.2$$

On the other hand, the time constant for a capacitor element C_n, which is located away from the cathode (or close to the anode), can be expressed as:

$$\tau_n = C_n \cdot (R_1 + R_2 + R_3 \dots + R_n) \quad 3.3$$

Comparing these two time constants of C₁ and C_n, the time constant for C_n is clearly higher than that of C₁, and because of this higher time constant, C_n will not be able to respond to high frequency AC signals within the time period, as the time period of the AC signal will be small. The time period is given by,

$$T_P = \frac{1}{f} \quad 3.4$$

The time constant for these individual capacitor elements increases as we move away from the cathode (or towards C_n as shown in Figure 3.6) because of the increase in resistance. Therefore, if the frequency of the AC signal becomes even higher (or the period becomes smaller), capacitor elements that are closer to C_n will also be unable to respond to the AC signal within the time period. As more of these capacitive elements stop responding to the

AC signal, the total capacitance of the main capacitor will start decreasing, and eventually the capacitance of Tantalum-MnO₂ capacitors rolls-off at higher frequencies.

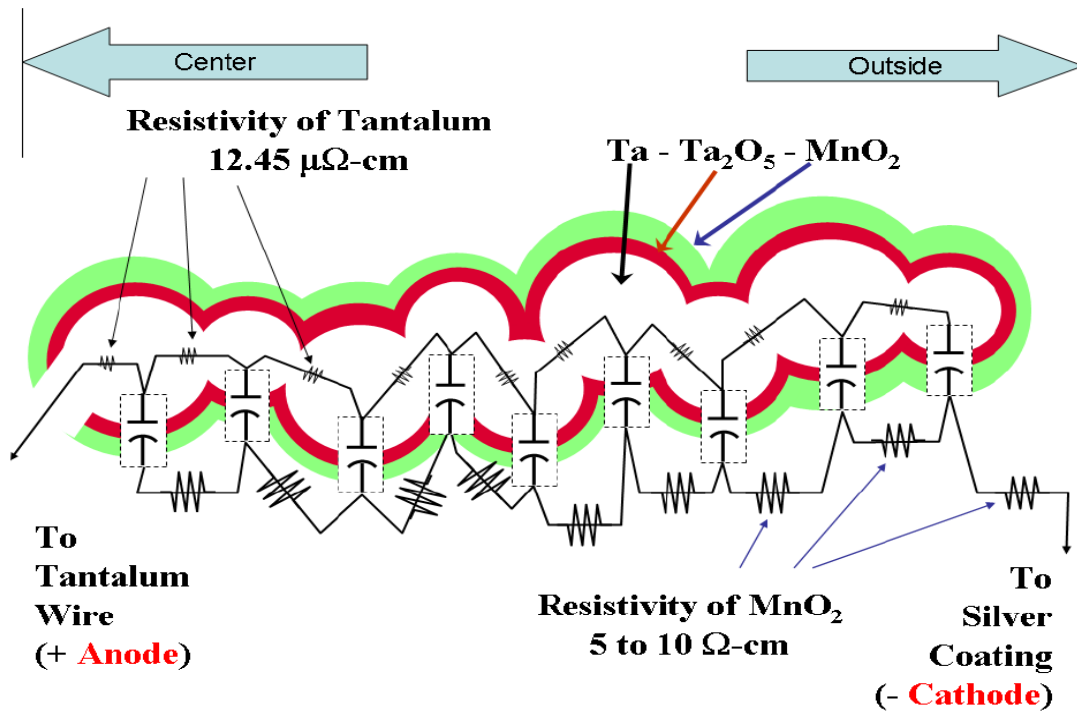


Figure 3.5. RC-ladder physical structure in Tantalum capacitors [21]

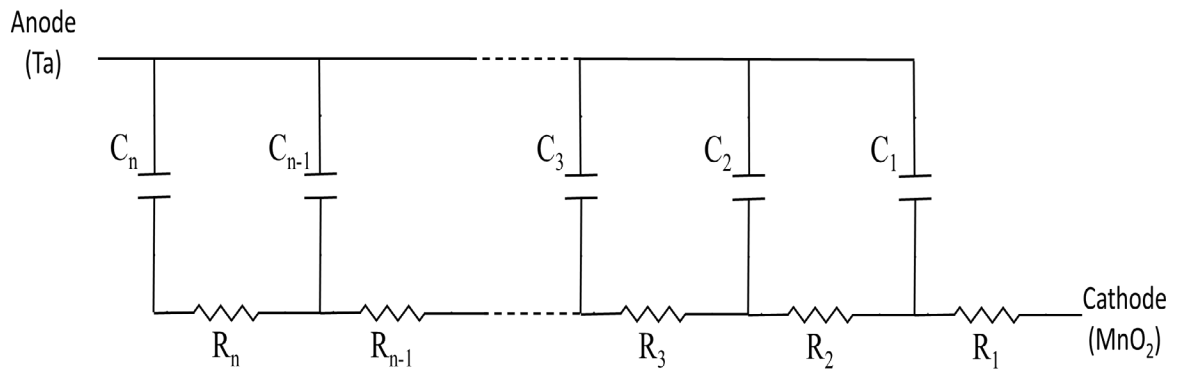


Figure 3.6. RC ladder network

3.5 Self-Healing Property of Tantalum-MnO₂ Capacitors

All Tantalum capacitors have impurities that may come from the anode and/or the electrolyte, and because of that there are defects created within the dielectric. In Wet Tantalum capacitors, these defects or fault sites are reformed by electrochemical processes during the capacitor operation. In Solid Tantalum capacitors, that is not possible. However, MnO₂ has its own way of healing these defect sites. When subjected to a high voltage, the defect sites create a path for leakage current and the current through these sites concentrates in a small area of the MnO₂. This concentrated current creates a local hot spot, and MnO₂ become unstable at this high temperature (usually around 470°C) and becomes oxidized to its lower oxide state, Mn₂O₃. The resistivity of this lower oxide state is much higher than MnO₂ and blocks the flow of the current past the defect site. This process is called the self-healing property of Tantalum-MnO₂ capacitors, and it is illustrated in Figure 3.7. As illustrated in Figure 3.7, the defect site in the dielectric might be a crack or an impurity, which is shown as Nickel in the figure, or both. Without the self-healing property of Tantalum-MnO₂ capacitors, the crack and the impurity in the dielectric will result in a leakage current in the capacitor and, thereby, failure of the capacitor. Therefore, once the fabrication of the capacitor is completed and ready for electrification, it goes through a process called aging. The aging process activates the self-healing mechanism of the Tantalum-MnO₂ capacitor and eliminates the fault sites by stressing the capacitor at a high voltage [19].

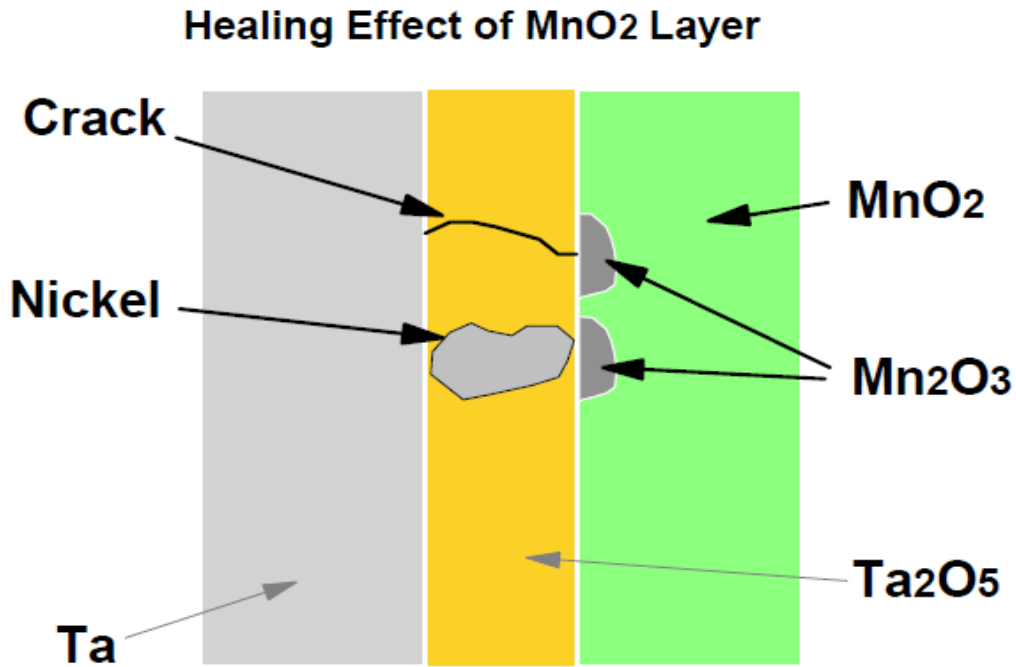


Figure 3.7. Self-healing property of a Tantalum-MnO₂ capacitor [4]

3.6 Failure Modes of Tantalum-MnO₂ Capacitors

For the self-healing process to occur the current must be sufficient. If the current through the fault site is too low, there would not be enough heat generated to convert MnO₂ into its lower oxide state, and the fault site would not be healed. If the current through the fault site is too high, in addition to heating the MnO₂ and converting it to its lower oxide state, the dielectric also becomes heated. If the heat is sufficiently high, the dielectric itself gets converted from its amorphous or glassy structure to a crystalline structure, which usually occurs at a temperature around 520°C [8]. This crystalline structure spreads out across the dielectric structure. The crystalline structure of the dielectric is much more conductive than the amorphous structure, which leads to a high flow of current through the

fault site, which in turn lead to an increase in the heat generation. While all this is taking place, MnO_2 is releasing oxygen when converted to its lower oxide state, Mn_2O_3 , and the tantalum contact that is on the fault site is getting heated. The heated tantalum then starts to absorb the free oxygen and create an exothermic reaction. The exothermic reaction results in an ignition resulting in a catastrophic failure in the capacitor. The sequence of this ignition process is illustrated in Figure 3.8. As illustrated in Figure 3.8, a small crack in the dielectric, could lead to an ignition of the whole capacitor.

"Ignition"

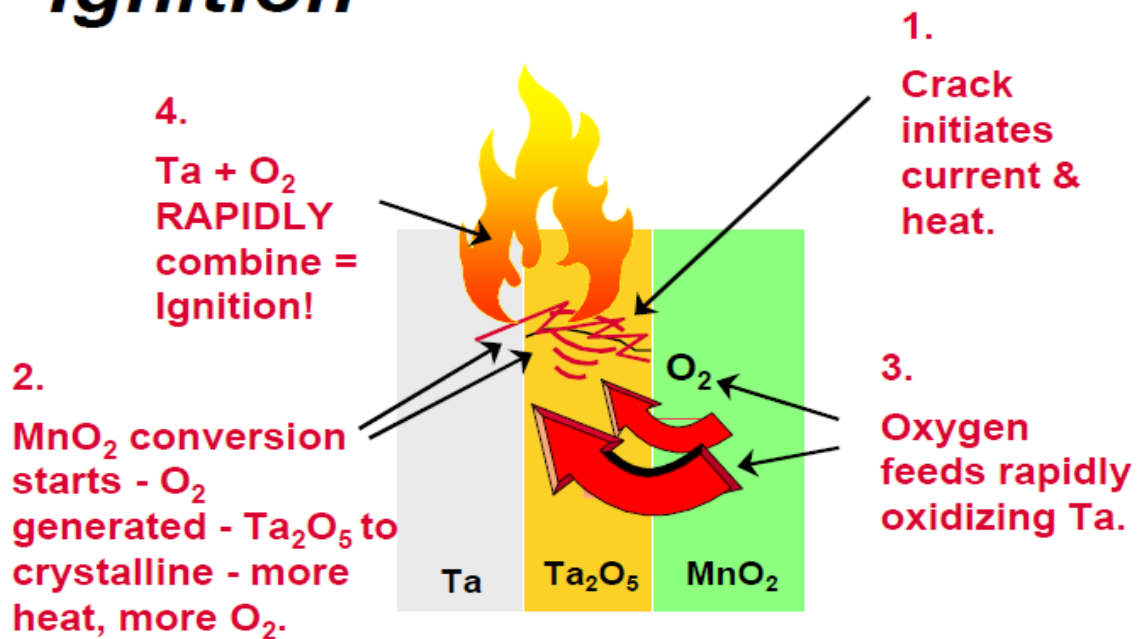


Figure 3.8. Ignition sequence of a Tantalum- MnO_2 capacitor [19]

In addition to the issue of ignition with Tantalum- MnO_2 capacitors, there is also a mechanical issue with having MnO_2 as a cathode. As explained earlier, the deposition of

MnO₂ occurs by dipping the tantalum slug into a Mn(NO₃)₂ solution and drying it at 270°C, which converts the liquid Mn(NO₃)₂ into solid MnO₂. This process is repeated several times until the dielectric layer is fully covered by MnO₂. The three materials (Ta, Ta₂O₅, and MnO₂), which constitute the capacitor have different coefficients of thermal expansion, and in addition to that MnO₂ is inelastic and brittle by nature. So, when the capacitor is heated to high temperatures repeatedly during the deposition process, the mismatch in coefficients of thermal expansion creates a mechanical stress inside the capacitor, which eventually leads to a crack in the dielectric layer. This crack leads to a leakage current and failure in the capacitor. The cracks usually occur at the wedges. In Figure 3.9 the mechanical stress in Tantalum-MnO₂ capacitor is illustrated. As shown in Figure 3.9, the mechanical stress that is created due to the mismatch in the coefficients of thermal expansion between Ta, Ta₂O₅, and MnO₂, results in a crack in the capacitor, especially at the wedges. These cracks will lead to a leakage current in the capacitor, and subsequently failure of the capacitor.

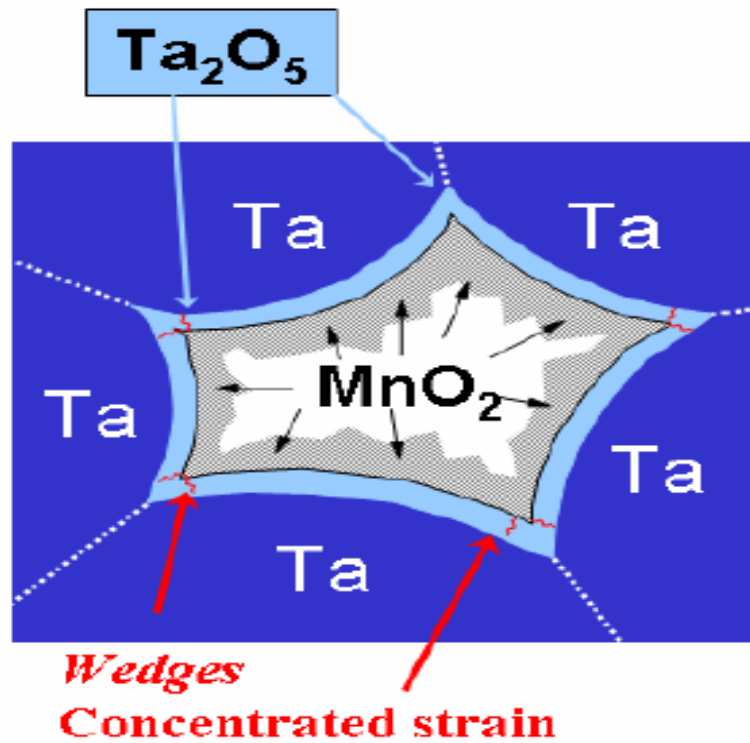


Figure 3.9. Mechanical stress of a Tantalum- MnO_2 capacitor [22]

Despite the ignition and the dielectric crack issues, Tantalum- MnO_2 capacitors are manufactured and used widely throughout the world. The driving force behind finding a replacement for MnO_2 in Solid Electrolytic capacitors was the need for a highly conductive cathode, which would result in lower ESR and an improved high frequency performance in Solid capacitors.

CHAPTER 4

POLYMER TANTALUM CAPACITORS

4.1 Introduction

In order to replace MnO_2 as a cathode in a Tantalum Electrolytic capacitor, higher conductive materials were used, such as tetracyano-quinodimethane (TCNQ) and conductive polymers. TCNQ is a charge-transfer salt. It has a conductivity of 1 S/cm, which is 10 times greater than that of MnO_2 . Conductive polymers have even higher conductivity than TCNQ, ranging from 10 S/cm to 500 S/cm. Conductive polymers were discovered by Shirakawa, MacDiarmid and Heeger in 1977 [23], which they received a Nobel Prize for in 2000 [24]. The first Polymer Tantalum capacitor was made in Japan in the early 1990s. The conductive polymers that were used at the time were polypyrrole (PP) [25, 26, 27] and polyaniline (PANI) [28]. Then later, poly(3,4- ethylenedioxythiophene) (PEDOT) was discovered and became the most popular conductive polymer in the Solid Tantalum Electrolytic capacitors [29]. PEDOT has higher conductivity, and is relatively more stable and insensitive to environmental conditions than any other polymer. Polymer Tantalum capacitors, however, did not start with great performance or high reliability. They started out with low working voltage, high leakage current, and low reliability, which limited their applications to risk-tolerant commercial electronics. After going through transformations over the years, the current Polymer Tantalum capacitors have high working voltage, low leakage current, and high reliability, which makes them attractive for critical applications.

4.2 Benefits of Polymer Tantalum Capacitors

Polymer Tantalum capacitors have a self-healing capability similar to Tantalum-MnO₂ capacitors. The self-healing mechanism in Polymer Tantalum capacitors can be explained by two possible mechanisms [19]. The first self-healing mechanism is related to the low-threshold temperature of polymers, which means the low evaporating temperature of polymers. When current concentrates in a fault site of the dielectric oxide and creates a high temperature, the polymer that is near the fault site becomes heated. As the heating continues, the polymer reaches a temperature where it starts to evaporate. This evaporation of the polymer creates a vacant site in the cathode near the fault site, which blocks any further flow of the leakage current and thus, prevents failure of the capacitor. This self-healing mechanism of Polymer Tantalum capacitors is illustrated in Figure 4.1 (a). The vacated sites in the polymer are illustrated in Figure 4.1 (a), where a leakage current is coming from the crack and the impurity, which is Nickel in this case, in the dielectric. The second self-healing mechanism is related to the oxidation of polymers. As the polymer near the fault site becomes heated, the heated part of the polymer becomes oxidized by absorbing the available oxygen. Since an oxidized polymer has higher resistance, it blocks any further flow of the current. This self-healing mechanism of Polymer Tantalum capacitors due to the oxidation of the polymers is illustrated in Figure 4.1 (b). As illustrated in Figure 4.1 (b), the oxidized polymer parts are marked in aqua color, which prevents any further flow of leakage current from the crack or impurity in the dielectric. Both of these self-healing mechanisms prevent the leakage current and provide an advantage to Polymer Tantalum capacitors.

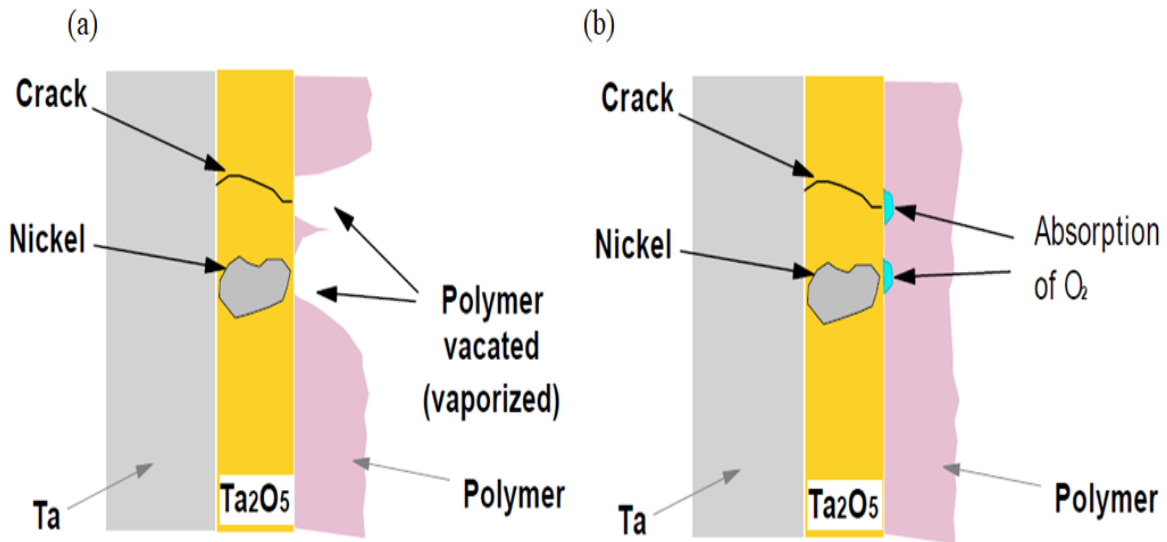


Figure 4.1. Self-healing mechanism of a Polymer Tantalum capacitor due to evaporation in the polymer layer (a) and due to oxidation in the polymer layer (b) [19].

Polymer Tantalum capacitors have higher frequency stability than Tantalum-MnO₂ capacitors and one of the lowest values of equivalent series resistance. One of the main reasons for this is the low resistivity of conductive polymers as compared to that of MnO₂. Due to this high conductivity of polymers, the effect of the RC-ladder effect is lower in Polymer Tantalum capacitors. For Polymer Tantalum capacitors, the capacitance roll-off begins at a higher frequency than that of Tantalum-MnO₂ capacitors. In Figure 4.2 capacitance as a function of frequency for both MnO₂ and Polymer Tantalum capacitors is illustrated [19]. As shown in Figure 4.2, the capacitance of the Polymer Tantalum capacitor remains stable for far longer than in Tantalum-MnO₂ capacitors.

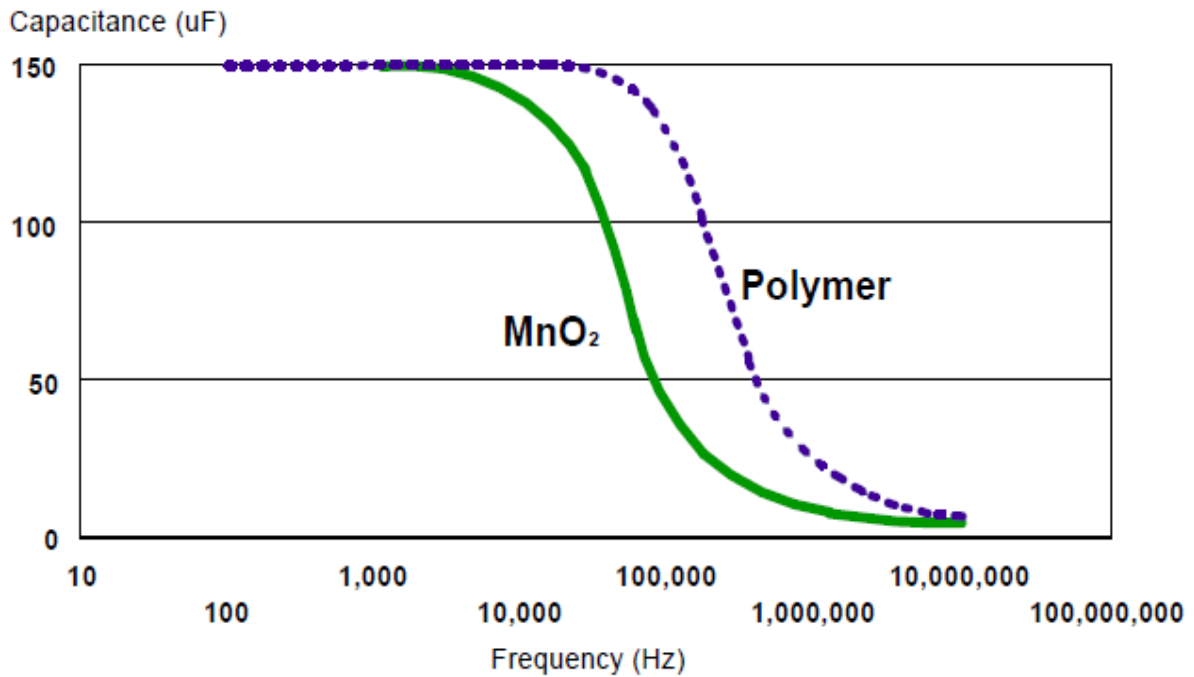


Figure 4.2. Capacitance roll-off in Tantalum-MnO₂ (T495D 150μF) and Polymer Tantalum (T520D 150 μF) capacitors [19].

Finally, another advantage Polymer Tantalum capacitors have over Tantalum-MnO₂ capacitors is that, unlike Tantalum-MnO₂ capacitors, Polymer Tantalum capacitors do not experience an ignition or crack failure. Polymers contain almost no oxygen, which is the main source of ignition and catastrophic failure in Tantalum-MnO₂ capacitors. Because of this lack of oxygen, there would not be any exothermic reaction in Polymer Tantalum capacitors that would create a dramatic failure in the device. The other failure mode that occurs in Tantalum-MnO₂ capacitors, but not in Polymer Tantalum capacitors, is the stress induced cracks. The mismatch in the coefficient of thermal expansions between Ta, Ta₂O₅, and MnO₂, creates a mechanical stress inside the capacitor. In addition to that,

the physical property of MnO_2 being brittle and inelastic contributes significantly to the crack. However, in Polymer Tantalum capacitors, the mechanical forces that are created because of the mismatch in coefficient of thermal expansions are not significant enough to create any crack. This is because during the process of depositing the polymer onto the dielectric, the drying process occurs at a lower temperature than that of MnO_2 . Furthermore, a polymer is a soft and elastic material, which has the capability to absorb any mechanical stress created inside the capacitor. Therefore, Polymer Tantalum capacitors do not experience ignition failure or mechanically induced cracks.

4.3 Fabrication of Polymer Tantalum Capacitors

The fabrication of Polymer Tantalum capacitors is similar to Tantalum- MnO_2 capacitors, with the main difference being that instead of using MnO_2 , a polymer is used as a cathode. The polymer that is used in this research work is a water dispersion of poly(3,4- ethylenedioxythiophene) (PEDOT) doped with poly (styrene sulfonate)(PSS) to increase the conductivity of the PEDOT; therefore, from here on the polymer in reference is PEDOT doped with PSS. There are two main methods of depositing PEDOT onto the dielectric oxide, Ta_2O_5 : in-situ and prepolymerized PEDOT. In-situ oxidative polymerization of PEDOT is performed by polymerization of 3, 4-ethylenedioxythiophene with iron (III) toluenesulfonate in a ratio of 3:1 [30]. Prepolymerized PEDOT is performed by dipping a tantalum slug that is covered with Ta_2O_5 into a waterborne dispersion of nanoscale PEDOT particles and drying it afterward at room temperature and then at 150°C [30]. The PEDOT deposited using this process is also known as slurry PEDOT. There is

another PEDOT cathode formation method commonly referred to as hybrid PEDOT. Hybrid PEDOT is a combination of both in situ and pre-polymerized PEDOT. In hybrid PEDOT, the in-situ PEDOT method is applied for internal impregnation of the porous anode and a pre-polymerized PEDOT dispersion is applied as an external part of the cathode [31]. Hybrid PEDOT is usually used for low voltage Polymer Tantalum capacitors, because low voltage anodes have a relatively small pore structure which makes it difficult to impregnate with pre-polymerized PEDOT only. In all of the three methods, a cathode is formed by depositing the PEDOT onto the dielectric oxide layer.

Polymer Tantalum capacitors manufactured using prepolymerized PEDOT, as compared to in-situ polymerization, show low leakage current (DCL), high breakdown voltage (BDV), high working voltage (WV), and high volumetric efficiency (CV/cc) [30, 32]. The reason for this improved performance of prepolymerized PEDOT cathodes as compared to its counterpart is the resulting potential energy barrier at the dielectric/PEDOT interface. For in-situ polymerized PEDOT, the residuals of the oxidizer and monomer in the polymerization process create a surface charge at the dielectric/PEDOT interface which lowers the potential barrier, resulting in an increase in leakage current and a decrease in breakdown voltage [30]. Whereas for prepolymerized PEDOT, the potential barrier at the dielectric/PEDOT interface increases as there is no significant surface charge at the interface and thus, resulting in a lower leakage current and a higher breakdown voltage.

Another advantage of prepolymerized PEDOT over in-situ polymerized PEDOT cathodes is that it possesses its own self-healing mechanism [30]. The defect sites in the dielectric oxide create a path for a leakage current, increasing the temperature in the defect

site. This temperature separates the PEDOT and the dopant (poly (styrene sulfonate))(PSS), or changes the optimal ratio between them, near the fault site. This separation of the PEDOT and the dopant lowers the conductivity of the polymer very significantly. This low conductive area of the polymer that is near the defect site prevents any further flow of the leakage current, which also prevents any damage to the capacitor.

Furthermore, prepolymerized PEDOT solves the Polymer Tantalum capacitor's problem of low working voltages. During Tantalum capacitor evolution, evolving from Wet Tantalum capacitors to Tantalum-MnO₂ capacitors to Polymer Tantalum capacitors, one of the main outcomes was an enormous decrease in ESR. However, this decrease in ESR came at a cost of reducing the maximum working voltage and volumetric efficiency (CV/cc) of the capacitors. As discussed in Chapter 3, the maximum working voltage for Wet Tantalum capacitors was approximately 150 V, but for Tantalum-MnO₂ capacitors it was approximately 50 V. For Polymer Tantalum capacitors, the maximum working voltage went down to as low as 25 V. In Figure 4.3 the trends in ESR, maximum working voltage and volumetric efficiency of Tantalum capacitors are shown over the years. As shown in Figure 4.3, the ESR, the maximum working voltage, and the volumetric efficiency have decreased as the Tantalum capacitor technology progresses from one generation to another. The reason for the reduction in the maximum working voltage and the volumetric efficiency is the increase in leakage current and the decrease in breakdown voltage of Polymer Tantalum capacitors. However, KEMET Electronics in collaboration with Clemson University has discovered a way to keep the leakage current low while increasing the working voltage for Polymer Tantalum capacitors [30]. This was accomplished by

using prepolymerized PEDOT as a cathode. For all these reasons, prepolymerized PEDOT tends to be the better manufacturing process for Polymer Tantalum capacitors, and capacitors fabricated using this method are more reliable and stable than those fabricated with in-situ polymerized PEDOT.

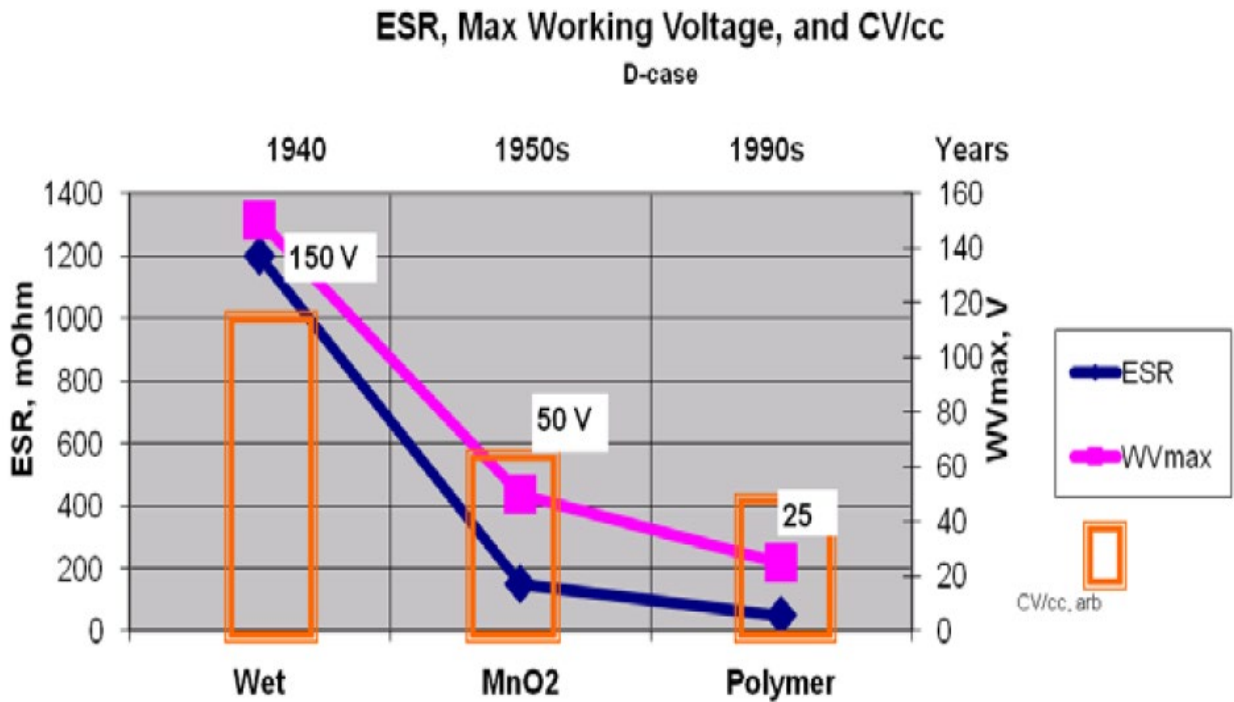


Figure 4.3. ESR, maximum working voltage and volumetric efficiency of D-case Tantalum capacitors [33]

4.4 Polymer Hermetic Sealed (PHS) Tantalum Capacitors

The next technology phase, after prepolymerized PEDOT Tantalum capacitors, was Polymer hermetic sealed (PHS) Tantalum capacitors. PHS Tantalum capacitors are

manufactured in using the same methods as any other Polymer Tantalum capacitors; however, before the final packaging is performed, which occurs after the coating of the carbon and silver layers, the capacitor is exposed to humidity, typically 85% relative humidity at a temperature of 85°C. The capacitor is then hermetically sealed to keep the moisture inside the package for a long time. A picture of a KEMET T550 PHS capacitor is shown in Figure 4.4. This controlled moisture inside PHS Tantalum capacitors helps in stabilizing the leakage current (DCL). In Figure 4.5 the DCL distribution of humid and dry PHS Tantalum capacitors that are measured at the rated voltage and 85°C for a duration of 2000 hours of life test is shown. As shown in Figure 4.5, the humid capacitor, which is shown in (a), has a much more stabilized leakage current than the dry capacitor, which is shown in (b). The moisture inside PHS Tantalum capacitors acts as a plasticizer for the polymer chains, which makes the chain movement easier by increasing the polymer mobility [34]. This property of the moisture allows polymer molecules to form a potential barrier at the dielectric/polymer interface by re-orientating themselves relatively quickly when an electric field is applied. The potential barrier then limits the flow of the current inside the capacitor. Therefore, PHS Tantalum capacitors have the distinct advantage of reduced leakage current.



Figure 4.4. KEMET T550 PHS capacitor [35].

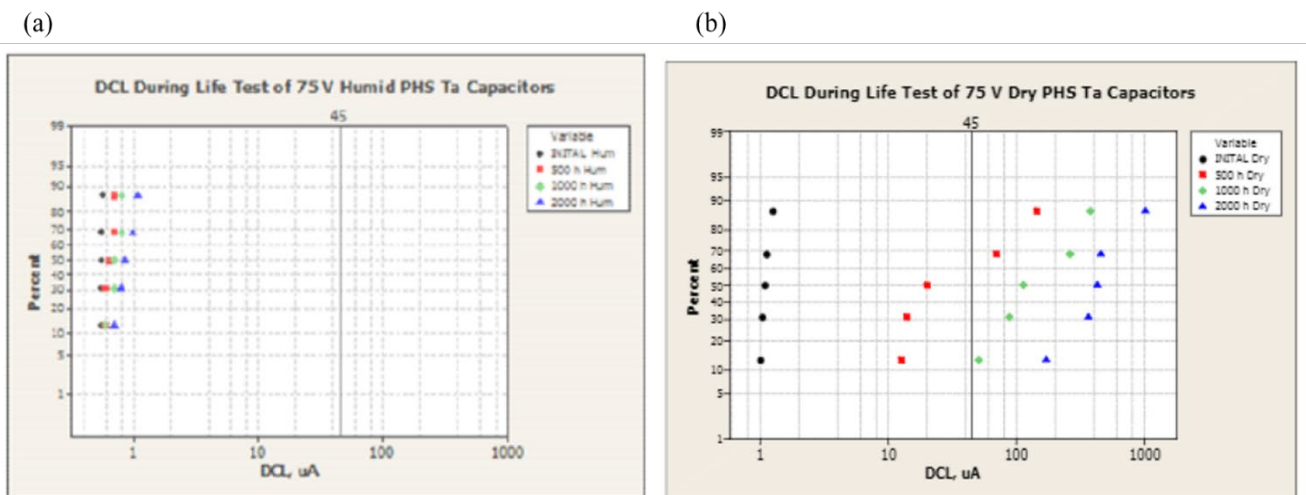


Figure 4.5. DCL distribution of humid (a) and dry (b) PHS Tantalum capacitors [36].

4.5 Flawless Dielectric Technology (F-Tech) and Simulated Breakdown Screening (SBDS)

Technologies that were recently discovered to improve the performance and reliability of Polymer Tantalum capacitors are flawless dielectric technology (F-Tech) [37] and simulated breakdown screening (SBDS) [38]. F-tech improves the performance of the capacitor by limiting defects in the dielectric. Polymer Tantalum capacitors are imperfect as are all other capacitors; there are defects and impurities in the dielectric layer which

affects the performance of the capacitor. The density and size of these defects in the dielectric are directly related to the density and size of local defects (or impurities) on the tantalum anode before the anodization process [16]. Therefore, the main sources of the defects in the dielectric are the tantalum anode and mechanical stress during the manufacturing and testing process. The defects that come from the anode are carbide and oxide inclusions. The carbide inclusions come from the residuals of the organic lubricant that is mixed with tantalum powder at the pressing, and the oxide inclusions come from the native oxide in the bulk of tantalum particles during their sintering in vacuum [16]. The carbide inclusions are responsible for micropores, an example of which is shown in Figure 4.6 (a). The oxide inclusions are responsible for crystal growth and cracks, an example of which is shown in Figure 4.6(b).

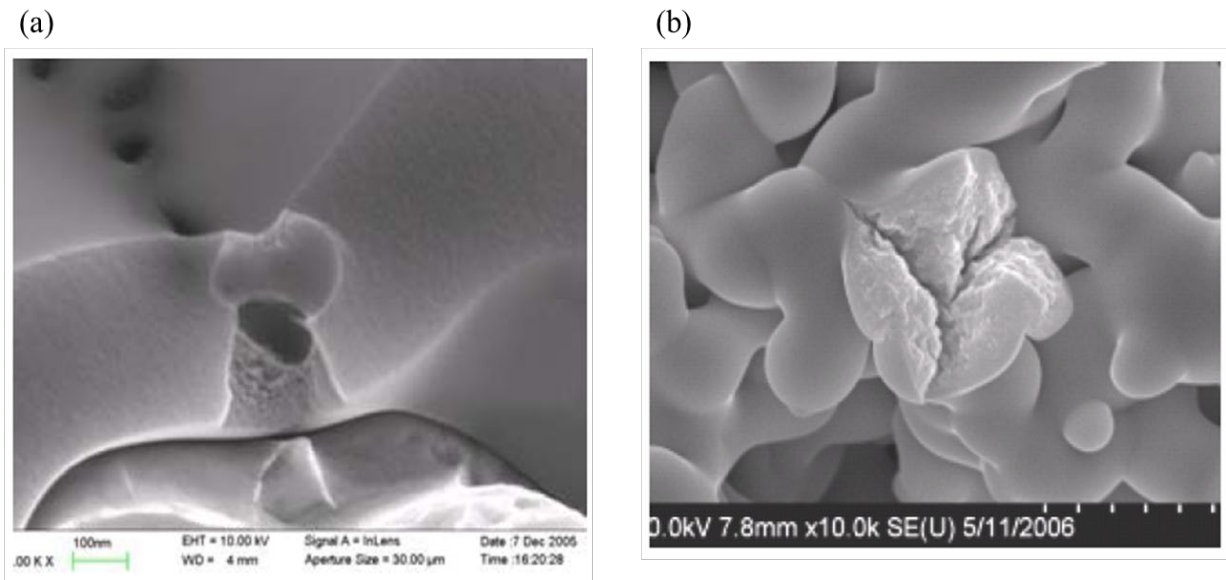


Figure 4.6. Micropores (a) and cracks (b) on the surface of the Ta_2O_5 dielectric that is formed on the tantalum anode. [33]

To avoid the carbons in the tantalum anode, F-tech uses an aqueous de-lubrication instead of the traditional thermal de-lubrication [16]. In the thermal de-lubrication, the anode is heated and pressed in vacuum to decompose and evaporate the organic lubricant, and some carbons from these decomposed organic lubricants are absorbed by the tantalum anode. Whereas in an aqueous de-lubrication, the soluble organic lubricant is washed out with water from the pressed tantalum anode [37], which makes the tantalum anode carbon inclusion free.

To reduce oxygens from the tantalum anode, F-tech uses magnesium vapor after the anode sintering process in vacuum is completed [16]. Magnesium atoms are absorbed onto the surface of the tantalum powder and react with oxygen in the tantalum, resulting in magnesium oxide, which is then leached from the tantalum surface in a diluted aqueous solution of sulfuric acid and hydrogen peroxide, resulting in a reduction of oxygen inclusions in the tantalum anode.

To avoid defects that may appear in the dielectric layer from a mechanical stress during the manufacturing and testing process, F- tech welds the tantalum wire to the anode after the pressing and sintering of the tantalum anode is completed, while traditionally the lead wire is embedded inside the powder before any pressing and sintering are performed. Application of this “flawless” technology allows Polymer Tantalum capacitors to be manufactured that are essentially defect free, which increases the performance and reliability of the capacitor significantly. This is illustrated in Figure 4.7, where a SEM image of a Ta_2O_5 dielectric formed on an F-tech tantalum anode is shown. The dielectric is essentially defect free, as it is clearly shown in Figure 4.7.

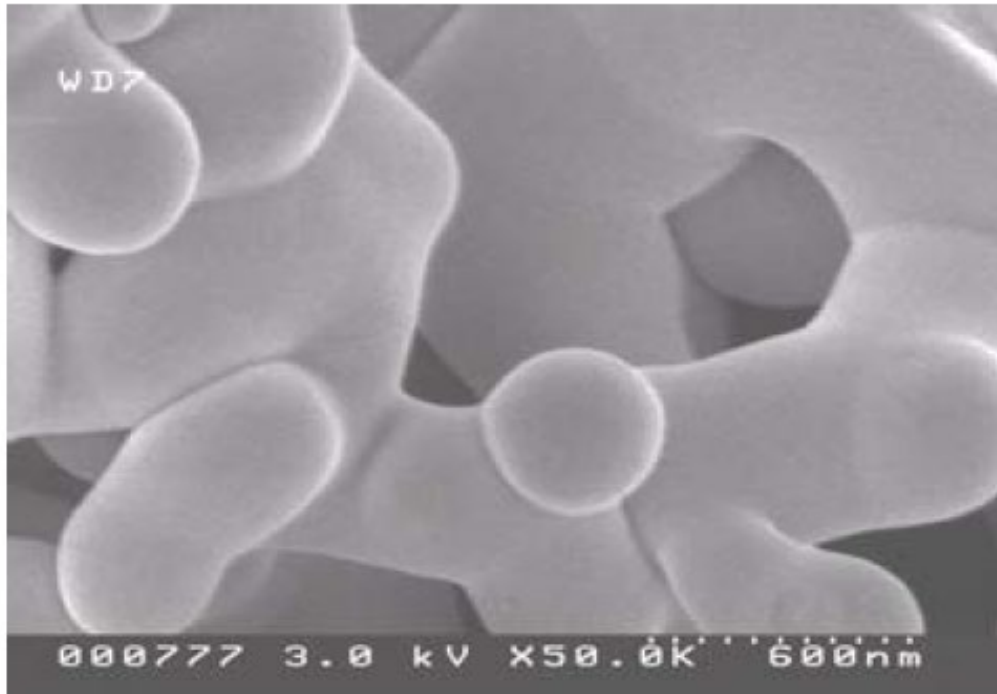


Figure 4.7. SEM image of a flawless Ta_2O_5 dielectric formed on an F-tech tantalum anode. [33]

Even with the application of the flawless dielectric technology, it is not guaranteed that 100% of the finished capacitors will be defect free. There will still be a small percentage of the finished capacitors that will have small defects on their dielectric layer. Furthermore, these defects might not be detectable using the traditional DC leakage test during the end of the line (EOL) testing because these defects are too small and might also be introduced into the dielectric layer by the overstressed tests and burn-ins [33]. Therefore, to effectively detect capacitors with hidden defects in their dielectric layer, a novel testing method called simulated breakdown screening (SBDS) test was developed [38]. This

testing method allows for the screening of low breakdown voltage in capacitors. An electrical circuit that is used for SBDS is shown in Figure 4.8. As shown in the SBDS circuit, the tested capacitor is connected in series with a high value resistor. A voltage that is above the average BDV is then applied to the capacitor under test, while the resistor limits the current that flows through the capacitor. The charging characteristic of the capacitor is then monitored using the voltage measurement across the capacitor, to detect the hidden (or small) defects. This method results in the capability of SBDS to detect small defects in the dielectric, which will contribute significantly to producing a capacitor that is nearly defect free.

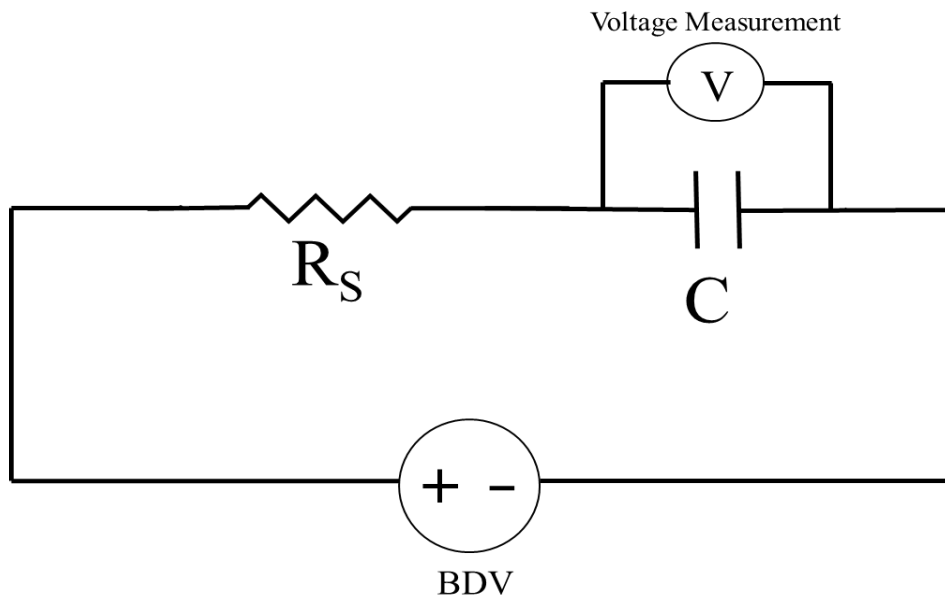


Figure 4.8. An electrical circuit used for simulated breakdown screening (SBDS)

CHAPTER 5

FABRICATION AND ELECTRICAL MEASUREMENTS

5.1 Fabrication of PHS Tantalum Capacitors

In this thesis work, we investigated the effects of environmental conditions on capacitance stability with temperature, frequency, and dc bias voltage in both dry and humid Polymer hermetic sealed (PHS) Tantalum capacitors with a wide range of working voltages and corresponding dielectric thicknesses. PHS Tantalum capacitors with four working voltages (WV), 15 V, 50 V, 75 V, and 100 V, were investigated, and five samples were measured from each working voltage.

The fabrication of the tantalum anodes for 15 V, 50 V, and 75 V working voltages was performed using 12,000 $\mu\text{C/g}$ tantalum powder, with an average particle size of 4.2 μm , pressed at 5.7 g/cc density into 1.32 g cylindrical pellets with resulting dimensions of 5.2 mm diameter and 10.7 mm height and sintered at 1650°C. The 100 V working voltage capacitor is considered as a high voltage capacitor, and the sizes of the tantalum powder particles are higher than the other working voltage capacitors. Thus, the fabrication of the tantalum anodes for 100 V working voltage was performed using 3,500 $\mu\text{C/g}$ tantalum powder, with an average particle size of 9.3 μm , pressed at 8.5 g/cc density into 1.96 g cylindrical pellets with resulting dimensions of 5.2 mm diameter and 10.7 mm height and sintered at 1850°C. The tantalum powders for both low and high working voltage capacitors were obtained from H.C. Starck, and the amount of major contamination in the powders were less than or equal to 10 ppm, except for the amount of oxygen, which

exceeded 1000 ppm primarily due to the oxygen in the native oxide of tantalum. The sintered tantalum anodes were then anodized in 0.1 wt. % phosphoric acid. During the anodization process, the dc current density was approximately 1 mA/cm² and the formation voltages were 2.75 times higher than the working voltages. At these conditions, the thicknesses of the anodic oxide films were 82.5 nm, 275 nm, 412.5 nm and 550 nm for 15 V, 50 V, 75 V and 100 V parts, respectively. These oxide thicknesses were calculated using the following equation:

$$d = a \cdot V_f \text{ Ratio} \cdot WV \quad 5.1$$

where a is the proportionality coefficient, which is 2 nm/V at 80°C, V_f Ratio is the formation voltage ratio, which is 2.75, and WV is the working voltage [39]. Pre-polymerized PEDOT doped with Poly Styrene Sulfonate (PSS) was then applied by dipping the sintered and anodized tantalum pellets into a waterborne dispersion of nanoscale PEDOT particles, followed by drying in air at room temperature and subsequently at 150°C. The molecular weights of PEDOT and PSS were about 1000-2500 g/mol and 400,000 g/mol, respectively. The particle size in the dispersion ranged from 10 μm to 40 nm. After application of external carbon and silver layers, the capacitors were assembled into nickel-plated brass cans with a glass insulator for positive external termination. Before sealing the hermetic cans, the capacitors were exposed to 50% relative humidity at room temperature for 24 hours (Humid parts). After the measurements of the humid parts were completed, the capacitors were dried in air at 125°C for 24 hours (Dry parts). In both Humid and Dry cases, capacitance values stabilized prior to the 24 hours

treatments and did not change during longer treatments. In Figure 5.1 a picture of the fabricated PHS capacitors that were used in this thesis work are shown; five samples for each dielectric thickness with a total of 20 samples.

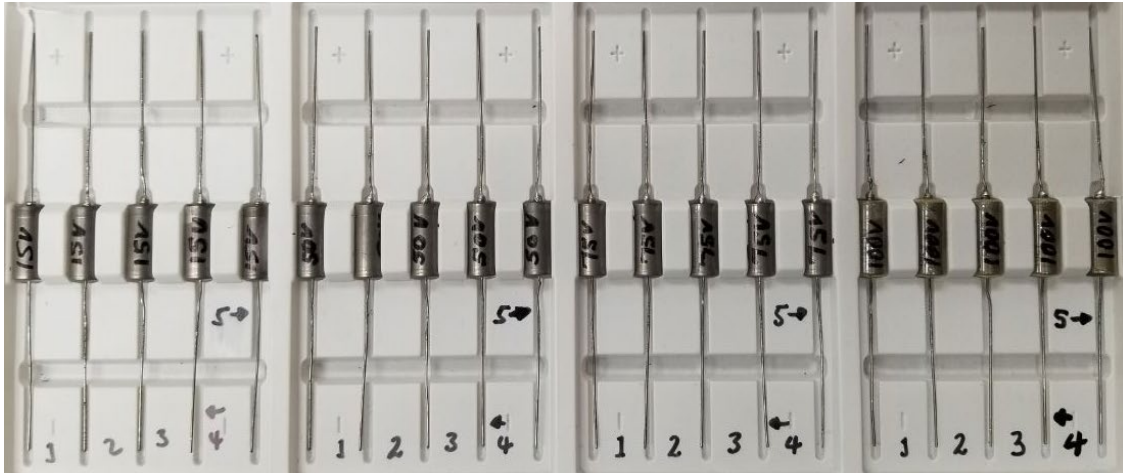


Figure 5.1. A picture of PHS Tantalum capacitors that are used in this thesis work.

5.2 Electrical Measurements

Capacitance measurements on humid PHS capacitors were performed using an Agilent E4980A Precision LCR Meter. The measurements were performed at various frequencies, temperatures, and dc bias voltages, on devices with the four different dielectric thicknesses as stated above. Essentially, three types of measurements were performed: capacitance versus frequency $C(f)$, capacitance versus temperature $C(T)$, and capacitance versus dc bias $C(V)$.

Capacitance versus frequency $C(f)$ measurements were performed at room temperature and zero dc bias voltage. The capacitance was recorded at the following frequencies: 20 Hz, 60 Hz, 120 Hz, 400 Hz, 1 KHz, 4 KHz, 10 KHz, and 40 KHz.

Capacitance versus dc bias $C(V)$ measurements were performed at room temperature and a frequency of 120 Hz. The capacitance was recorded for a wide range of dc bias voltages, from 0 V to the working voltage of the capacitor.

Capacitance versus temperature $C(T)$ measurements were performed at the frequencies listed above for various dc bias voltages ranging from 0 V to 10 V. These measurements were performed at several temperatures with the specific order of, Room Temperature, 0°C, -55°C, Room Temperature, 85°C, 105°C, Room Temperature, 125°C, and Room Temperature. The periodic capacitance measurements at room temperature were performed at zero dc bias and a frequency of 120 Hz for the primary purpose of verifying that the capacitor was not damaged from the temperature stress. An air bath oven was used for the high temperature measurements to heat the capacitors above room temperature, and a Dewar flask containing a mixture of dry ice and ethanol was used for the low temperature measurements. The temperature was monitored by attaching a thermocouple onto the capacitors, and a 15-minute wait time at the desired temperature was employed prior to performing the capacitance measurement in order to ensure that the temperature was stabilized inside the capacitor. To study the effects of moisture, the capacitors were dried as discussed above in the fabrication section, and all measurements were repeated on the dried capacitors.

CHAPTER 6

CAPACITANCE DEPENDENCE ON DIFFERENT ENVIRONMENTAL CONDITIONS

6.1 Introduction

The main goal of this research work was to investigate the capacitance stability of PHS Tantalum capacitors under different environmental conditions. The effects of temperature, frequency, and dc bias voltage in humid and dry PHS Tantalum capacitors with different dielectric thicknesses were investigated. The hermetic seal of the capacitors allowed us to maintain a stable humidity level in the capacitors during the electrical measurements.

The investigation is presented in three sections. In the first section, the effects of temperature on the capacitance of humid and dry PHS Tantalum capacitors with different dielectric thicknesses (82.5 nm, 275 nm, 412.5 nm, and 550 nm) are presented. We studied the capacitance loss and gain of both humid and dry PHS parts at different temperatures, from -55°C to 125°C , with respect to the capacitance at room temperature for all the dielectric thicknesses. We compared capacitance differences between humid and dry parts at different temperatures for all the dielectric thicknesses. The results are then explained using models that are consistent with the known theories. In the second section, the effects of frequency on the capacitance of humid and dry PHS Tantalum capacitors with different dielectric thicknesses are presented. We studied the capacitance loss as the frequency increased from 20 Hz to 40 KHz in both humid and dry PHS parts for all the dielectric thicknesses. The results are then explained with models that are consistent with the known

theories. In the third section, the effects of dc bias voltage in dry and humid PHS Tantalum capacitor with different dielectric thicknesses are presented. We studied capacitance dependence on dc bias voltage in both humid and dry PHS parts for all the dielectric thicknesses by varying frequency and temperature, separately. The results are then explained at the end.

6.2 Capacitance Dependence on Temperature

The first environmental condition that was investigated, which affects the capacitance of Polymer Tantalum capacitors, was temperature. In Figure 6.1 capacitance as a function of temperature ($C(T)$) in humid and dry PHS capacitors with different dielectric thicknesses, T_{ox} , measured at 120 Hz and zero bias voltage, is shown. The results show that, for all dielectric thicknesses of both humid and dry PHS capacitors, capacitance is directly related to temperature, meaning capacitance increases with temperature. Also, for all dielectric thicknesses, the capacitance of humid capacitors is higher than the capacitance of dry capacitors; however, the difference in their capacitance decreases both at low and high temperatures with respect to room temperature. The decrease in capacitance at low temperatures in comparison to the room temperature result (capacitance loss) is larger in humid capacitors than in dry capacitors, whereas the increase in capacitance at high temperatures in comparison to the room temperature result (capacitance gain) is higher in dry capacitors than in humid capacitors.

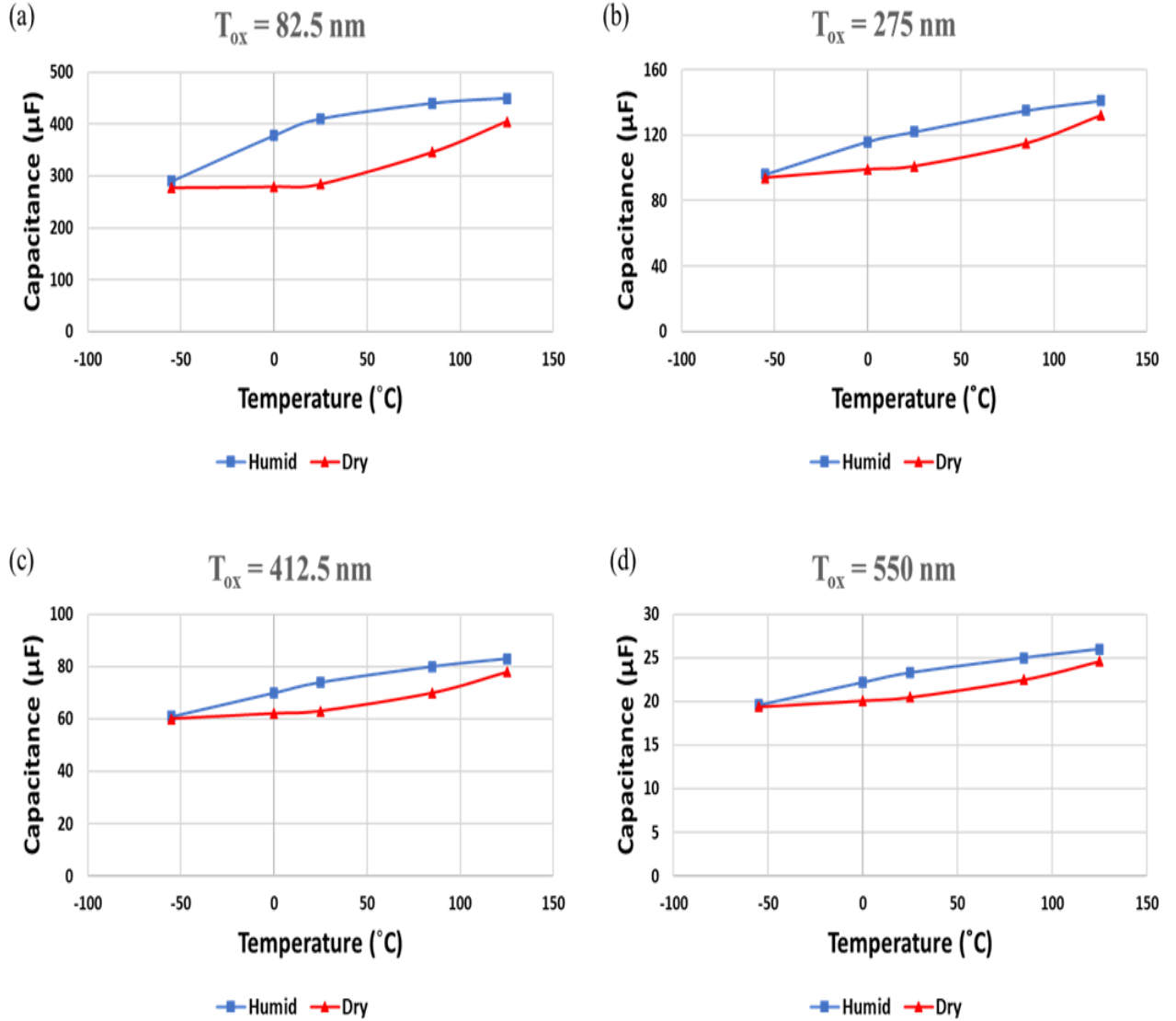


Figure 6.1. Capacitance dependence on temperature in humid and dry PHS capacitors measured at 120 Hz and 0 bias voltage for different dielectric thicknesses: (a) 82.5 nm, (b) 275 nm, (c) 412.5 nm, and (c) 550 nm.

The relative change in capacitance with temperature with respect to capacitance at room temperature, $C(RT)$, in humid and dry PHS capacitors for different dielectric thicknesses, is shown in Figure 6.2. The change in capacitance is calculated as:

$$\Delta C(\%) = \left[\frac{C(T) - C(RT)}{C(RT)} \right] \cdot 100 \quad 6.1$$

As shown in the figure, at low temperatures the capacitance loss in humid capacitors is higher than in dry capacitors. Furthermore, for the humid capacitors this capacitance loss is higher for thinner dielectrics, whereas for the dry capacitors this capacitance loss is approximately the same for all dielectric thicknesses. On the other hand, at high temperatures the capacitance gain in dry capacitors is higher than in humid capacitors. For the dry capacitors, this capacitance gain is larger for thinner dielectrics, whereas for the humid capacitors this capacitance gain is approximately the same for all dielectrics.

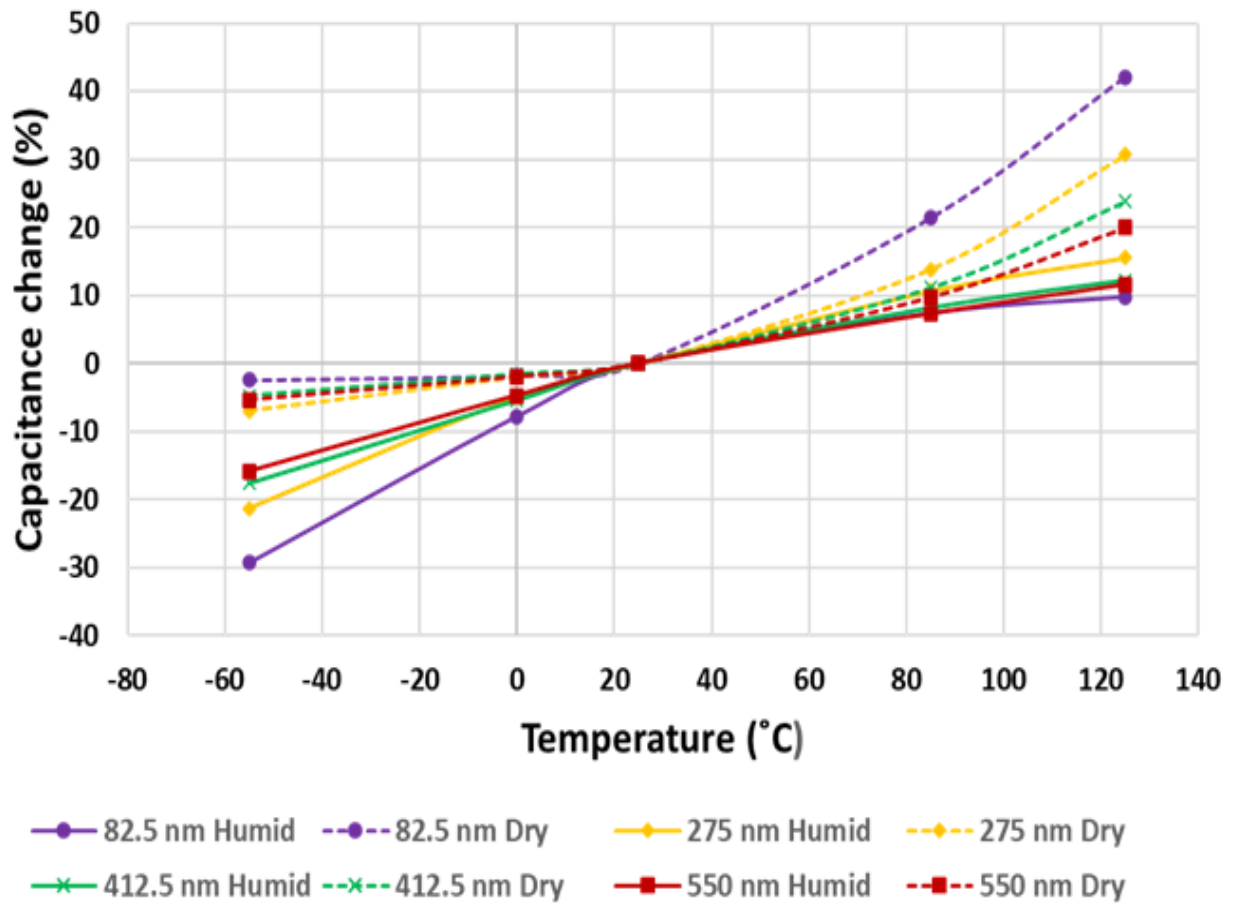


Figure 6.2. Relative change in capacitance with temperature with respect to capacitance at room temperature in humid and dry PHS capacitors, for various dielectric thicknesses.

In order to look more closely at the endpoints of very low temperature (-55°C) and very high temperature (125°C), the capacitance change (loss or gain) with respect to room temperature as a function of dielectric thickness for both humid and dry PHS capacitors was plotted and is shown in Figure 6.3. In Figure 6.3(a) the relative capacitance loss at $T = -55^{\circ}\text{C}$ with respect to room temperature is shown, where the capacitance loss is calculated as:

$$C_{loss}(\%) = \left[\frac{C(RT) - C(-55^\circ\text{C})}{C(RT)} \right] \cdot 100 \quad 6.2$$

In Figure 6.3(b) the relative capacitance gain at $T = 125^\circ\text{C}$ with respect to room temperature is shown, where the capacitance gain is calculated as:

$$C_{gain}(\%) = \left[\frac{C(125^\circ\text{C}) - C(RT)}{C(RT)} \right] \cdot 100 \quad 6.3$$

As can be seen in Figure 6.3, capacitance loss at -55°C in dry capacitors and capacitance gain at 125°C in humid capacitors are approximately identical for all dielectric thicknesses measured. These losses and gains in capacitance are similar to the temperature variation of the dielectric constant of the anodic Ta_2O_5 film [40]. However, capacitance losses at -55°C in humid capacitors are much larger than in dry capacitors, whereas capacitance gains at 125°C in dry capacitors are much larger than in humid capacitors, and in both cases the observed change is more significant for devices with thinner dielectrics. These results show the complicated effects of temperature on different dielectric thicknesses for humid and dry capacitors.

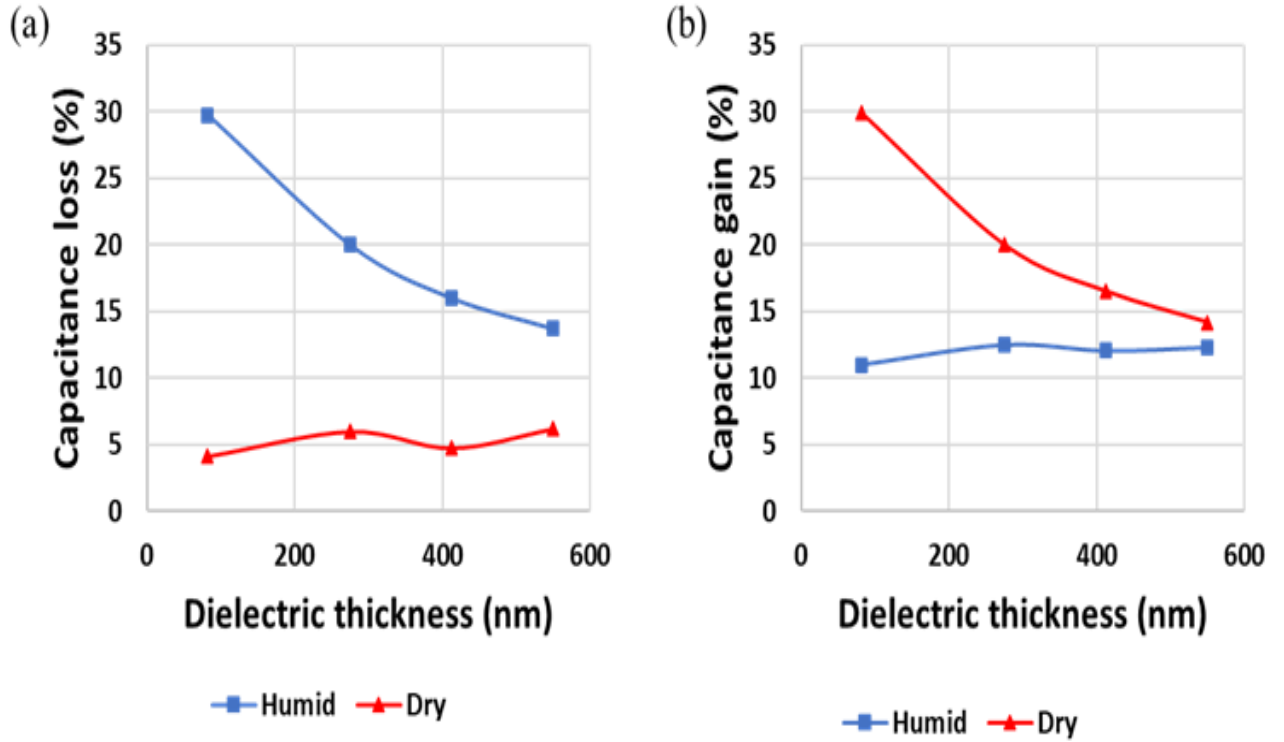


Figure 6.3. Capacitance loss at -55°C (a) and capacitance gain at 125°C (b) with respect to capacitance at room temperature versus dielectric thickness in humid and dry PHS capacitors.

To study the capacitance change between humid and dry conditions, the relative capacitance change between humid and dry conditions as a function of temperature was analyzed and is presented in Figure 6.4. The relative capacitance change was calculated as:

$$\Delta C(\%) = \left[\frac{C(\text{humid}) - C(\text{dry})}{C(\text{humid})} \right] \cdot 100 \quad 6.4$$

As shown in Equation 6.4, the capacitance change was calculated with respect to humid parts because humid parts have higher capacitance than dry parts, yielding a positive capacitance change. The difference in capacitance between humid and dry conditions is a maximum at room temperature and decreases for lower and higher temperatures, as shown in Figure 6.4. Furthermore, this capacitance difference is more pronounced for capacitors with the thinnest dielectrics. It appears that devices with thick dielectrics are less affected by the humidity inside the capacitor.

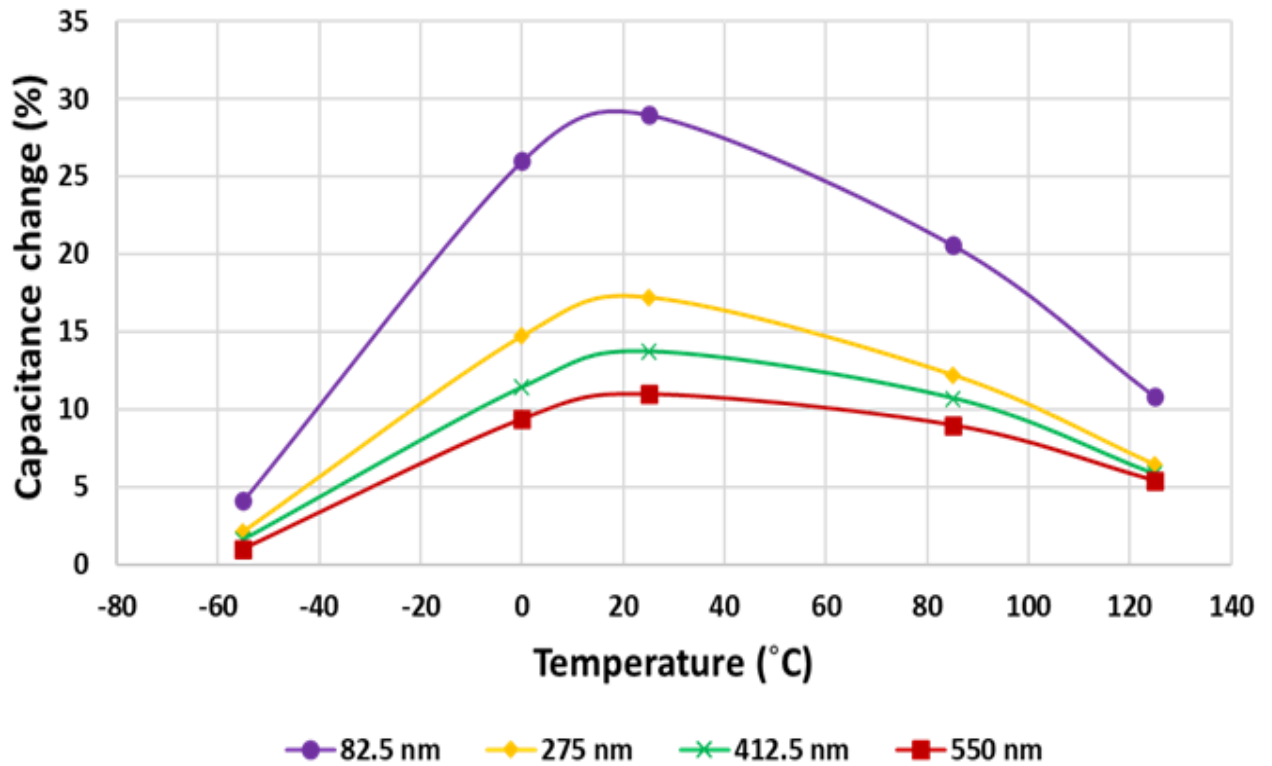


Figure 6.4. Relative capacitance change between humid and dry PHS capacitors as a function of temperature for different dielectric thicknesses.

The effects of humidity on the capacitance of Polymer Tantalum capacitors as well as the dependence on temperature can be explained by a model based on the integrity of the dielectric oxide/polymer interface [41]. When prepolymerized PEDOT is deposited onto the dielectric surface, because of the porous nature of the tantalum anode, not all of the surface of the dielectric will have a direct contact with the PEDOT. Some parts of the dielectric surface will not have a direct contact with the PEDOT surface, creating a free area between the two surfaces which does not contribute to the capacitance of the capacitor. This free area that is between the dielectric and PEDOT surfaces is illustrated in Figure 6.5(a). As shown in Figure 6.5(a), some areas of the dielectric surface do not have direct contact with the PEDOT layer. This usually occurs in dry parts, because in humid parts the free area is filled with water molecules that are absorbed during humidification. Therefore, under dry conditions, only the dielectric surface area that has a direct contact with the PEDOT surface contributes to the capacitance. Under humid conditions, when the capacitor is humidified, the free area of the dielectric decreases due to a thin layer of the absorbed water molecules, which increases the total conductive surface area and thus, the capacitance. In Figure 6.5(b) this increase in total conductive surface area for humid capacitors is illustrated. As shown in Figure 6.5(b) the PEDOT is now in complete contact with the dielectric.

In Figure 6.2, at low temperatures the capacitance loss in humid parts is larger than in dry parts as compared to capacitance at room temperature. This is because the surface conductivity of the dielectric in the free area of the humid parts decreases due to the low mobility of the ionic charge carriers [42]. Furthermore, in humid parts the adhesion that is

created in the free area of the dielectric oxide/PEDOT interface upon humidification is weak. Thus, the PEDOT layer can easily shrink at low temperatures, which decreases the conductive surface area of the dielectric in the humid parts. This shrinkage of the PEDOT layer can also occur in the dry parts to some extent; however, for the dry parts the capacitance loss at low temperatures is low and primarily caused by temperature variation of the dielectric constant of the anodic Ta₂O₅ film.

Also in Figure 6.2, at high temperatures the capacitance gain is higher in dry parts than in humid parts as compared to capacitance at room temperature. This is mainly because of the expansion of the PEDOT layer in dry parts upon heating, resulting in an increase in the conductive surface area of the dielectric and thus, the capacitance. The PEDOT layer in humid parts can also expand upon heating; however, the humid parts have already absorbed water molecules during humidification, leaving less room for additional expansion upon heating [41]. Thus, the capacitance gain in the humid parts at high temperatures is low and primarily caused by temperature variation of the dielectric constant of the anodic Ta₂O₅ film.

Therefore, the coverage of the dielectric oxide layer with PEDOT particles is very crucial to the effects of temperature on the capacitance of Polymer Tantalum Capacitors. The capacitance of humid PHS Tantalum parts is higher than that of dry parts for all dielectric thicknesses and for all temperatures observed. This is because humid parts absorb water molecules at the dielectric oxide/polymer interface, which increases the active conductive surface area of the dielectric and thus, the capacitance. At low temperatures,

the capacitance loss in humid parts is larger than in dry parts with respect to capacitance at room temperature for all the dielectric thicknesses. This high capacitance loss in humid parts at low temperatures is related to the low mobility of ionic charge carriers, which decreases the conductivity of the dielectric in the free area. At high temperatures, the capacitance gain is higher in dry parts than in humid parts with respect to capacitance at room temperature for all the dielectric thicknesses. This high capacitance gain in dry parts at high temperature is related to the expansion of the PEDOT layer upon heating, resulting in an increase in the active conductive surface area of the dielectric and thus, the capacitance.

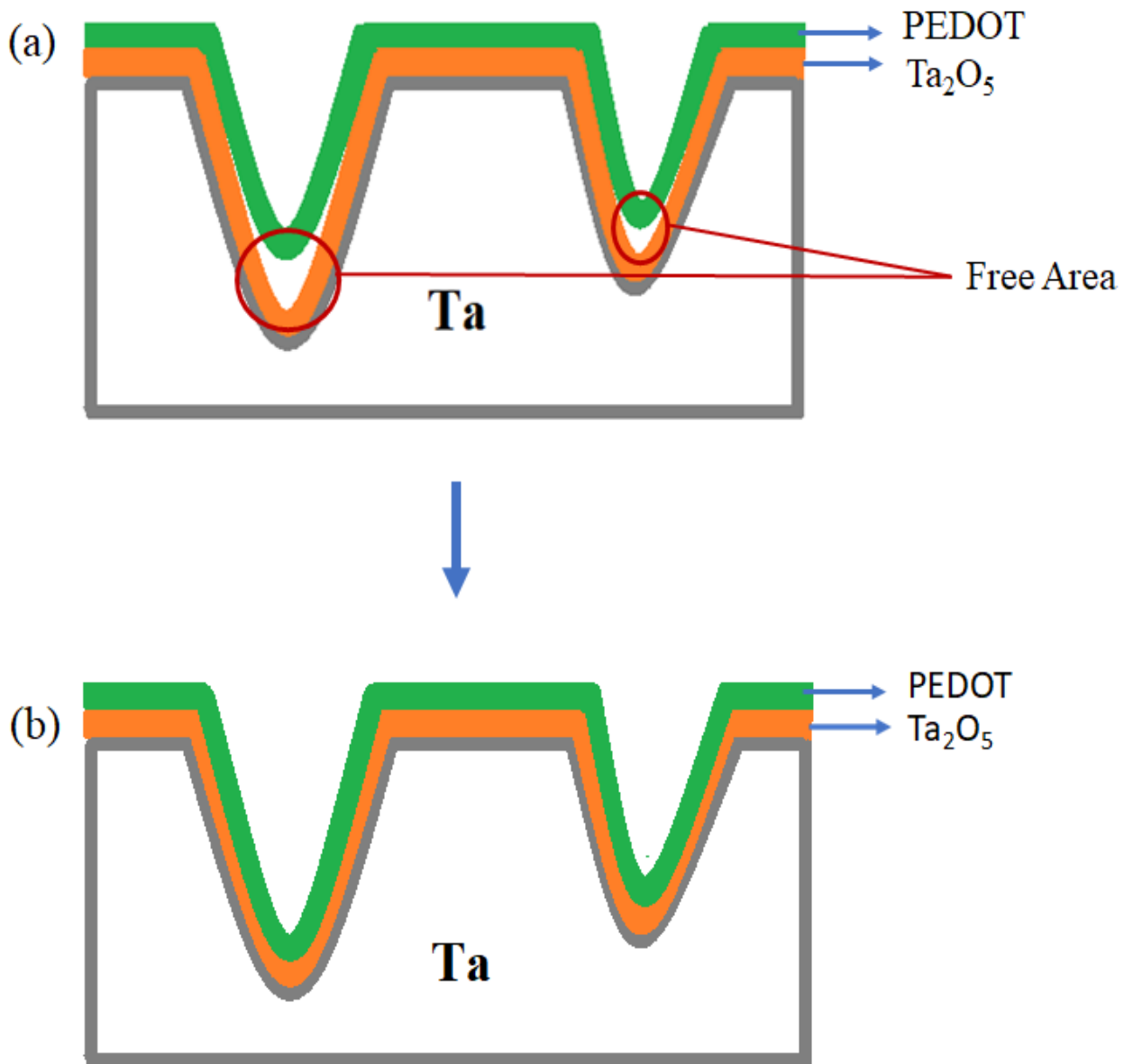


Figure 6.5. Free area between dielectric and PEDOT surfaces for dry capacitors (a) and closure of the free area under humid condition of the capacitor (b).

6.3 Capacitance Dependence on Frequency

Secondly, we studied the effects of frequency on the capacitance of Polymer Tantalum capacitors with different dielectric thicknesses under humid and dry conditions. Capacitance as a function of frequency for both humid and dry PHS capacitors measured at room temperature and zero bias voltage is shown in Figure 6.6. According to Figure 6.6, at lower frequencies capacitance in humid PHS capacitors reduces gradually with frequency while capacitance in dry PHS capacitors remains relatively unchanged, until the capacitance of both humid and dry parts begins to roll-off. To determine whether temperature has any impact on the frequency dependence of capacitance, the room temperature measurements shown in Figure 6.6 are repeated at different temperatures in the following sequence; -55°C , 0°C , 85°C , 105°C , and 125°C , and the results are presented in Figure 6.7. As shown in Figure 6.7, the results at different temperatures are relatively similar to the results at room temperature (Figure 6.6), showing the same frequency effects on the capacitance of both humid and dry capacitors. This means temperature does not have a significant role in capacitance dependence on frequency. Therefore, from here on the discussion of capacitance dependence on frequency is based on the room temperature measurement result that is shown in Figure 6.6.

From Figure 6.6, we see that at lower frequencies (below 1000 Hz) the capacitance of the humid parts decreases gradually with frequency, while the capacitance of the dry parts remains relatively unchanged. Similar to the capacitance loss at low temperatures in humid parts, capacitance loss with frequency in humid parts can be related to the low mobility of the ionic charge carriers which cannot follow the AC signal at higher

frequencies [42]. Eventually, the capacitance in both humid and dry capacitors begins to fall sharply at the “knee frequency”, and the capacitance of the humid parts approaches that of the dry parts. The “knee frequency” is a frequency where the capacitance begins to decline with a large slope.

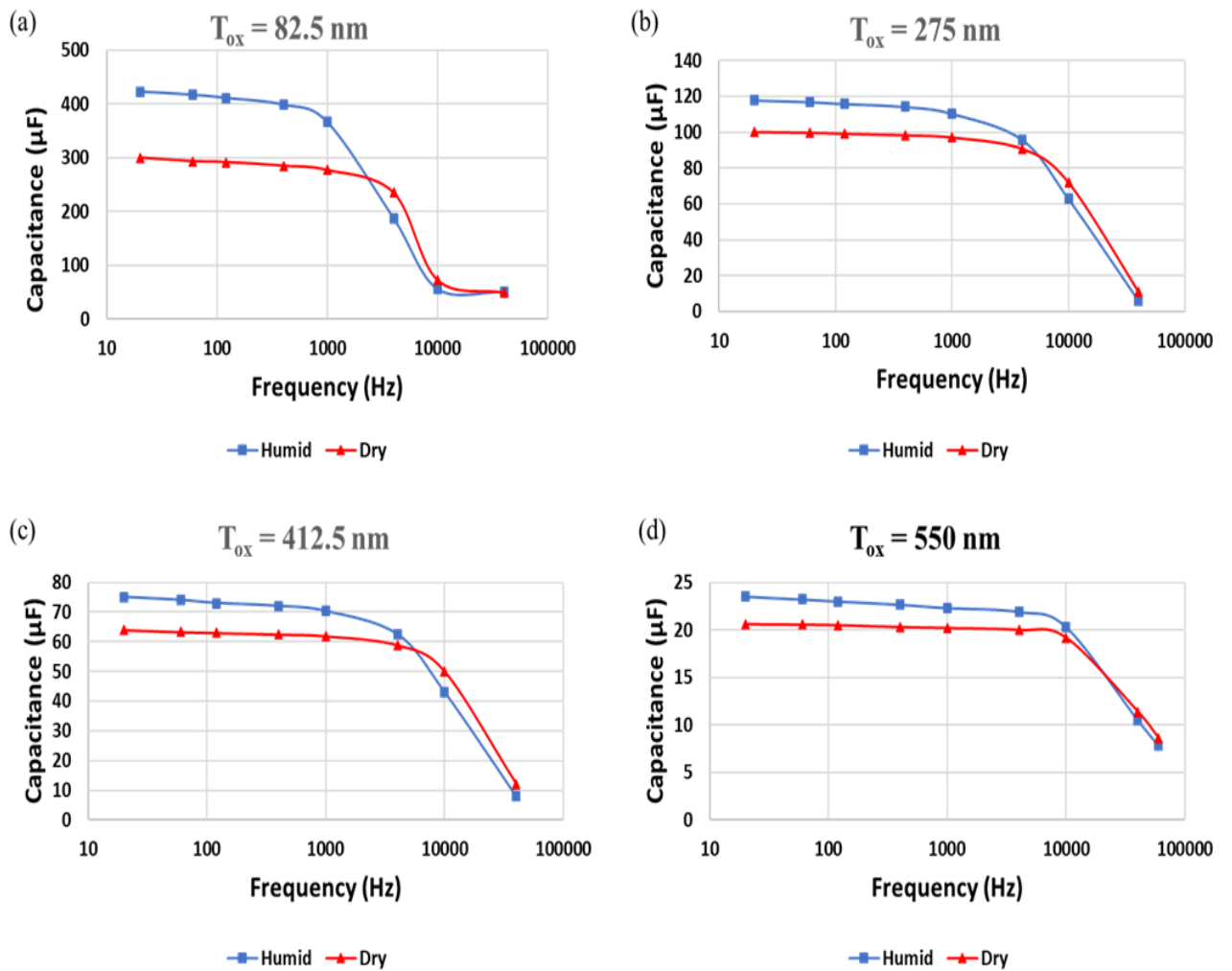


Figure 6.6. Capacitance dependence on frequency in humid and dry PHS capacitors measured at room temperature and 0 bias voltage for different dielectric thicknesses: (a) 82.5 nm, (b) 275 nm, (c) 412.5 nm, and (d) 550 nm

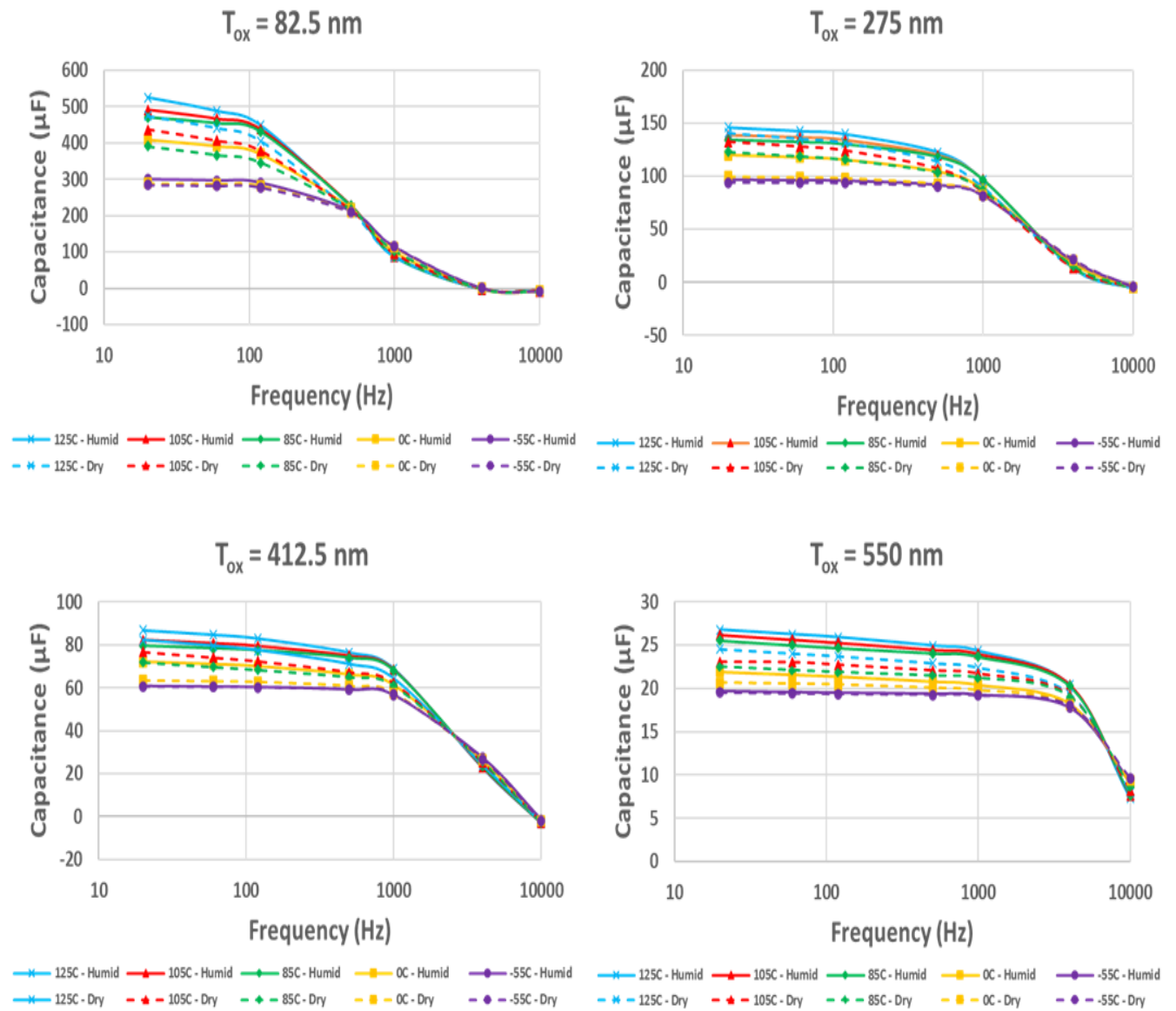


Figure 6.7. Capacitance dependence on frequency in humid and dry PHS capacitors measured at different temperatures for different dielectric thicknesses: (a) 82.5 nm, (b) 275 nm, (c) 412.5 nm, and (d) 550 nm

The “knee frequency” in tantalum capacitors with porous tantalum anodes has been explained by the RC-Ladder effect (distributed capacitance model), which is discussed in Chapter 3.4. This model presents the capacitor as a sum of the capacitances of multiple layers starting with the external layer of the anode, followed by the dipper layer, and finally the core of the anode. At the “knee frequency”, the period of the AC signal, where its equation is given in Equation 3.4 and rewritten below for convenience,

$$T_p = \frac{1}{f}$$

becomes smaller than the time constant of the core capacitive element, which is expressed as:

$$\tau = R \cdot C \tag{6.5}$$

where R is the equivalent resistant of the core capacitor, and C is the capacitance of the core capacitor. When the period of the AC signal (T_p) is less than the time constant of the capacitive element (τ), the core capacitive element cannot respond within the time period and thus no longer contributes to the total capacitance. Therefore, at frequencies above the “Knee” the capacitance begins decreasing sharply with applied frequency. As the frequency continues to increase further above the “knee frequency”, T_p also continues to decrease, and more capacitive elements that are closer to the core become unable to respond within

the time period and they can no longer contribute to the total capacitance which is already decreasing.

However, the “knee frequency” of Polymer Tantalum capacitors is higher than Solid Electrolytic (Ta-MnO₂) capacitors [19], which implies that Polymer Tantalum capacitors have a higher capacitance stability with frequency. This can be explained by the higher conductivity of the PEDOT cathode as compared to the conductivity of MnO₂ cathode. The conductivity of PEDOT cathode is also higher than that of the liquid electrolyte cathode of Wet Electrolytic capacitors. The difference in conductivity between these cathodes becomes larger at lower temperatures where there is a small change in the conductivity of PEDOT, which is a p-type nearly degenerate semiconductor [43], some reduction in the conductivity of MnO₂, an n-type semiconductor with narrow band gap [44], and a high reduction in the conductivity of the liquid electrolyte approaching the gel state with low ionic mobility at low temperature (-55°C) [45].

In addition to the RC-ladder effect, which can explain the “knee frequency” transition of Polymer Tantalum capacitors, there are other minute secondary transitions that are observed before the “knee frequency” is reached. These transitions can be observed in Figure 6.6 by minor changes in the capacitance versus frequency dependence slope of each humid and dry curve in all of the dielectric thicknesses. These transitions might not have a significant effect on the general electrical behavior of the capacitors, but they will certainly contribute to the understanding of the operation of Polymer Tantalum capacitors. As shown in Figure 6.6, these transitions are more visible in humid parts, where the slope of the humid parts is a little higher than that of the dry parts at lower frequencies. These

secondary transitions are related to the mobility of the conductive polar segments of the polymer cathode. The polar segments are smaller branches (or sub-chains) that are attached to the main polymer chain.

Polar segments of polymers respond to an alternating electric field [46, 47]. The response ability of these polar segments is associated with a relaxation time, τ_{REL} , which is the time needed for the segments to return to equilibrium or reach a new equilibrium after a disturbance caused by the applied electric field. This relaxation time is affected by the polar segment size; for example, large polar segments have a longer relaxation time. The relaxation process is characterized by a driving force, P , and it can be expressed as:

$$P = P_0 \exp\left(-T_P/\tau_{REL}\right) \quad 6.6$$

where T_P is the signal period. The polar segments response to the electric field is strong at lower frequencies, where $T_P > \tau_{REL}$, in which case the polar segments of the polymers are following the applied electric field. However, at higher frequencies, where $T_P < \tau_{REL}$, practically no relaxation takes place; polar segments of a certain size are immobilized. The minor transitions occur when the magnitude of T_P approaches the magnitude of τ_{REL} . In comparison to dry capacitors, humid capacitors have relaxation times that are smaller because of the water related plasticization in humid capacitors, and therefore, the secondary transitions are more pronounced and occur at lower frequencies in humid capacitors.

The relative change in capacitance with frequency with respect to capacitance at 20 Hz (the lowest frequency used in this work), $C(20 \text{ Hz})$, in both humid and dry PHS

capacitors for different dielectric thicknesses was measured at room temperature and the results are shown in Figure 6.8. The capacitance change is calculated as:

$$\Delta C(\%) = \left[\frac{C(f) - C(20\text{Hz})}{C(20\text{Hz})} \right] \cdot 100 \quad 6.7$$

It can be seen in Figure 6.8 that the “knee frequency” is lower in thinner dielectric Polymer Tantalum capacitors and it increases with increasing dielectric thickness. Not only is the “knee frequency” lower for the thinner dielectric Polymer Tantalum capacitors, but so is the effective series resistance (ESR). The ESR of humid and dry PHS capacitors was measured at 100 kHz as a function of dielectric thickness and is shown in Figure 6.9. It is clear that the ESR increases with dielectric thickness for both humid and dry samples. Another important observation from this result is that there is practically no difference between the ESR of humid and dry PHS capacitors.

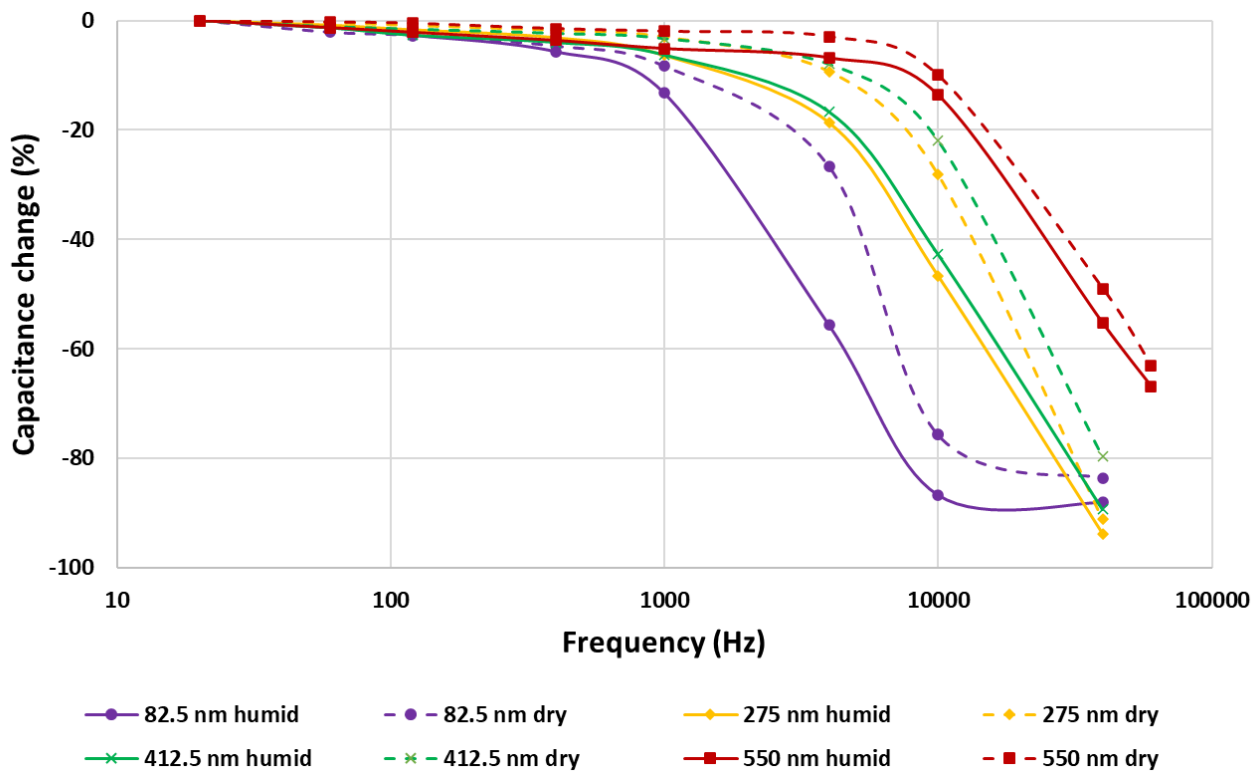


Figure 6.8. Relative change in capacitance with respect to capacitance at 20 Hz in humid and dry PHS capacitors measured at room temperature.

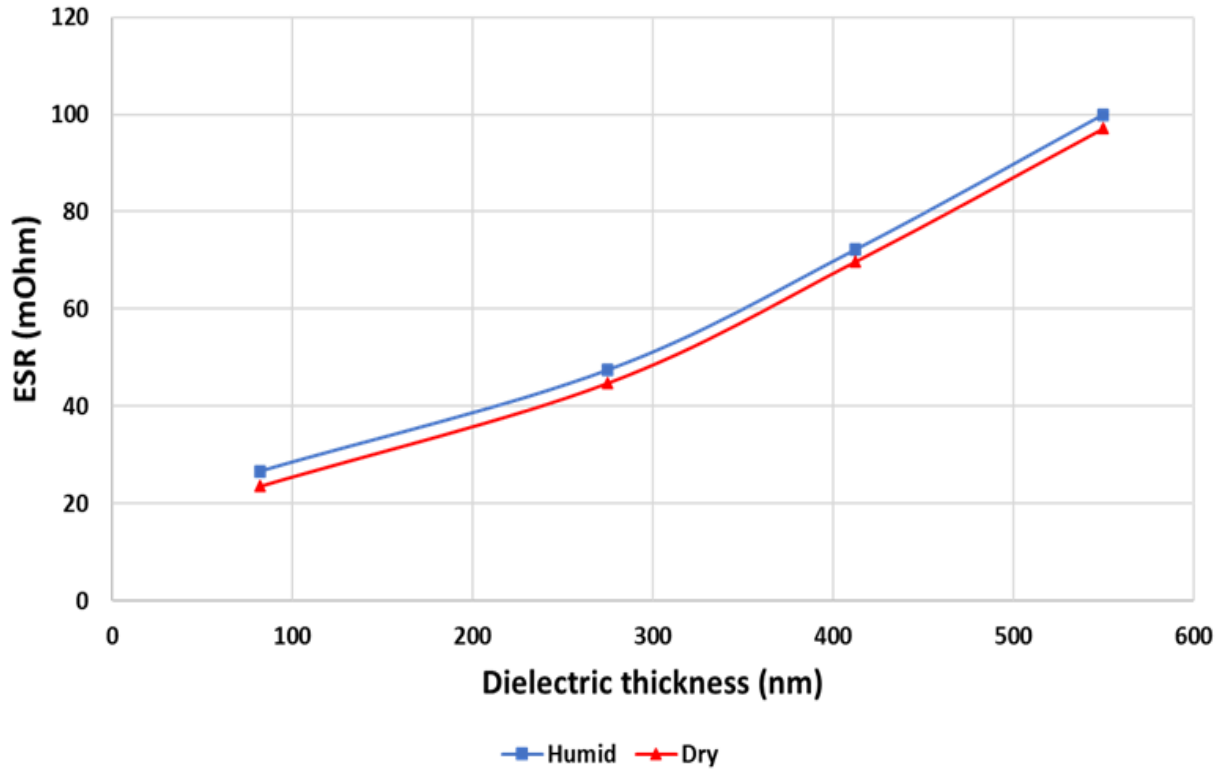


Figure 6.9. ESR, measured at 100 kHz, as a function of dielectric thickness in humid and dry PHS capacitors.

The results presented in Figure 6.8 and Figure 6.9 show a lower “knee frequency” and lower ESR in Polymer Tantalum capacitors with thinner dielectrics. Moreover, there is only a small difference between the “knee frequency” of humid and dry capacitors, except for the thinnest dielectric (82.5 nm) capacitors. These observations require explanations beyond the RC-ladder effect. For the same tantalum anode, thinner dielectric Polymer Tantalum capacitors have a higher capacitance and, thereby, a lower reactance, as well as a lower self-resonance frequency. The equations for reactance (X_C) and self-resonance frequency (f_{SR}) are given in Equation 6.8 and 6.9, respectively.

$$X_C = \frac{1}{2\pi fC} \quad 6.8$$

$$f_{SR} = \frac{1}{2\pi(LC)^{1/2}} \quad 6.9$$

where f is the frequency, C is the capacitance, and L is the parasitic inductance of the capacitor. The self-resonance frequency of a capacitor is the frequency at which the capacitance resonates with the parasitic inductance of the capacitor, resulting in the lowest impedance of the capacitor. As illustrated in Figure 6.10, capacitors behave as a pure capacitor until the self-resonance frequency is reached, where the impedance reaches its lowest point. The impedance ($|Z|$) is given by,

$$|Z| = \sqrt{ESR^2 + X_C^2} \quad 6.10$$

Above the self-resonant frequency, capacitors no longer behave as a capacitor, but behave as an inductor. Therefore, the lower reactance and self-resonance frequency could explain the lower “knee frequency” in the capacitors with thinner dielectrics as compared to those with thicker dielectrics. As shown in the frequency response curve for the capacitor with an 82.5 nm dielectric thickness in Figure 6.8, the capacitance levels off at about 10 kHz and thereafter begins to increase. This is especially noticeable for the humid capacitors. The behavior described here usually occurs at or near the self-resonance frequency. Thus, it seems reasonable that lower reactance and lower self-resonance frequency in the thinner

dielectrics can adequately explain the lower “knee frequency” and lower ESR in the thinner dielectric Polymer Tantalum capacitors.

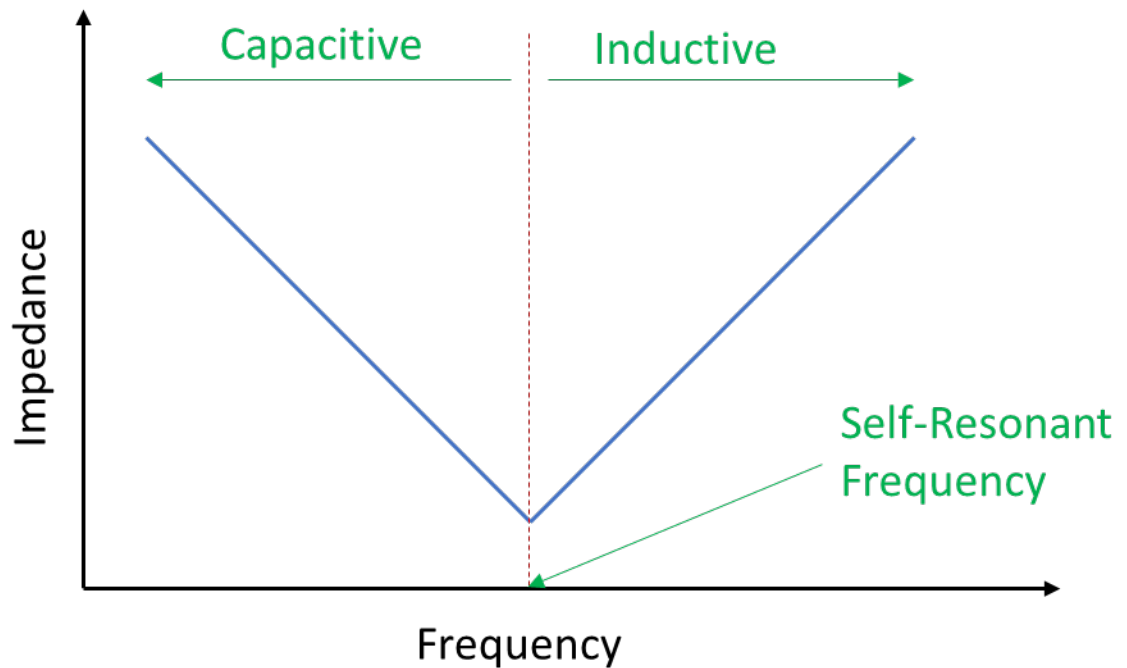


Figure 6.10. Illustration of impedance as a function of frequency, showing the self-resonant frequency

6.4 Capacitance Dependence on DC Bias Voltage

Finally, the capacitance stability of Polymer Tantalum capacitors with dc bias voltage was studied. In Figure 6.11 the capacitance dependence on dc bias voltage in both humid and dry capacitors measured at room temperature and 120 Hz is shown. To further study the capacitance stability with dc bias voltage, capacitance-voltage measurements were performed at different temperatures keeping the frequency constant (at 120 Hz) and

at different frequencies keeping the temperature constant (at room temperature). In Figure 6.12 the capacitance as a function of dc bias voltage in humid and dry PHS capacitors for different dielectric thicknesses measured at different temperatures and at 120 Hz is shown, and in Figure 6.13 the capacitance as a function of dc bias voltage in humid and dry PHS capacitors for different dielectric thicknesses measured at different frequencies and at room temperature is shown. All these results clearly indicate one thing. The capacitance is not dependent on dc bias voltage, irrespective of varying frequency and temperature, in both humid and dry PHS capacitors for all dielectric thicknesses.

Capacitance instability with bias voltage in dry Polymer Tantalum capacitors presented in Reference [48] can be related to an increase in DCL at higher voltages. If capacitors have high DC leakage currents, measurements of their capacitance will be inaccurate since LCR meters are measuring displacement current and cannot distinguish between it and the leakage current. Due to technologies, such as “flawless” (F-Tech) and simulated breakdown screening (SBDS), used in the fabrication of Polymer Tantalum capacitors for this work, DCL was low and stable in both humid and dry capacitors at all voltages less than or equal to the working voltages.

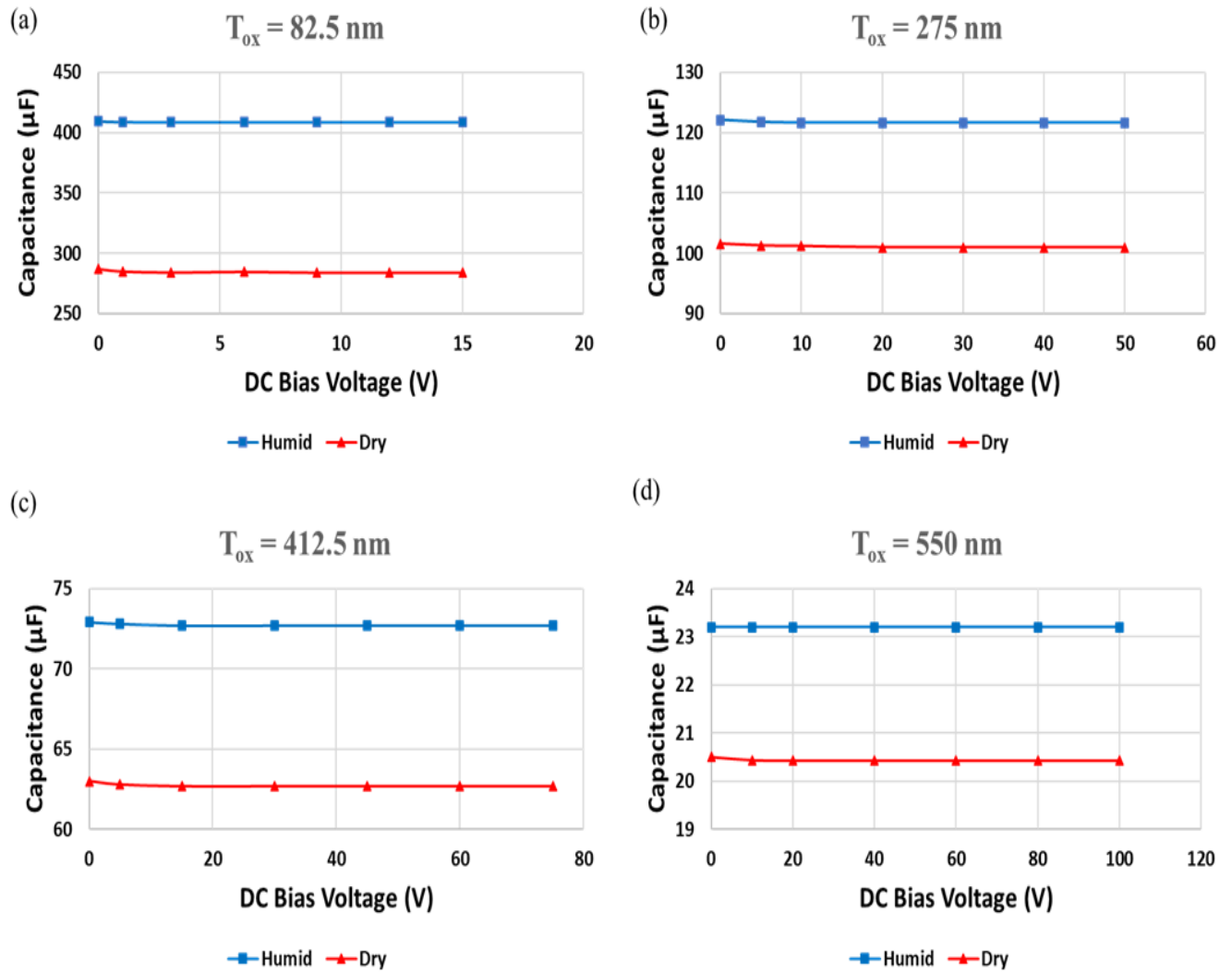


Figure 6.11. Capacitance dependence on dc bias voltage in humid and dry PHS capacitors measured at 120 Hz and room temperature for different dielectric thicknesses: (a) 82.5 nm, (b) 275 nm, (c) 412.5 nm, and (d) 550 nm

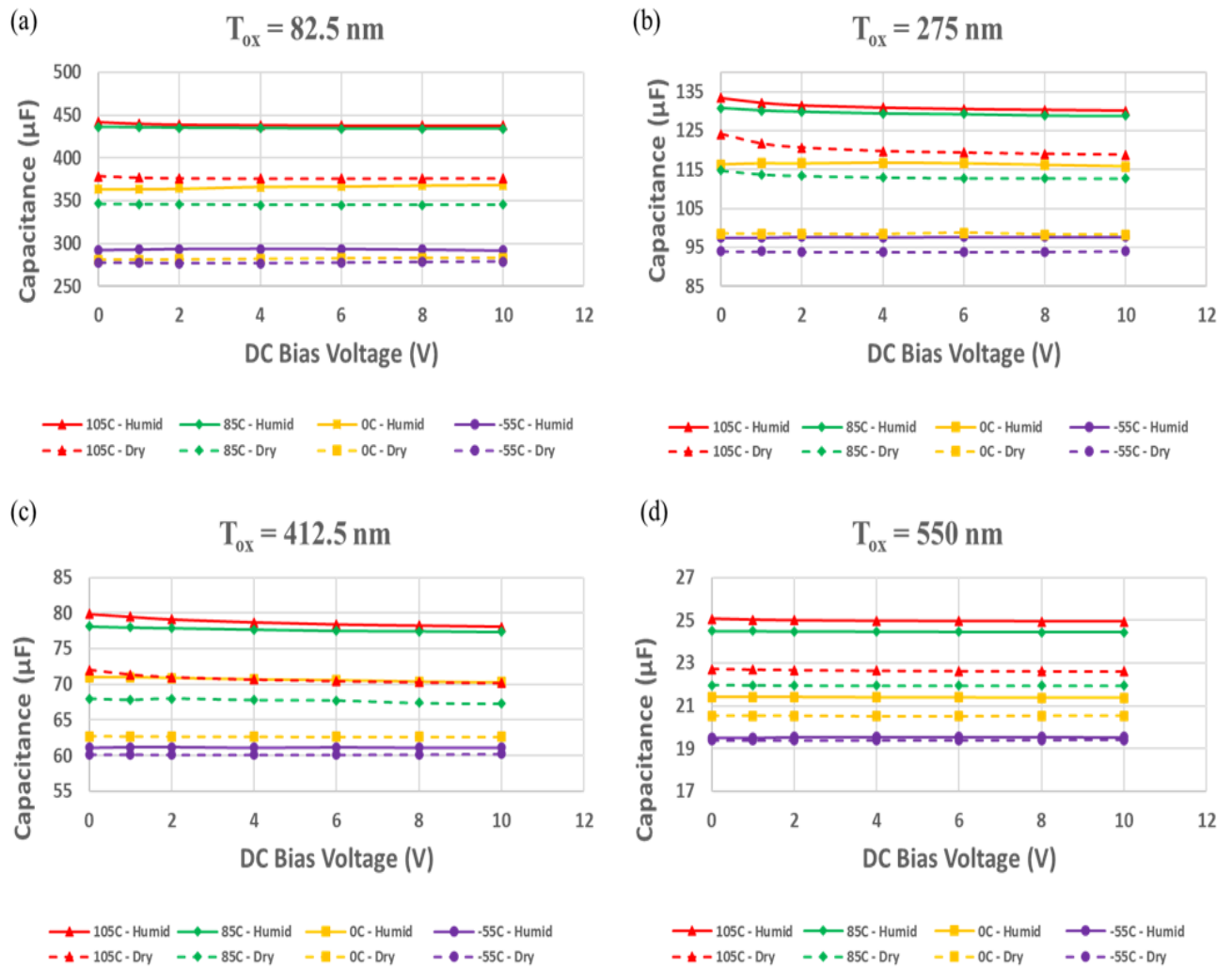


Figure 6.12. Capacitance dependence on dc bias voltage in humid and dry PHS capacitors measured at different temperatures and 120 Hz for different dielectric thicknesses: (a) 82.5 nm, (b) 275 nm, (c) 412.5 nm, and (d) 550 nm

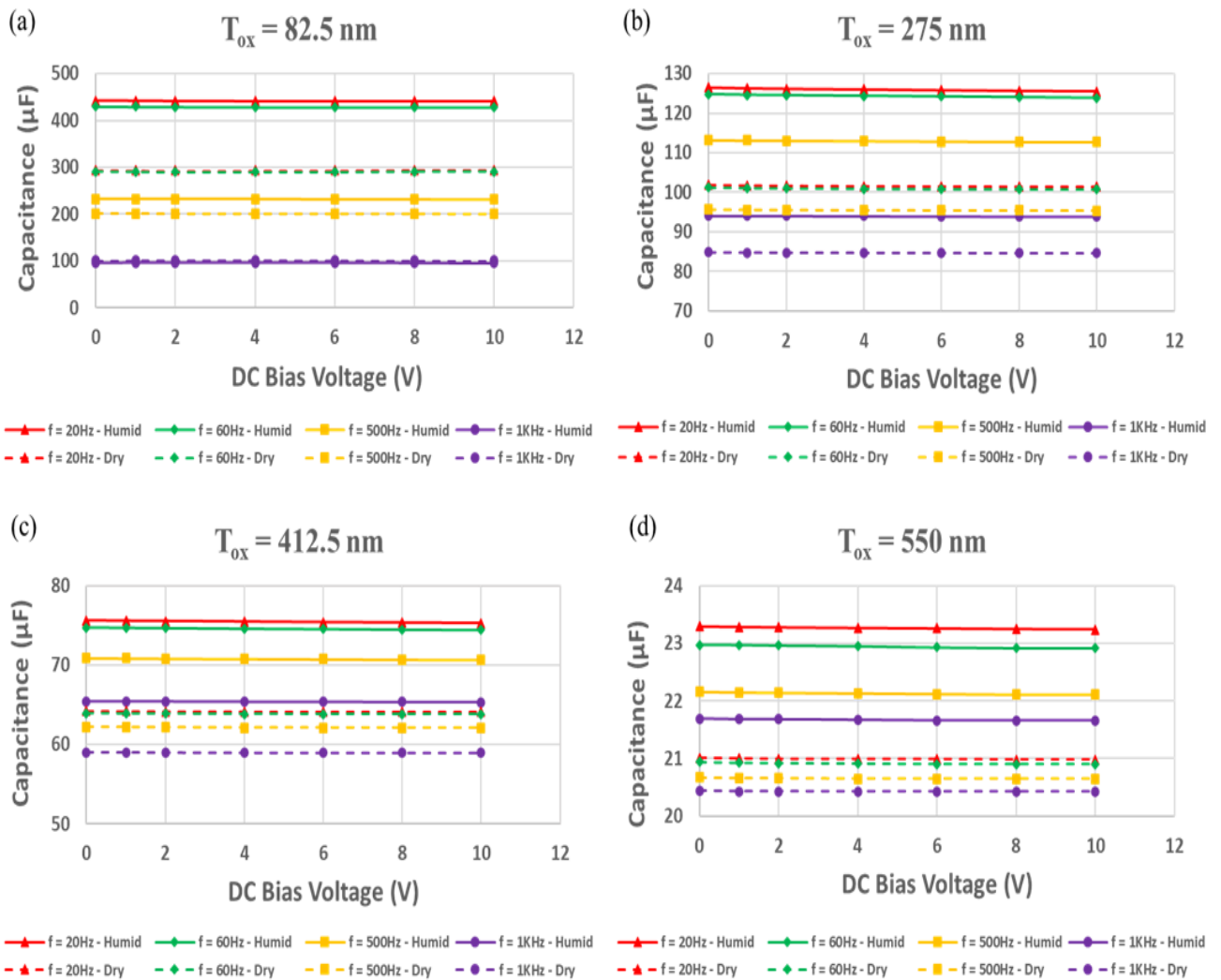


Figure 6.13. Capacitance dependence on dc bias voltage in humid and dry PHS capacitors measured at different frequencies and room temperature for different dielectric thicknesses: (a) 82.5 nm, (b) 275 nm, (c) 412.5 nm, and (d) 550 nm

6.5 Conclusion

The effects of temperature, frequency, and dc bias voltage on the capacitance stability of Polymer Tantalum capacitors with different dielectric thicknesses were investigated under both humid and dry conditions. The results from the electrical measurements and corresponding explanations were presented in this chapter. Some of the observations are summarized below.

The capacitance of humid capacitors is higher than that of dry capacitors for all dielectric thicknesses and for all temperatures observed. This is mainly because under humid conditions the conductivity of the dielectric surface increases in the free area where there is no direct contact between the dielectric and PEDOT. This increase in the surface conductivity of the dielectric, provided by the thin layer of absorbed water molecules during humidification, results in a higher total surface area and thus, a higher capacitance. At lower temperatures, the capacitance loss in humid parts is larger than in dry parts with respect to capacitance at room temperature for all dielectric thicknesses. This capacitance loss in humid parts is related to the lower mobility of the ion charge carriers in the humid parts, which decreases the conductivity of the dielectric in the free area. At high temperatures, the capacitance gain is higher in dry parts than in humid parts with respect to capacitance at room temperature for all dielectric thicknesses. This capacitance gain in dry parts is related to the expansion of the PEDOT layer upon heating, increasing the conductive surface area of the dielectric and thus, the capacitance.

At lower frequencies, the capacitance of the humid capacitors decreases slowly with frequency, whereas the capacitance of dry capacitors remains relatively unchanged.

This capacitance decrease with frequency in humid parts can be related to the low mobility of the ionic charge carriers which cannot follow the AC signal at higher frequencies. Eventually, the capacitance in both humid and dry capacitors falls sharply at the “knee frequency”. This capacitance loss at the “knee frequency” is related to the RC-Ladder effect. Finally, we saw that there is practically no capacitance dependence on dc bias voltage for both humid and dry Polymer Tantalum capacitors.

CHAPTER 7

SUMMARY AND CONCLUSION

In this thesis, capacitance stability of Polymer Tantalum capacitors was investigated under humid and dry environmental conditions with different dielectric thicknesses. Capacitance dependence on temperature ($C(T)$), capacitance dependence on frequency ($C(f)$), and capacitance dependence on dc bias voltage ($C(V)$) of both humid and dry Polymer Tantalum capacitors with different dielectric thicknesses were investigated.

The coverage of the dielectric oxide surface with PEDOT particles plays a critical role in the effect of environmental conditions on Polymer Tantalum capacitors. The porous nature of the tantalum anode prohibits a complete direct contact between the surface of the dielectric oxide and PEDOT layer, decreasing the active conductive surface area of the dielectric. Since capacitance is directly related to the conductive surface area of the dielectric oxide/PEDOT interface, a decrease in the conductive surface area results in a decrease in the capacitance. Under humid conditions, because of the absorbed water molecules, the conductivity of the dielectric surface increases in the free area where there is no direct contact between the dielectric and PEDOT. This increase in surface conductivity of the dielectric results in a higher total surface area and, thereby, a higher capacitance in humid parts in comparison to the capacitance in dry parts. At lower temperatures, the conductivity of the humidified dielectric surface decreases due to the lower mobility of the ionic charge carriers, which increases capacitance loss with temperature in humid parts in comparison to dry parts. At higher temperatures, the PEDOT layer in dry parts expands upon heating, increasing the active conductive surface area and,

thereby, increasing the capacitance gain with temperature in dry parts in comparison to humid parts. Therefore, the integrity of the dielectric oxide/PEDOT interface is very crucial in the capacitance variation with temperature in Polymer Tantalum capacitors.

Frequency is another parameter that was investigated, which affects the capacitance stability of Polymer Tantalum capacitors. At lower frequencies, the capacitance of the humid capacitors decreases gradually with frequency, while the capacitance of the dry parts remains relatively unchanged. This capacitance decrease with frequency in humid parts can be related to the low mobility of the ionic charge carriers which cannot follow the AC signal at higher frequencies. Eventually, the capacitance in both humid and dry capacitors begins to roll-off at the “knee frequency”. This steep drop in capacitance at the “knee frequency” is related to the RC-Ladder effect. The RC-Ladder effect models capacitors as a sum of the capacitances of multiple layers starting with the external layer of the anode to the core of the anode. As the frequency increases, the capacitive elements that are closer to the core stop responding to the applied frequency since the period of the AC signal is less than the time constant of the capacitive element, and thus, no longer contributes to the total capacitance. As the frequency continues to increase further above the “knee frequency”, the time period of the AC signal also continues to decrease, and more capacitive elements that are closer to the core become unable to respond within the time period and are no longer able to contribute to the total capacitance. This decrease in capacitance with frequency shows the effect of frequency on the capacitance of Polymer Tantalum capacitors.

The effect of frequency on the stability of capacitance is more pronounced in thinner dielectric Polymer Tantalum capacitors as compared to those with thicker dielectrics. This can be explained using the lower reactance and lower self-resonance frequency of thinner dielectrics, which leads to a lower “knee frequency” in Polymer Tantalum capacitors with thinner dielectrics.

To improve the environmental stability of Polymer Tantalum capacitors, working on the integrity of the dielectric oxide/PEDOT interface will be very important. This interface can be improved using three possible methods. The first method is usage of a coarser tantalum powder during the fabrication of the tantalum anode, which increases the pore size and improves the impregnation of the tantalum anode with prepolymerized PEDOT particles [41]. However, this method reduces the volumetric efficiency of the capacitor, and for this reason most lower voltage capacitors are made with fine powders. The second method to improve the integrity of the dielectric oxide/PEDOT interface is by depositing the PEDOT using in-situ polymerization instead of prepolymerized PEDOT [41]. In-situ polymerization provides better coverage of the dielectric surface with PEDOT molecules. The frequency response also improves due to the smaller size molecules in in-situ PEDOT in comparison to the molecule size in prepolymerized PEDOT. However, in-situ polymerization has its own disadvantages. It leaves residual by-products of the chemical reactions inside the polymer cathode which are impossible to completely wash out, and these by-products affect the breakdown voltage (BDV) and dc leakage current (DCL) of the capacitor [32]. The third method to improve the integrity of dielectric oxide/PEDOT interface is by adding a coupling agent called amine silane to the dielectric

surface prior to depositing prepolymerized PEDOT [41]. Applying amine silane improves the adhesion between the dielectric and the PEDOT, increasing the active conductive surface area of the dielectric and reducing the capacitance difference between humid and dry capacitors.

APPENDICES

Appendix A

Guide for Heating the Sample and Performing High Temperature Capacitance

Measurements

1. Attach a thermocouple on the sample (DUT C1) that is connected to a Digital Multimeter, to monitor the temperature of the sample during heating.
2. Connect long wires to both ends of the sample (external ends of the anode and the cathode), where the other ends of these wires are connected to the Keithley 8101-PIV Test Box at SMU 1 and SMU 4. The Test Box is then connected to the Agilent E4980A Precision LCR meter, which is used to measure the capacitance and the equivalent series resistance of the sample.
3. Insert the sample into an Erlenmeyer flask.
4. Insert the Erlenmeyer flask into an Air Bath Oven.
 - The Air Bath Oven controls the temperature by regularly heating and circulating the air inside the oven.
 - The Air Bath Oven that is used in this work can be heated up to 220°C with a resolution of 1°C.
5. The temperature inside the oven is controlled by the temperature controller of the oven; however, the temperature of the sample is monitored by the Digital Multimeter that is connected to the thermocouple that is attached to the sample
 - When the temperature on the Digital Multimeter reaches the desired value, record the temperature, and wait 15-minute at the desired temperature prior

to taking a capacitance measurement to ensure the temperature inside the sample is stabilized.

6. For high temperature capacitance measurements, first start at room temperature, and then at 85°C and 105°C, respectively, and back to room temperature to ensure the sample is not damaged from the high temperatures, and then at 125°C and back to room temperature again to check if the sample is not damaged from the high temperature.

Appendix B

Guide for Cooling the Sample and Performing Low Temperature Capacitance

Measurements

1. Attach a thermocouple on the sample (DUT C1) that is connected to a Digital Multimeter, to monitor the temperature of the sample during cooling.
2. Connect long wires to both ends of the sample (external ends of the anode and the cathode), where the other ends of these wires are connected to the Keithley 8101-PIV Test Box at SMU 1 and SMU 4. The Test Box is then connected to the Agilent E4980A Precision LCR meter, which is used to measure the capacitance and the equivalent series resistance.
3. Insert the sample into an Erlenmeyer flask.
4. Insert the Erlenmeyer flask into a Dewar, that contain a mixture of dry ice and ethanol, slowly while monitoring the temperature on the Digital Multimeter.
 - When the temperature on the Digital Multimeter reaches the desired value, record the temperature, and wait 15-minute at the desired temperature prior to taking the capacitance measurement, to ensure the temperature inside the sample is stabilized.
5. For low temperature capacitance measurements, first start at room temperature, and then at 0°C and -55°C, respectively, and back to room temperature to ensure the sample is not damaged from the low temperatures.

Appendix C

Guide for Performing Capacitance and Equivalent Series Resistance (ESR)

Measurements Using the Agilent E4980A Precision LCR Meter

1. Turn on the Agilent E4980A Precision LCR Meter by pushing the power button and wait for at least 30 minutes prior to taking measurements to allow the LCR meter to warm up.
2. Make sure the High current (H_{CUR}) and the High potential (H_{POT}) terminals are connected into one High output terminal using a T-connector, and the Low current (L_{CUR}) and the Low potential (L_{POT}) terminals into one Low output terminal.
3. Connect the High and the Low output terminals into the Keithley 8101-PIV Test Box using Triaxial cables at SMU 1 and SMU 4.
4. Connect the external wire connectors of the sample at SMU 1 and SMU 4.
5. Push “Meas Setup” button on the LCR meter and use the Up, Down, Left, and Right triangular arrow buttons to adjust the parameters as desired. Here are some of the parameters that are frequently used for measurements in this work.
 - a. FUNC: adjusts to series and parallel circuit mode of capacitance, inductance, and resistance measurements. In this work, parallel circuit mode ($C_P - R_P$) is used for capacitance measurements and Series circuit mode ($C_S - R_S$) is used for equivalent series resistance (ESR) measurements.
 - b. FREQ: adjusts frequency as desired.

- c. BIAS: adjusts the dc bias voltage as desired. However, in order to have a dc bias voltage, the “DC BIAS” button must be pushed in first.
 - d. LEVEL: adjusts the voltage level of the AC signal. 1 V is used in this work.
6. Once all the parameters are adjusted to the desired values, press “Display Format” to go back to the screen which will show the measurement results.
 7. Record the measurement results from the screen.

Appendix D

Procedure for Measuring Capacitance of Polymer Hermetic Seal (PHS) Capacitors

1. Measurements of capacitance as a function of frequency ($C(f)$)
 - $f = 20 \text{ Hz}, 60 \text{ Hz}, 120 \text{ Hz}, 500 \text{ Hz}, 1 \text{ kHz}, 4 \text{ kHz}, 10 \text{ kHz}, 40 \text{ kHz}$
 - $V = 0 \text{ V}$
 - $T = \text{RT}$ (Room Temperature)
2. Measurements of capacitance as a function of dc bias voltage ($C(V)$)
 - $V = 0 \text{ V}, 1 \text{ V}, 2 \text{ V}, 4 \text{ V}, 6 \text{ V}, 8 \text{ V}, 10 \text{ V} \dots, \text{WV}$ (working voltage).
 - $f = 120 \text{ Hz}$
 - $T = \text{RT}$
3. Repeat step 1 and 2 for $T = \text{RT}, 0^\circ\text{C}, -55^\circ\text{C}, \text{RT}, 85^\circ\text{C}, 105^\circ\text{C}, \text{RT}, 125^\circ\text{C}, \text{RT}$
 - Wait for 15-minute at each temperature prior to taking measurements.
 - This will help to make sure that the temperature is stabilized inside the capacitor.
 - **RT** and **125°C** measurements must be performed at 120 Hz and 0 V.
 - For measurements at **125°C**, the total time (waiting + measurement) should not exceed 1-hour range.
 - Staying for more than an hour at 125°C might damage the device.

4. Measurements of Capacitance as a function of frequency and dc bias voltage ($C(f, V)$)

- $V = 0 \text{ V}, 1 \text{ V}, 2 \text{ V}, 4 \text{ V}, 6 \text{ V}, 8 \text{ V}, 10 \text{ V}$
- $f = 20 \text{ Hz}, 60 \text{ Hz}, 120 \text{ Hz}, 500 \text{ Hz}, 1 \text{ kHz}$
- $T = RT$

5. KEMET dries the samples.

- Drying is performed at 125°C for 24 hours

6. Repeat steps 1 – 4 for dry samples.

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