Characterization of Tantalum Polymer Capacitors

NEPP Task 1.21.5, Phase 1, FY05

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Abstract

Solid-electrolyte tantalum capacitors were first developed and commercially produced in the 1950s. They represented a quantum leap forward in miniaturization and reliability over existing wound-foil wet electrolytic capacitors. While the solid tantalum capacitor has dramatically improved electrical performance versus wet-electrolyte capacitors, especially at low temperatures, today's electronic circuits require even better performance.

In response to this need, steady improvements in the equivalent series resistance (ESR) of tantalum capacitors have been made. Low ESR is the most important attribute of capacitors used to filter and de-couple power for high-speed digital electronics. While the first patented tantalum capacitor was claimed to have ESR of roughly 2.0 ohms, a similar capacitor today has ESR of about 0.1 ohms. Even so, today's digital electronics frequently require capacitors to have ESR in the low milliohms, a level that can be achieved with conventional tantalum capacitors only by connecting many in parallel.

A substantial fraction of the ESR of a tantalum capacitor comes from its solid electrolyte material, manganese dioxide (MnO_2). While MnO_2 is substantially more conductive than almost all wet electrolytes, especially at low temperatures, capacitor manufacturers search for higher conductivity materials to replace MnO_2. Today's solid electrolyte material of choice is the conductive polymer PEDT (polyethylene-dioxythiophene) which has up to 100 times MnO_2's conductivity and has generally acceptable compatibility with tantalum pentoxide, the tantalum capacitor's dielectric.

With the introduction of conductive polymer electrolyte, remarkable improvements in capacitor ESR are possible. But ESR isn't the only capacitor performance characteristic to benefit. For lower-voltage capacitors, improved dielectric strength and long-term reliability are also observed. Also, substantially more capacitance stability with frequency is observed. But there are also limitations to the technology including marginal material stability at elevated temperatures, muted self-healing capability, and reduced dielectric reliability at high rated voltages.

This document briefly describes the origin of MnO_2-based solid tantalum capacitors, their methods of processing and construction, and their defining electrical characteristics versus the wet electrolytic capacitors they replace. The case for improved electrolyte conductivity is briefly presented and conductive polymer is identified as the candidate material of choice to replace MnO_2 in the solid tantalum capacitor. The defining electrical characteristics of capacitors made with conductive-polymer solid electrolyte are described.

Typical processing options and material issues related to conductive polymer electrolyte are identified. Details of the step-by-step processing of typical tantalum polymer capacitors from tantalum powder to assembled and encapsulated devices are photographically presented. The electrical performance, dielectric robustness, reliability, and environmental stability of tantalum polymer capacitors are discussed in some detail. Competitive testing of these capacitors will occur during the FY06 task. Results of this competitive evaluation will be published in FY06 as the phase two deliverable of this project.

Introduction

The solid-electrolyte tantalum capacitor was invented by Bell Laboratories in the early 1950s as a miniaturized, low-voltage support component for circuits employing their newly invented transistor. Before this invention a few tantalum capacitors were manufactured from tantalum foil, but almost all electrolytic capacitors were made from etched aluminum foil. Wet-electrolyte aluminum electrolytic capacitors provided substantially more capacitance per unit volume than other capacitor technologies of the time, but they were dramatically bulky by today's standards. Some of the bulk resulted from the need to operate at the relatively high voltages of vacuum tube circuits (> 100Vdc).

Whether tantalum or aluminum, these first-generation metal-foil electrolytic capacitors all employed wet electrolytes to make the electrical connection from the circuit to the negative side of the capacitor's dielectric. The positive electrical connection was made directly to the metal foil upon which the metal-oxide dielectric was grown by electrochemical anodization. The foil was typically chemically etched prior to anodization to increase its surface area and thereby increase the capacitance of the finished capacitor.

One consequence of making the negative connection to the dielectric with a wet electrolyte is poor low-temperature performance. This is true because electrolyte conductivity falls at low temperatures as charge carriers become less mobile. Another problem is that the wet electrolyte can slowly escape from the capacitors, causing them to gradually go open-circuit. Though big improvements have been made over the last half-century, these two problems still cause trouble for wet-electrolyte, wound-foil electrolytic capacitors.

A New Kind of Capacitor

The scientists at Bell Labs realized that low-voltage transistorized circuits not only promised significant miniaturization, but also promised higher reliability than was possible with vacuum-tube circuits. They also saw the need for smaller, more reliable capacitors to complement the transistors. Their solution was a capacitor physically different from anything seen before.

This capacitor was made with tantalum instead of aluminum. But instead of chemically etching tantalum metal foil to increase its surface area prior to growing the insulating dielectric film on it, as is commonly done with aluminum electrolytic capacitors, the surface area of the tantalum metal was increased by a different method. The surface area was increased by compacting finely-divided tantalum powder into a porous slug and then carefully sintering the powder particles together at high temperature while maintaining much of the slug's porosity. After this sintering step, the dielectric film was electrochemically grown on the porous slug's internal and external surfaces. The result was a compact element with dielectric grown on a remarkably high surface area, much higher than could be achieved in the same volume by etching tantalum foil. This was the first substantial innovation of Bell Labs' capacitor, but not the only one.

In conventional wound-foil electrolytic capacitors, the exposed negative-polarity surface of the dielectric is contacted with a wet or gelled electrolyte which provides the electrical path from the dielectric to the external circuit. The electrical path the external circuit is completed via a nearby high-surface-area etched-foil cathode that also contacts the electrolyte. It is possible to make the negative connection to the dielectric of a porous-slug tantalum capacitor in a similar fashion using wet electrolyte and a high-surface-area cathode. Indeed "wet" tantalum capacitors are made this way. However, such construction does not solve the problem of poor performance at low temperatures, or the possibility that the electrolyte may escape from the capacitor over time (it should be noted that modern, hermetically-sealed wet tantalum capacitors are very reliable and rarely leak, but they are also relatively heavy and expensive).

The second substantial innovation of Bell Labs' capacitor was the use of a dry or solid electrolyte in place of the wet electrolyte used in conventional wet electrolytic capacitors. The exposed negative surface of the tantalum capacitor's dielectric is contacted by coating it with the semi-conducting crystalline solid, manganese dioxide (MnO_2). This is accomplished by dipping the porous slug into manganous nitrate solution and then heating it to convert the liquid manganous nitrate that contacts the dielectric into solid MnO_2. To facilitate good internal coverage, the concentration of the manganous nitrate solution is kept low, and many dip and convert cycles are usually required to adequately contact the dielectric. The end result is a solid and dry functional capacitor element composed of tantalum metal as one electrode, high-quality dielectric, and another electrode, MnO_2, contacting the other surface of the dielectric. However, MnO_2 is not a material easily connected to external circuits, so a few finishing steps are needed to make a practical capacitor from the functional capacitor element.

Once the dielectric's surface is so contacted, the externally-exposed MnO_2 is covered with a finely divided carbon layer which is then covered with a conductive metallic shell. This outer shell facilitates a low-resistance negative connection to the external circuit via a metallic terminal. The positive connection is typically made by welding a metallic terminal to a stub of tantalum wire that is connected to the metallic surface of the porous tantalum slug. These terminal connections were accomplished with wire leads in earlier tantalum capacitors, but have evolved into surface-mount-compatible terminations in recent years. The finished capacitor is then covered with a protective case.

Not only was the new tantalum capacitor smaller, but it also had better electrical performance and reliability than the existing wet electrolytic capacitors. The small size resulted from the pressed, porous slug made of finely divided tantalum powder. The improved reliability was mainly achieved because the MnO_2 electrolyte couldn't escape or "dry out."

The first process for manufacturing commercially viable tantalum capacitor was patented in 1960 by Richard Millard of Sprague Electric Company. The patent application was filed in 1955, not long after the device was described by Bell Labs. A significant improvement patented by Millard was the "reform" step in which the dielectric of the capacitor was repaired after each dip-and-convert cycle of MnO_2 deposition. This repair was accomplished by application of voltage while the capacitor element was immersed in a suitable electrolyte. This process improvement dramatically reduced the leakage current of the finished capacitors. Millard also described ranges of temperature and time for the MnO_2 deposition process that improved total achieved capacitance and lowered ESR.

A copy of the Millard's drawing of the patented capacitor appears in Figure 1. Visible in Millard's drawing are the fundamental construction details described above: central porous slug with dielectric coating filled with MnO_2 (10 and 11), positive leadwire connected to the slug (12), outer MnO_2 coating (14), carbon coat (16), outer metallic electrode (18), negative leadwire (20), and protective case (22).

A schematic drawing of the tantalum capacitor element of Figure 1 appears in Figure 2. The tantalum powder particles are simplified to spherical shape, magnified, and arranged in simplistic fashion to exaggerate the porosity available for impregnation with MnO_2. The particles are shown partially melted together and to the tantalum wire to form a continuous metallic structure. Dielectric appears on the exposed surface area of the tantalum metal and the dielectric is covered with MnO_2 both inside and outside of the porous structure. The external surface of the MnO_2 is covered with a layer of carbon and the carbon is covered with a metallic coat. Sprayed copper was a preferred metallic coating in Millard's patent, but he also mentioned zinc, tin, silver, and gold as suitable alternatives. In contrast with the schematic drawings of Figures 1 and 2, a high-magnification picture of the actual internal structure of a tantalum capacitor element appears in Figure 3.

Conventional MnO_2-based tantalum capacitors are constructed in substantially similar fashion today. The most notable differences involve today's use of highly pure, more finely divided tantalum powder for increased surface area (higher capacitance) in a given volume, use of silver-filled paint for the metallic coating, and use of the "chip" packaging configuration which lacks conventional leadwires but instead has short surface-mount terminations. Some typical high-reliability military-style surface-mount tantalum chip capacitors appear in Figure 4. A more detailed description of the materials and assembly of modern tantalum capacitors appears in a later section.

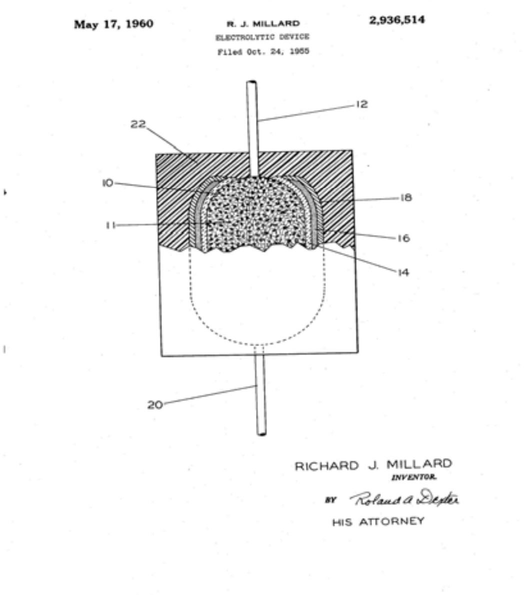


Figure 1. Patent Drawing of First Commercially Viable Tantalum Capacitor.

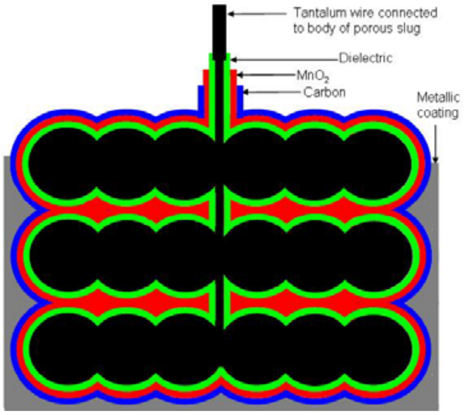


Figure 2. Schematic Drawing of Tantalum Capacitor Element of Figure 1.

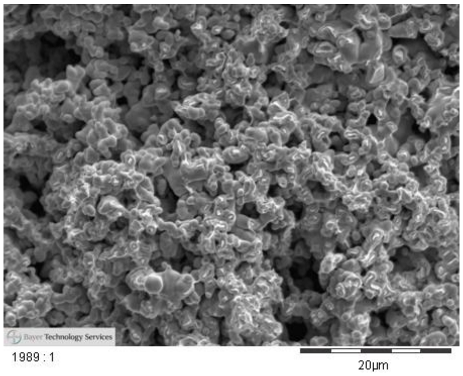


Figure 3. Actual Internal Structure of Tantalum Capacitor Element (Photograph Courtesy of Bayer).

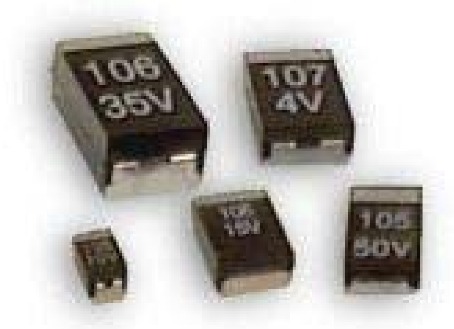


Figure 4. Modern Surface-Mount Tantalum Chip Capacitors.

Defining Characteristics of Conventional Tantalum Capacitors

The compelling characteristics of tantalum capacitors are small size, high reliability, and good parametric performance over broad ranges of frequency and temperature. As mentioned earlier, the small size of tantalum capacitors results from the porous pressed powder structure of the capacitor element. Modern tantalum capacitors are fabricated from powders that can deliver very high electrical charge storage characteristics when compared to other competing capacitor technologies.

Volumetric Efficiency

Tantalum powder "charge" is specified as a capacitance-voltage product called CV. A typical high-charge powder might be advertised as having 50,000 CV/gram of charge. What this means is that under ideal circumstances, one gram of this powder should be sufficient to produce a capacitor having a product of capacitance times dielectric formation voltage of roughly 50,000 μF-volts. The dielectric formation voltage is the maximum voltage achieved across the dielectric when the dielectric is created on the exposed surface of the tantalum metal during chemical anodization in a suitable electrolyte. During dielectric formation, tantalum ions and oxygen ions unite and "form" the dielectric tantalum pentoxide after they travel to roughly the midpoint of the existing oxide layer under the influence of an applied electric field.

If such a 1-gram capacitor element made from 50,000 CV/g powder had dielectric formed to 50 volts, it should ideally achieve a capacitance of 1000μF. Since the dielectric formation voltage is roughly 3-4 times the final rated voltage of the capacitor, this would be roughly a 16V rated tantalum capacitor. Unfortunately, it's difficult to achieve the advertised charge and still have a reliable capacitor, but it's not uncommon to achieve a substantial fraction of the advertised charge.

Early tantalum capacitors were made from powders having fairly low charge, roughly in the neighborhood of 1000 CV/g. Such powder could be used for making capacitors with fairly high rated voltages (>50V). Some modern powders claim to exceed 100,000 CV/g, but are limited to use at relatively low voltages because the powder particles are so small that formation of the dielectric consumes the tantalum that connects the individual particles together when the formation voltage exceeds a predictable value. Nevertheless, low-voltage capacitors with remarkably high capacitance are now possible, and development of even higher-charge powders and processing methodology continue.

High Reliability

It was stated earlier that much of the reliability improvement possible with tantalum capacitors was due to the use of solid electrolyte that couldn't escape from the capacitor. This is certainly true in comparison with wet-electrolyte aluminum capacitors which have predictable wearout based on the leak rate of the package seal. But there is another factor contributing to the good reliability of tantalum capacitors. This factor is the inherent self-healing properties of the MnO_2 dielectric coating.

There are two different ways that MnO_2 promotes self-healing. First, there is a thermodynamic tendency for oxygen in the dielectric to slowly diffuse into the pure tantalum substrate metal that supports it. This tendency is encouraged, exponentially, by temperature and the presence of electric field in the dielectric. Of course the presence of electric field is the normal condition for operating capacitors. Oxygen vacancies resulting from this oxygen diffusion degrade the insulating properties of the dielectric and lead to increased leakage current and ultimately to dielectric breakdown. MnO_2 is an oxygen rich material that readily supplies oxygen to the dielectric to replace oxygen lost to the substrate via diffusion. Thus MnO_2 impedes this degradation mechanism, improving reliability.

Second, MnO_2 can be converted into a less conductive oxide, typically Mn_2O_3, upon exposure to high temperatures, generally higher than 450^oC. Very high local current densities exist at small flaws in the dielectric (cracks, impurities, etc.) when voltage is applied to the capacitor. The result is localized heating of the dielectric. This heat is conducted to the MnO_2 coating, converting it into the less conductive Mn_2O_3. This process limits the local current flow and "heals" the flaw site.

Improved Electrical Performance

It was mentioned earlier that a weakness of wet-electrolyte capacitors is poor performance at low temperatures as the electrolyte becomes less conductive. The capacitor characteristics directly affected by low electrolyte conductivity are capacitance roll-off with frequency, dissipation factor, and ESR.

Because of the porous slug structure of the tantalum capacitor, electrical signals from the external circuit must be conducted to the inner parts of the capacitor's structure through the electrolyte. AC voltage drops occur along the way in the electrolyte's resistance and these voltage drops limit the percentage of the signal that reaches the core of the capacitor. If little of the external circuit's signal reaches the capacitor's core, then capacitance that exists there is largely invisible to the circuit and the effective capacitance is reduced.

At very low frequencies, there is enough time for the capacitance inside the slug to fully charge to the externally applied voltage and all of the slug's capacitance is "seen" by the external circuit. But at higher frequencies, the rate of charging inside the slug is limited by RC time constants along the electrolyte's path, and the slug's internal capacitance cannot "keep up" with time-varying changes of circuit voltage. A good electrical model of this behavior is the RC ladder transmission line. The RC ladder model predicts a frequency beyond which the effective capacitance of the structure begins to predictably decline, a phenomenon known as "capacitance roll-off."

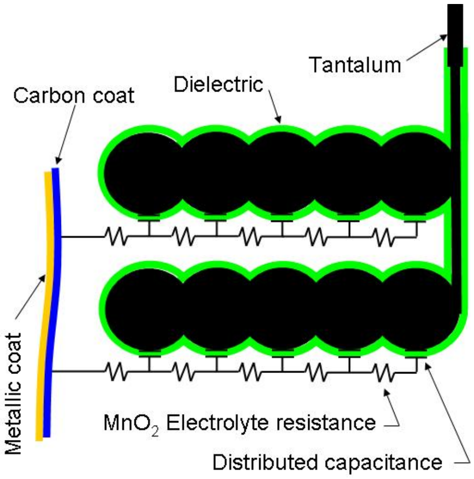


Figure 5. Schematic Representation of the Origin of the RC-Ladder Model of Tantalum Capacitors Based on Diagram of Figure 2.

A schematic view of the internal structure of a tantalum capacitor element, highlighting the physical origin of the RC ladder and the capacitance roll-off effect, appears in Figure 5. Computer models of the high-frequency behavior of tantalum capacitors are based on this model with individual values of R and C chosen to reflect the specific geometry of the capacitor element in question. Such models can predict the frequency-dependant characteristics of tantalum capacitors with high accuracy.

Capacitance roll-off behavior is easily verified in the laboratory. The effect is demonstrated by observing capacitance decrease while increasing the resistance of the electrolyte, increasing the measurement frequency, or both. Alternatively, reducing the resistance of the electrolyte increases the frequency where roll-off begins. Typical wet-electrolyte capacitors tend to experience substantial capacitance roll-off above roughly 1 kHz at room temperature and at much lower frequencies at very low temperatures. In contrast, conventional MnO_2 tantalum capacitors have substantially stable capacitance until well above 10 kHz because of the increased conductivity of MnO_2 versus wet electrolytes.

Another direct consequence of the resistance along the electrolyte's path is elevated energy loss. An ideal capacitor is a perfect energy storage device and will return all of the energy stored in it. Real capacitors always have some resistance in addition to their capacitance, and this resistance is the root cause of energy loss. Energy loss in capacitors is quantified by the parameters dissipation factor (DF) and ESR.

DF is the ratio of energy lost to energy stored in the capacitor over a full cycle of applied alternating voltage, while ESR is the equivalent value of resistance that if connected in series with an ideal capacitor would perfectly simulate the energy loss mechanisms in the capacitor. Both of these parameters grow numerically as the conductivity of the electrolyte falls. At low temperatures, wet electrolytes are very poor conductors and wet-electrolyte capacitors demonstrate very high DF and ESR at low temperature.

Conventional MnO_2–based solid tantalum capacitors have much better (lower) DF and ESR at low temperatures because of the improved conductivity of MnO_2 at low temperatures versus common wet capacitor electrolytes. MnO_2 still loses conductivity at low temperatures, just not as quickly as wet electrolytes do. At -55^{o}C, DF and ESR of a conventional MnO_2 tantalum capacitor are not likely to degrade by more than a factor of two, but many wet-electrolyte capacitors become essentially non-functional at that temperature and are not generally intended for use below roughly -40^{o}C. In contrast, MnO_2 tantalum capacitors retain useful performance as low as -80^{o}C.

The remaining essential electrical property of conventional tantalum capacitors is DC leakage current, or rather the absence of it. One important characteristic of capacitors is that they should block DC currents. Real capacitors do not perfectly block DC current, but the current that "leaks" through the dielectric is usually very small. Typical values of leakage current for MnO_2-based tantalum capacitors usually fall well below catalog limits which are commonly set at 0.01CV, where C is the capacitance in μF and V is the rated voltage. For example, a 100μF, 10V capacitor would have a room-temperature leakage current limit of 10μA, but would typically have a measured DC leakage at 10V of less than 1 μA. Typically measured leakage currents for MnO_2-based tantalum capacitors at rated voltage range from roughly 0.1 nA to about 100 μA.

Defining Characteristics of Tantalum Capacitors Made with Conducting-Polymer Electrolyte

Much was said earlier about the benefits of solid electrolytes (no loss of electrolyte over time) and of more conductive electrolytes (less capacitance roll-off, lower DF, and lower ESR). The primary reason for the existence of tantalum capacitors made with conducting-polymer electrolyte (called "tantalum polymer capacitors") is that conducting polymers are significantly more conductive than MnO_2, perhaps up to 100 times more conductive. The direct benefits of this increased conductivity are lower ESR and improved high-frequency performance.

Lower ESR

While the conductivity of some conducting polymers may be as much as 100 times higher than that of MnO_2, the improvement in capacitor ESR is not this dramatic. What is typically seen is reduction of capacitor ESR by a factor of between 2 and 4. The discrepancy is due to several factors. First, not all of the ESR of a tantalum capacitor comes from its electrolyte. There are other sources of resistance, including the resistance of the tantalum, carbon, conductive metal coat, termination metal, and associated interfaces. There is even a component of ESR that comes from dielectric loss, but this is usually very small at higher frequencies. A second reason for the discrepancy is that creating conductive polymer inside a slug with fine pores is much more difficult that creating conductive polymer on the surface of a flat glass slide in the laboratory. The polymer film inside the tantalum slug must be produced one thin layer at a time and the individual layers must communicate well with each other electrically, a difficult task. This process will be described in more detail later.

In spite of the current practical limitations of the technology, dramatically low ESR has been achieved in tantalum polymer capacitors. Currently, single-anode capacitors with 100 kHz ESR under 7 mΩ have been manufactured, and multiple-anode tantalum polymer capacitors have been made with ESR under 3 mΩ. Such low ESR in combination with high capacitance makes the tantalum polymer capacitor the fastest growing segment of the tantalum capacitor industry.

Better High-Frequency Performance

The higher conductivity of the conductive polymer electrolyte improves the high-frequency capacitance of these capacitors. Capacitance roll-off of tantalum polymer capacitors remains low until well above 100 kHz. This characteristic substantially improves the filtering performance of these capacitors in DC-DC converters and other circuits that operate in this frequency range. The filtering characteristics of such circuits depend on both capacitance and ESR, so filtering effectiveness improves more than would be anticipated by simply considering improvements in ESR alone. Typical MnO_2-based tantalum capacitors could lose up to 50% of their capacitance at 100 kHz, while tantalum polymer capacitors typically retain more than 90% of their capacitance at 100 kHz.

Superior Reliability for Lower Rated Voltages

But low ESR in the absence of good reliability would not be very compelling. It turns out that almost all tantalum polymer capacitors have better reliability than equivalent MnO_2 tantalum capacitors. It is thought that the low-temperature deposition of the conducting polymer into the tantalum slug does less damage to the capacitor's dielectric than is done by the high-temperature conversion of manganous nitrate into MnO_2.

Almost all of the polymer processing is done in the neighborhood of room temperature while MnO_2 generation is done at temperatures in excess of 250^oC and typically involves more processing cycles. The low-temperature processing and relative softness of the resulting polymer are thought to produce less damage to the dielectric than occurs from frequent thermal cycling of the tantalum slugs after the early deposition cycles of the hard, crystalline MnO_2.

Two experimental observations support this hypothesis. First, the ultimate breakdown voltages of capacitor elements impregnated with polymer are higher than those impregnated with MnO_2 for similar dielectric thickness, and far fewer lifetest failures are observed under highly accelerated conditions (e.g., 1.5Vr @ 85^oC) for tantalum polymer capacitors versus MnO_2-based tantalum capacitors.

Some Flies in the Ointment

Unfortunately, not all the news is positive. Generally speaking, tantalum polymer capacitors are more sensitive to high temperature than are MnO_2-based tantalum capacitors, their leakage current is higher, and for the higher rated voltages, the breakdown and lifetest advantages disappear. No tantalum polymer capacitors are presently rated higher than 25V and the reliability of those that are is less than spectacular.

All conductive polymers appear to be inherently less thermally stable than MnO_2. This is likely the result of superior bond strength in the inorganic, crystalline MnO_2 versus the bond strength in organic polymers. Quantitatively, MnO_2 begins to break down at temperatures above roughly 450^oC while common conductive polymers begin to break down at temperatures closer to 200^oC.

It is also known that exposure to oxygen at temperatures much higher than 105^oC can substantially increase the resistance of the conductive polymers used in capacitors. For this reason, capacitors advertised for use at 125^oC are made with extra attention paid to careful sealing of the capacitor element within the protective epoxy case. It appears that the epoxy molding material captures the small amount of oxygen that diffuses through the case at 125^oC before it can reach the conductive polymer within the capacitor element. But if the integrity of the case epoxy is disturbed by defects such as cracks or pin holes, ESR deteriorates significantly over the course of 1,000 hours exposure to 125^oC, a common lifetest duration.

Also, the DC leakage current of tantalum polymer capacitors is generally higher than that of MnO_2-based tantalum capacitors. The reasons for this higher leakage current are not fully understood, but it is thought that the higher leakage results from residues of the polymerization process, higher conductivity of the polymer itself with respect to MnO_2, and less effective self-healing properties of the conductive polymer. Regardless of the reasons, the practical effect is that catalog leakage limits for tantalum polymer capacitors are typically 10 times higher than for MnO_2-based tantalum capacitors, and there isn't usually as much of a gap between actual leakage and the catalog limit as is common for MnO_2-based tantalum capacitors.

Finally, the reliability of *higher-voltage* tantalum polymer capacitors is no longer superior to that of MnO_2-based tantalum capacitors of similar rated voltage, and in some cases it is inferior. The reasons for the reduced reliability of higher-voltage tantalum polymer capacitors are not precisely known, but it is suspected that at least two factors may contribute.

First, the oxygen replenishment function that MnO_2 performs is not present in the conductive polymer. It may be that this reliability-enhancement mechanism may simply be more important at higher voltages than at lower voltages where the reliability of tantalum polymer capacitors is clearly superior to MnO_2-based tantalum capacitors.

Second, although self-healing does occur in the conductive polymer due to degradation of the polymer's conductivity at high temperatures, this self-healing mechanism is not thought to be as effective as the self-healing mechanism of MnO_2-based tantalum capacitors. Decomposition of the conductive polymer is thought to leave behind carbonaceous residues which retain some conductivity, and carbon touching the dielectric's surface is known to enhance the conductivity of tantalum pentoxide dielectric by the mechanism of direct electron injection.

No Exothermic Ignition Mechanism

Although the absence of readily available oxygen in the conductive polymer may work against realization of reliable high-voltage tantalum polymer capacitors, it is certainly a benefit during capacitor failure. When MnO_2-based tantalum capacitors fail, it is not uncommon that sufficient heat is produced at the failure site to release substantial local oxygen. This oxygen can combine chemically with the tantalum substrate in an uncontrolled exothermic reaction which causes catastrophic instantaneous ignition of the MnO_2-based tantalum capacitor.

The dividing line between controlled, successful self-healing and catastrophic ignition is not clearly drawn. But generally speaking, MnO_2-based tantalum capacitors made from higher CV/gram powders and those with only lightly sintered connections between their tantalum particles appear to be more susceptible to ignition. Also, capacitors used in low impedance, high-current circuits are more susceptible to ignition rather than self-healing in response to dielectric faults.

This uncontrolled ignition mechanism *does not occur* in tantalum polymer capacitors because there is no plentiful supply of oxygen adjacent to the dielectric. However, tantalum polymer capacitors do fail in the short-circuit mode, and if the available current from the circuit is substantial, it is possible to achieve sustained combustion of the capacitor and of the surrounding circuitry simply due to the substantial heat generated by the high fault currents.

Materials and Processing

In principle, the processing of tantalum polymer capacitors is quite similar to the processing of conventional MnO_2-based tantalum capacitors. The major change is the substitution of conducting polymer for the MnO_2. But other small materials changes may be made to optimize ESR reduction and reduce sensitivity to reflow conditions. These smaller changes are of no more significance than the typical variability seen between different manufacturers of a generically similar product. So the focus of this section will be on materials and processes unique to the manufacture of tantalum polymer capacitors.

A variety of materials are available to replace MnO_2 as the solid electrolyte in a tantalum capacitor. Four possible materials will be described: tetracyano-quinodimethane (TCNQ) salts, polyaniline (PANI), polypyrole (PPY), and polyethelyne-dioxythiophene (PEDT). Other conductive polymers exist that have the necessary conductivity to replace MnO_2, but they have not been successfully employed in capacitor manufacturing because of a variety of shortcomings such as poor stability. Two examples are polyphenylenevinylene (PPV) with conductivity of 10-16 S/cm and iodine-doped polyacetylene with conductivity of 100 S/cm.

TCNQ

The first material, tetracyano-quinodimethane (TCNQ) is not strictly a polymer, but rather a charge-transfer salt that forms linear chains of molecules which are stacked in layers. Highly polarizable donor molecules contribute electrons that provide conduction along the chains. One such donor molecule is N-methyl phenazinium (NMP).

TCNQ salts made with NMP have been reported to have conductivity exceeding 100 S/cm. This is much higher conductivity than $MnO_{2,}$ which is generally considered to have conductivity in the neighborhood of 0.1 to 1 S/cm. However, the conductivity of TCNQ is typically in only one dimension (along the chain), so structures that depend on three-dimensional conductivity must rely on compositions that consist of shorter chains in random orientation and effective electrical communication among the chains. This generally reduces the effective conductivity of the material for capacitor applications.

TCNQ is commonly used in wound aluminum foil electrolytic capacitors for power supply applications. There has been good success with this application. Typical ESR performance of these devices is roughly 20-30 mΩ. The salt is melted and drawn into the pores of the etched aluminum foils and the separator material and allowed to cool. Sanyo is a major supplier of these devices (OS-CON).

TCNQ has not found much use in porous tantalum slugs, likely because of difficulties impregnating the much deeper porosity of tantalum anodes and temperature limitations. While common aluminum foil is only etched to depths of roughly 30 microns, porous tantalum slugs have pores which reach to their core. These pores are 10 to 50 times deeper and present a more formidable challenge for complete impregnation.

Finally, there is very little separation between the temperatures needed to melt and impregnate the TCNQ salt and temperatures that begin to decompose the material. Capacitors made with TCNQ are not generally stable above roughly 85^{o}C, a temperature that would be too limiting for capacitors made from relatively expensive metal tantalum. But this temperature limit is frequently acceptable for less-expensive aluminum capacitors in less-demanding applications.

PANI

Polyaniline (PANI) is the most thermally stable conductive polymer but is easily de-doped in the presence of water. Conductivities up to 10 S/cm have been reported which are high enough to provide a substantial advantage over MnO_2, but sensitivity to moisture discourages use of PANI in tantalum capacitors. Higher molecular weight dopants are being investigated to overcome the moisture limitation, but at the present time, PANI is not used in any commercially available tantalum capacitors. However, the material has found application in double-layer super-capacitors and other electronic applications. Another concern is the possible generation of carcinogenic byproducts upon decomposition.

PPY

Polypyrole (PPY) is the first intrinsically conductive polymer successfully used to manufacture both aluminum and tantalum capacitors. The basic raw materials are commonly available and relatively inexpensive. Aluminum capacitors based on PPY are manufactured by Panasonic (SP Cap), Rubycon, and others. Tantalum capacitors based on PPY are manufactured by NEC and Sanyo (POS-CAP).

PPY is suitable for both chemical polymerization and electro-chemical polymerization in tantalum capacitors. In the chemical polymerization process, the porous element is alternately dipped in monomer and oxidizer solutions with appropriate drying steps between. Contact between the monomer and oxidizer initiates polymerization. Afterwards, excess non-reacted materials must be washed out of the porous slug. A suitable dopant material is added either to the monomer or oxidizer solution to enhance electrical conductivity by providing free electrons. The basic materials are highly reactive and care must be taken to control the reaction in order to deposit meaningful amounts of polymer inside the porous slug. Other factors that control the conductivity and morphology of the resulting polymer are temperature and pH.

The electrochemical process involves deposition of a suitable conductive seed layer inside the porous slug. This layer is electrically contacted and the slug is dipped in a doped monomer solution. Electric current is passed through the seed layer into the doped monomer solution stimulating the oxidation reaction that grows the doped polymer on the seed layer. A significant advantage of the electrochemical process is that it provides enhanced polymer thickness and uniform coverage on the edges and corners of the porous slug because of the enhanced electric field at these locations. A disadvantage is the relative difficulty getting the polymer to form inside the porous structure because of the limited electric field present there.

PEDT

Polyethelyne-dioxythiophene (PEDT) is the most popular conductive polymer for use in tantalum capacitors. It has high electrical conductivity (up to 300 S/cm) and is both thermally stable at fairly high temperatures (above 200^{o}C in oxygen-free environments) and relatively insensitive to moisture. Another advantage is that the polymerization reaction is less aggressive which provides a wider processing window.

A variety of dopants are available and it is thought that PEDT's physical and electrical properties can be optimized for specific dielectrics and operating voltages by judicious choice of dopant. One disadvantage is that while PEDT can be polymerized via the electrochemical process, little success has been achieved in tantalum capacitors with this process. Another disadvantage is the relatively high cost of the raw materials.

In the capacitor industry, PEDT is deposited in tantalum anodes by either the "two-pot" chemical polymerization method described above for PPY, or by a "one-pot" method. In the "one-pot" method, monomer, oxidizer, and dopant are combined in one container with additional ingredients that slow the polymerization process. The porous tantalum slug is dipped in the solution and the polymerization reaction continues inside the slug. It is also possible to use both processes, i.e., internal polymerization via the "two-pot" method and external polymerization via the "one-pot" method.

A variety of manufacturers use PEDT in tantalum capacitors. Among them are KEMET (KO-Cap), NEC (Neo-Cap), EPCOS (TOPcap), Vishay (255D), AVX (TCJ), and others.

Construction Details

Typical construction of tantalum polymer capacitors is best illustrated with pictures. Figures 6 through 14 serve this purpose. It should be noted that the pictures were taken of samples that came from several different part types, so there may be small discrepancies from picture to picture that can be detected by the experienced eye. Also, the samples were exposed to a good bit of incidental human handling and may not accurately represent optimum factory uniformity.

Figure 6 is a magnified view of 50 kCV/g tantalum powder prior to being pressed into a porous tantalum slug. The powder particles typically stick together in porous bundles called agglomerates. The smallest agglomerates visible in the picture are roughly 5-10 μm in size and are made up of individual particles that are roughly 0.1 to 1 μm in size. The powder is coated with an organic binder material that aids powder flow as it is dispensed into the presses that form the compacted, but still porous tantalum slugs. The binder also provides lubrication during slug pressing.

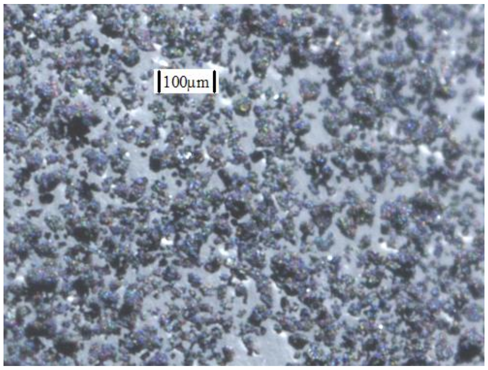


Figure 6. Tantalum Powder Agglomerates (~150X).

Figure 7 is a picture of a porous tantalum slug that has a tantalum anode wire pressed into it. The slug of Figure 7 has been first heated in a vacuum to a temperature high enough (typically >200°C) to decompose the organic binder, and then further heated to roughly 1,600°C to sinter the individual powder particles together. The objective is to form good mechanical connections between the particles and between the particles and the anode wire without unnecessarily compromising the slug's porosity and internal surface area. The degree of sintering is controlled by time and temperature, and various properties of the finished capacitor can be fine-tuned during this process step.

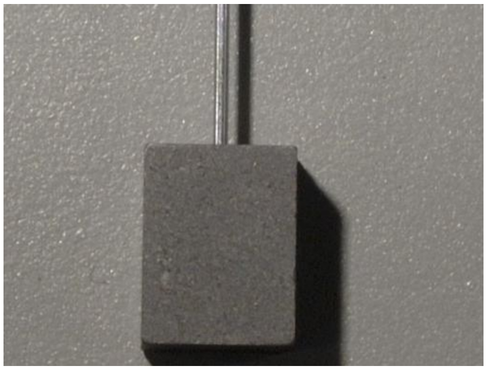


Figure 7. Sintered Porous Tantalum Slug with Pressed-in Anode Wire (~15X).

Figure 8 shows several tantalum slugs attached to a common conductive bar. The slugs have been immersed in a suitable electrolyte and dielectric has been "formed" on the exposed tantalum surface by electrolytic anodization. During anodization, tantalum ions migrate from the surface of the tantalum metal to a point roughly halfway through the existing dielectric where they combine with similarly migrating oxygen ions that are supplied by the electrolyte. The result is partial consumption of the underlying tantalum metal and growth of the tantalum pentoxide dielectric on the remaining metal's surface. The color change is due to the refractive properties of the dielectric film which grows to a thickness consistent with roughly 20 angstroms per volt of applied formation voltage.

The peak formation voltage is usually about 3 to 4 times higher than the rated voltage of the finished capacitor. So for a 6.3 volt capacitor, 20V would not be an unusual formation voltage. 20V dielectric would be roughly 400 angstroms or 40 nm thick. For the smallest tantalum particles which could be 0.1 μm or 100 nm thick, there isn't very much tantalum metal left after oxide this thick is grown. Indeed, at much higher formation voltages, oxide formation consumes enough of the tantalum metal in the smaller particles to effectively disconnect them from the rest of the slug. The end result is reduced available surface area and less CV/gram than can be achieved at lower formation voltages.

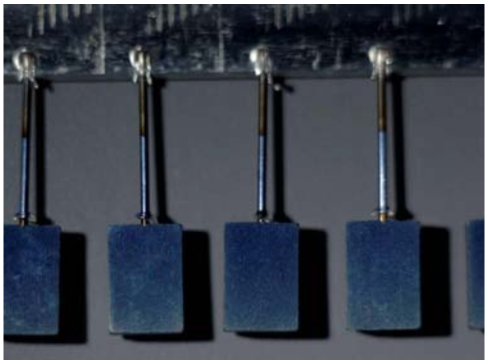


Figure 8. Anodized ("formed") Tantalum Slugs.

Figure 9 is a picture of tantalum slugs after dielectric formation that have been impregnated with conductive polymer. The color of this polymer lies somewhere between very dark blue and black. The objectives of this stage of the process are to create a uniform, highly conductive layer of polymer on all of the internal surface of the slug and then to create a uniform, dense layer of polymer on the outer surface of the slug. Electrically, the outer layer of polymer adds unwanted ESR to the finished device, but this is an acceptable tradeoff for the mechanical protection that the layer provides to the very thin dielectric that lies just below it.

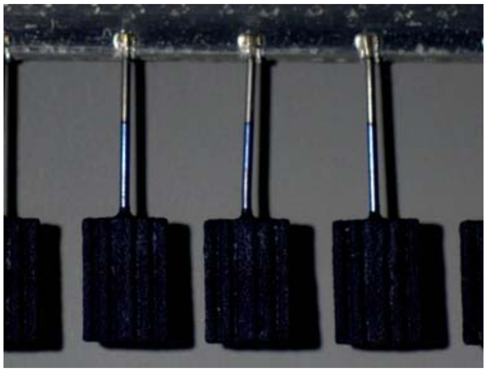


Figure 9. Anodized Slug Impregnated with Conductive Polymer.

Figure 10 shows the polymer coated slugs after addition of a carbon layer and a coating of conductive silver paint. The carbon layer provides a good interface between the polymer and the silver flakes in the paint. At this stage of processing, the capacitor elements are fully functional and have electrical properties very similar to those of the finished capacitors. Initial electrical testing is done at this point to assess the quality of the elements before they proceed further in the process.

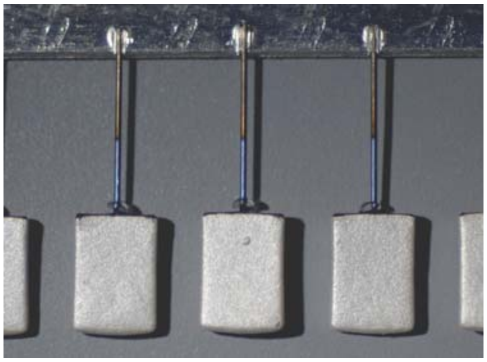


Figure 10. Fully Functional Tantalum Capacitor Elements after Coating with Carbon and Silver Paint.

Figure 11 shows a portion of the metal leadframe strip to which the individual capacitor elements will be attached in the early stages of the capacitor assembly process. The precise dimensions of the leadframe vary from manufacturer to manufacturer, but the function is the same. The leadframe provides a means to process many capacitor elements at the same time to improve efficiency during mass production.

Small dollops of conductive silver adhesive have been placed on the offset metal surfaces of the leadframe in preparation for insertion of the individual capacitor elements. This adhesive will subsequently be cured at elevated temperature to make a low-resistance connection between the leadframe metal and the silver paint layer of each capacitor element. Uniformly-spaced guideholes appear in the leadframe. They exist to aid transport and provide precise positioning during the various manufacturing steps.

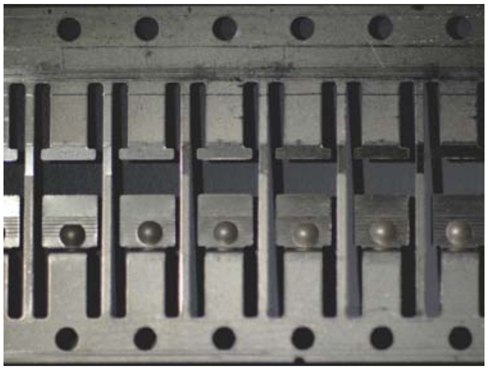


Figure 11. Stamped Leadframe with Conductive Silver Adhesive Applied to Offset Surface.

In Figure 12, one sees capacitor elements electrically connected to the leadframe. The positive connection is made by resistance welding of the anode wire to the leadframe. The negative connection is made by curing the silver adhesive which forms a conductive layer between the leadframe and the silver paint on the elements. The silver adhesive is cured by heating until the epoxy binder cross links. During the curing process, there is some shrinkage which draws the silver particles together and into contact with the surfaces of the leadframe and silver paint.

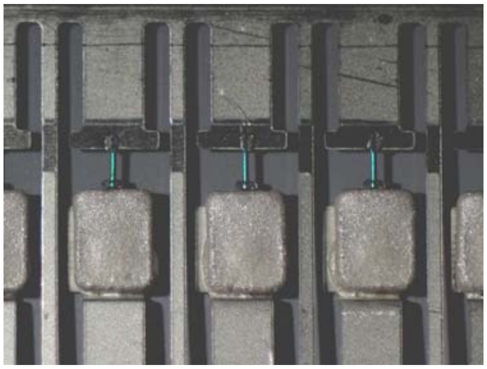


Figure 12. Capacitor Elements Assembled to Leadframe by Welding the Anode Wire and Curing the Silver Adhesive.

The next step is to mold a protective epoxy case around each element. The result appears in Figure 13. The molded epoxy cases have been laser marked and the individual capacitors have been electrically isolated from each other to facilitate electrical testing.

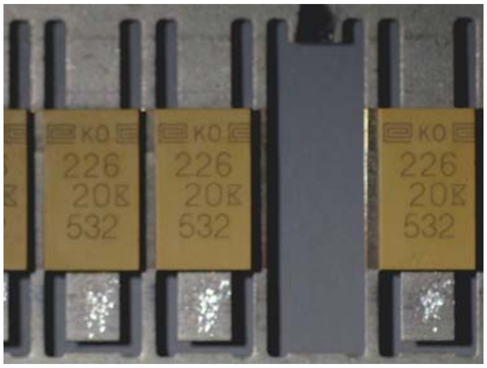


Figure 13. Epoxy Case Molded around Assembled Capacitor and Laser Printed.

Each capacitor can now be aged and electrically tested. These specific capacitors were part of an experiment, and evidence of multiple probe contacts is easily observed on the lower (negative) terminal. One capacitor is missing in Figure 13. This capacitor did not meet specifications and was removed from the leadframe strip during electrical testing. During high-volume production, sub-standard capacitors are physically removed to prevent them from being shipped to a customer.

After electrical testing, the surviving capacitors are cut from the leadframe strip. The terminal metal that exits from the molded case is trimmed to a suitable length and is then bent and formed around the bottom edge of the capacitor. This step is performed on both terminals and the capacitor is inserted and sealed inside a standardized plastic carrier tape. The carrier tape is designed to feed hundreds or thousands of capacitors to automated equipment that places the capacitors on customers' circuit boards. The capacitors appear in the carrier tape in Figure 14. One capacitor has been removed from the tape and inverted to show its surface mount terminals.

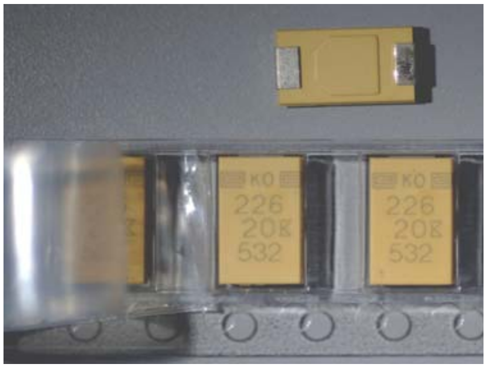


Figure 14. Finished Capacitors in Carrier Tape after Leads are Trimmed and Bent around Bottom Edges (7.3mm X 4.3mm).

Typical Electrical Performance and Reliability

Manufacturers of tantalum polymer capacitors often make available to their customers typical electrical performance and reliability data. Occasionally, such data can also be found in technical papers. It can be reasonably assumed that these public data are selected to show the capacitors in a generally favorable light, but nevertheless they provide much useful information. In this section, some typical performance data from several manufacturers will be presented to give a basic overview of the performance characteristics of tantalum polymer capacitors.

Unfortunately, there is considerable variability in the test conditions as well as the format of the available data. Moreover, there is no direct overlap of specific part types represented (capacitance and rated voltage). Thus little competitive information can be gleaned from these data, but much general information can be gathered from the various part types and test conditions. In the FY06 continuation project, capacitors of the same part types will be anonymously purchased from a variety of suppliers. These capacitors will be subjected to uniform testing to provide a better understanding of the relative performance and reliability of several manufacturers' product.

The presently available data will be presented in four categories. The first data category is typical electrical performance which is intended to highlight the "as manufactured" electrical behavior of tantalum polymer capacitors. The second data category is typical dielectric robustness which is intended to demonstrate the generally superior breakdown performance of tantalum polymer capacitors in high inrush current applications. The third data category is reliability performance which is intended to highlight differences in expected failure rates and distribution of times-to-failure between tantalum polymer capacitors and MnO_2-based tantalum capacitors. The last data category is environmental stability which is intended to highlight shifts in electrical performance after initial exposure to environmental and reflow conditions as well as after long-term exposure to heat, voltage, and humidity.

Typical Electrical Performance

The statistical distribution of 120Hz capacitance among 12 capacitors in a sample of 150μF, 6.3V Vishay-Sprague tantalum polymer capacitors appears in Figure 15. These capacitance values are not significantly different from what would be expected for tantalum capacitors manufactured with MnO_2 cathode material. The median value of the distribution falls somewhat short of the nominal capacitance value, but all devices fall within +/-10% limits.

It is not unusual for the median capacitance of tantalum capacitors of all vendors to fall somewhat short of the nominal capacitance value. One reason is that almost all efforts to improve device robustness result in reduced capacitance, so the primary focus is often placed on simply exceeding the minimum tolerance limit while providing the most robust design. Another related reason is that there is no economic incentive to put any more expensive tantalum powder into a design than is absolutely necessary to meet specification limits.

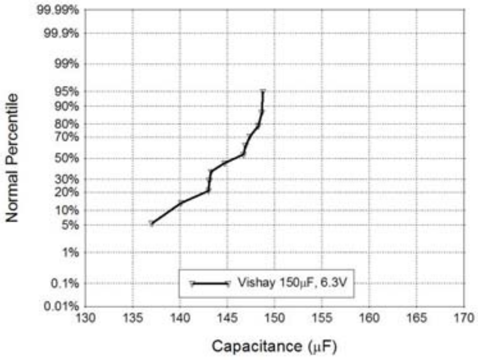


Figure 15. Typical 120Hz Capacitance Data for 150μF, 6.3V Tantalum Polymer (Data Courtesy of Vishay-Sprague)

120Hz dissipation factor (DF) data appear in Figure 16 for the same 12 tantalum polymer capacitors whose capacitance appears in Figure 15. Again the data are no different than would be expected for an MnO_2-based tantalum capacitor. At 120Hz, the dissipation factor is largely governed by dielectric loss rather than cathode conductivity, and the dielectric is the same for both styles of tantalum capacitor. The DF limit for these capacitors is 12% and it is clear that these devices comfortably comply.

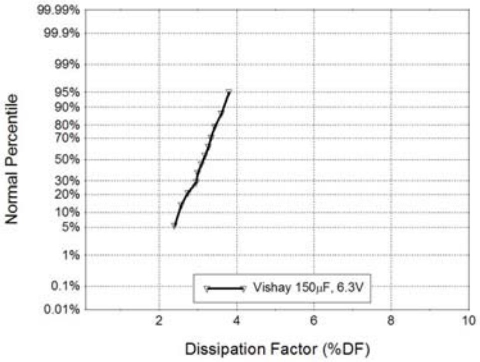


Figure 16. Typical 120Hz Dissipation Factor Data for 150μF, 6.3V Tantalum Polymer (Data Courtesy of Vishay-Sprague)

The DC leakage current data for the Vishay-Sprague capacitors of Figures 15 and 16 appear in Figure 17. The leakage values are log-normally distributed and the spread of the distribution is similar to the spread of DC leakage values for MnO_2-based capacitors. However, the median value of leakage is much higher for these tantalum polymer capacitors than would be normal for MnO_2-based tantalum capacitors.

In Figure 17, the dashed vertical line represents the typical DC leakage current limit for a 150μF, 6.3V device while the solid vertical line represents the limit for a tantalum polymer device. It's clear that one of these capacitors would not have met the MnO_2 limit and several others are pretty close. This is typical for tantalum polymer capacitors from all manufacturers. Tantalum polymer capacitors generally have much higher leakage current than is true for comparable MnO_2-based capacitors, and the median value of the distribution is usually closer to the catalog limit for tantalum polymer capacitors than is true for MnO_2-based capacitors.

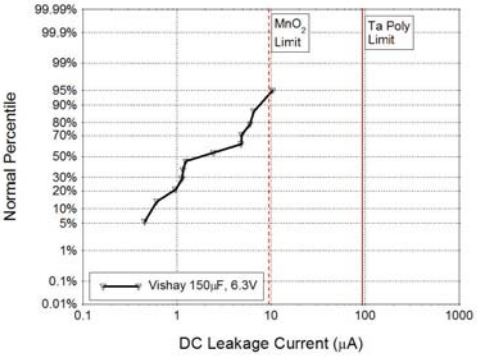


Figure 17. Typical DCL Data for 150μF, 6.3V Tantalum Polymer Capacitor (Data Courtesy of Vishay-Sprague)

Typical impedance and ESR data for a KEMET 330μF, 6.3V tantalum polymer capacitor appear in the swept-frequency plot of Figure 18. This plot was generated with the KEMET-Spice capacitor modeling program that is available without cost to customers. Similar software is available from other manufacturers as well. While the data of Figure 18 are not laboratory-measured data, they are remarkably similar to such laboratory-measured data.

In addition to interactive graphs, the software can provide numerical values for the discrete components of an equivalent electronic circuit that behaves very much like the actual capacitors over a wide range of frequencies. These equivalent circuit models can then be incorporated into a larger computer models of a customer's circuit to simulate expected capacitor behavior over wide ranges of frequency, temperature, and voltage. These models are typically based on the RC-ladder structure that was schematically described in Figure 5.

Generally speaking, there is little difference in the overall appearance of impedance and ESR graphs for tantalum polymer capacitors and MnO_2-based tantalum capacitors, with the exception that the ESR is lower for the tantalum polymer capacitors at frequencies above roughly 1kHz. These lower ESR values reflect the improved conductivity of the polymer cathode material.

Near resonance, the impedance values for tantalum polymer capacitors are lower than for MnO_2-based tantalum capacitors, reflecting the lower ESR. However, the impedance away from resonance is essentially similar for both polymer- and MnO_2-cathode devices. The downward slope of the impedance curve prior to resonance is dominated by the capacitive reactance and the upward slope after resonance is dominated by inductive reactance. These parameters are similar for both capacitor styles.

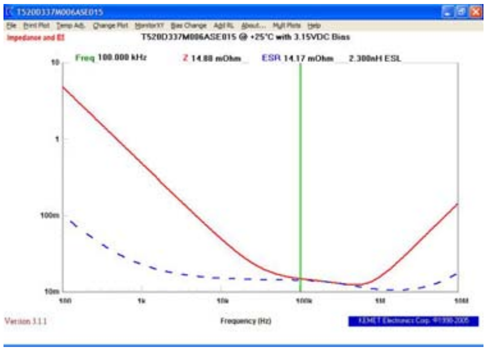


Figure 18. Modeled Impedance and ESR versus Frequency Curve for 330μF, 6.3V Tantalum Polymer Capacitor (Data from KEMET Spice Model Software).

Figure 19 presents a comparison of the capacitance roll-off behavior of various styles of tantalum capacitors. It was stated earlier that less capacitance roll-off is observed at a given high frequency if the resistance values in the RC-ladder of Figure 5 are lower as would be the case for use of a conductive polymer cathode having higher conductivity than MnO_2. Less capacitance roll-off is also observed if the physical length of the ladder is shortened. This is analogous to reduced loss in a short transmission line versus a longer transmission line fabricated from the same materials.

Both of these concepts are validated by the data of Figure 19. The most poorly performing device is the single-anode MnO_2-based capacitor which demonstrates initiation of roll-off slightly above 1kHz. If the single MnO_2-based capacitor element is replaced by three very thin MnO_2-based elements connected in parallel, significant roll-off doesn't occur until frequencies above 10kHz. This demonstrates the beneficial effect of reducing the length of the RC-ladder structure by making the capacitor elements thinner.

The remaining curve demonstrates the superior performance that is achieved by combining the benefits of multiple thin capacitor elements with the conductivity enhancement provided by the conducting polymer. It is expected that a single-anode tantalum polymer device would have performed similarly to the multiple-anode MnO_2 device, but the multiple-anode tantalum polymer capacitor demonstrates clearly superior performance. For this capacitor, significant roll-off is postponed until frequencies well above 100kHz.

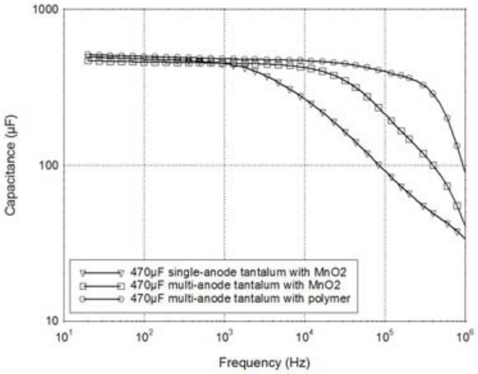


Figure 19. Typical Capacitance Roll-off with Frequency for Various Tantalum Capacitors (Data from KEMET; CARTS-Europe 2002, pg. 64).

Typical Dielectric Robustness

Not all tantalum capacitors from a given lot have similar dielectric robustness. It is not unusual for the breakdown voltages during rapid charging to vary over a range of 2:1 to 3:1 or more. Of course there is not much concern about the devices at the high end of the range, it is the relatively few at the low end of the range that cause almost all of the problems with turn-on failures.

Figure 20 contains dielectric breakdown data collected on large samples of 220µF, 10V, MnO_2-based tantalum capacitors. There are 5 curves that represent statistical distributions of breakdown voltage when large samples of capacitors from a randomized population were rapidly charged through various series resistances (the resistance includes the capacitor's ESR). Although not specifically pertinent to the topic at hand, it is clear from the data that the breakdown voltages are significantly affected by the value of series resistance, this effect can be quantified, and higher series resistance leads to higher breakdown voltages.

For a value of total series resistance of 0.35Ω, it is seen that the breakdown voltages range from 8V to 26V or 0.8 to 2.6 times rated voltage, a range of 3.25:1. This is fairly typical performance for MnO_2-based tantalum capacitors. Had these capacitors been 100% surge current tested at full rated voltage during production testing, probably none of the capacitors would have failed below rated voltage. This would have tightened the range to 2.6:1.

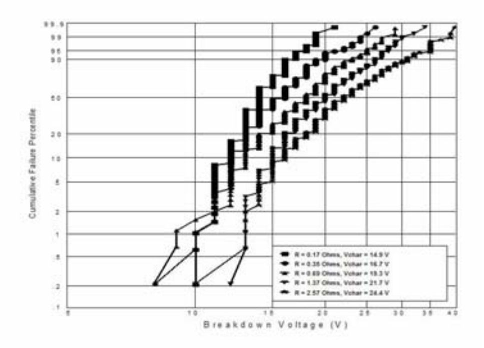


Figure 20. Breakdown Voltages for 220µF, 10V Tantalum MnO_2 Capacitors under High Inrush Current Conditions with Various Series Resistance Values (Data from KEMET; CARTS 2001, pg. 153).

In contrast, Sanyo provided similarly-collected breakdown data for some 150µF, 10V tantalum polymer capacitors. These data appear in Figure 21 and are generally representative of 10V tantalum polymer capacitors.

The external series resistance was 0.33Ω and it is estimated that the ESR of the capacitors was roughly 20mΩ. Thus the total series resistance was approximately 0.35Ω, the same total series resistance as was used to generate the 0.35Ω MnO_2-based curve of Figure 20. The range of breakdown voltages is 1.75 to 2.6 times rated voltage, or roughly 1.5:1. This is a much smaller spread of breakdown voltages than was seen for the MnO_2-based tantalum capacitors in Figure 20. It is common that the range of breakdown voltages for tantalum polymer capacitors is smaller than observed for MnO_2-based devices and that the first breakdown occurs at much higher voltage.

The first significant observation is that both styles of capacitors had maximum breakdown voltage of 2.6 times rated voltage. While this exact agreement is probably coincidental, the similarity of the values is noteworthy, and likely represents the existence of an upper limit to dielectric robustness that is related to the dielectric formation voltage (likely to be in the neighborhood of 3 times rated voltage).

The second observation is that the first breakdown for the tantalum polymer capacitors occurs at 1.75 times rated voltage. This is roughly twice as high as the lowest voltage seen for the MnO_2-based capacitors. While the precise numerical value of this advantage varies somewhat with manufacturer and rated voltage, tantalum polymer capacitors consistently outperform equivalent MnO_2-based capacitors on this test.

As was previously mentioned, it is thought that this improved robustness against high inrush current results from a combination of the reduced processing temperatures during polymerization and the relative softness of the polymer with respect to hard, crystalline MnO_2. It is also thought that this advantage is *not* due to the electrical properties of the polymer or its processing chemistry. This hypothesis is supported by the increased DC leakage current seen in tantalum polymer capacitors as is demonstrated in Figure 17.

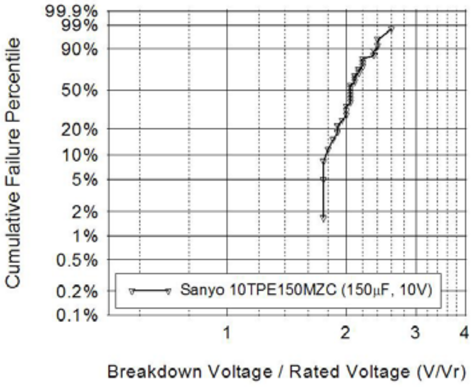


Figure 21. Breakdown Voltages for 150μF, 10V Tantalum Polymer Capacitors under High Inrush Current Conditions with ~0.35Ω Series Resistance (Data Courtesy of Sanyo).

Typical Reliability Performance

The most absolute measure of reliability for tantalum capacitors is time-to-failure during low-impedance DC lifetests. While other important reliability tests exist, it still remains true that when failure rates are discussed, it is data from hot, dry, DC lifetests that dominate the discussion. Early lifetesting was typically performed at 85^{o}C and rated voltage. However, unless the sample sizes are exceedingly large, it takes a very long time to collect a useful amount of failure data in a practical time frame at these conditions.

To address this issue, accelerated lifetests were developed. Times-to-failure can be reliably accelerated by use of voltages higher than rated voltages and/or temperatures above 85^{o}C. The data of Figure 22 are times-to-failure for a population of MnO_2-based tantalum capacitors that were tested at 1.32 times rated voltage at 85^{o}C. Estimates vary, but the acceleration formula of MIL-PRF-55365 indicates that the time acceleration due to this applied voltage is approximately 400. The data are plotted on a Weibull scale that generates straight lines from data that fit a Weibull distribution.

One characteristic of such data is that if the Weibull β parameter (slope of the data) is less than one, the failure rate of the devices is decreasing in time. Manufacturers take advantage of this fact to “Weibull grade” tantalum capacitors to known reliability levels by lifetesting capacitors long enough at accelerated conditions to weed out enough of the early failures that the failure rate falls to the desired low level.

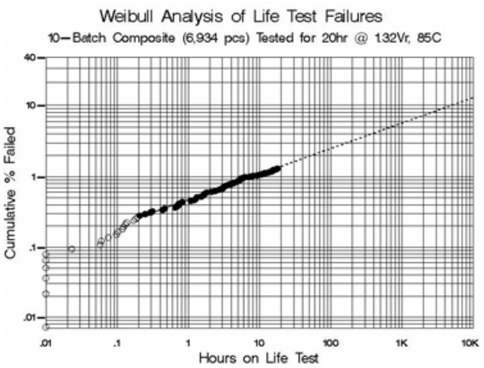


Figure 22. Typical Time-to-Failure Performance of MnO_2 Tantalum Capacitors during Weibull Failure Rate Grading (Data Courtesy of KEMET).

For the data of Figure 22, the β parameter is 0.36 which is much less than 1. If one works through the calculations presented in MIL-PRF-55365 using the data of Figure 22, he finds that after 10 hours of lifetesting at 1.32 times rated voltage, the failure rate has fallen from a very high initial value to less than 0.1% per 1000 hours. Armed with this information, typically gathered on a sample of capacitors from a given lot, the manufacturer would then subject the rest of the lot to low-impedance lifetest for 10 hours at 85°C and 1.32 times rated voltage and ship the survivors with confidence that the surviving population would demonstrate the same 0.1%/1000 hour failure rate. This strategy has been used with much success to establish the failure rate of MnO_2-based solid tantalum capacitors for military and aerospace applications.

However, when one attempts to follow the same path with tantalum polymer capacitors, the results are not the same. Generally, even after hundreds of hours at 1.32 times rated voltage and 85C, no failures are observed at all, or if there is a rare failure, it occurs at the very start of the test and no more failures are subsequently observed. So what value of β do you use if no failures occur? How do you estimate the failure rate if there are no failures?

Basically the whole approach doesn't work very well for almost all tantalum polymer capacitors because of the shortage of failures. **But this is a good thing**. What it means is that these capacitors are inherently more reliable than MnO_2-based tantalum capacitors. Indeed, field experience indicates very few failures, and almost all of those occur immediately after turn on. Moreover, it is thought that the few turn-on failures (usually measured in parts per million) are predominantly the result of damage to the dielectric that is caused by the thermo-mechanical stresses of reflow mounting rather than by defects resulting from the manufacturing process (the MnO_2 impregnation process is thought to be the cause of almost all early failures of MnO_2-based capacitors).

Because of the shortage of lifetest failures of tantalum polymer capacitors, there was curiosity regarding the expected life of these devices. To explore this question, very highly accelerated lifetests were performed. Figure 23 shows time-to-failure for four such lifetests on 100μF, 6V tantalum polymer capacitors. The test voltage was 9.6V, or 1.6 times rated voltage. Test temperatures ranged from 85°C to 145°C. These data and data collected at other combinations of voltage and temperature lead to acceleration models that predicted very long life at rated voltage and 85°C. Specifically the first failure under maximum rated conditions for the capacitors whose data appear in Figure 23 is not expected for roughly 100 years. Little de-rating is needed for reliable application of these capacitors, and the industry typically recommends derating by only 20% instead of 50% for MnO_2-based tantalum capacitors.

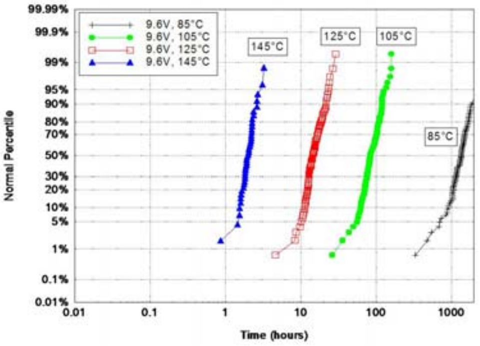
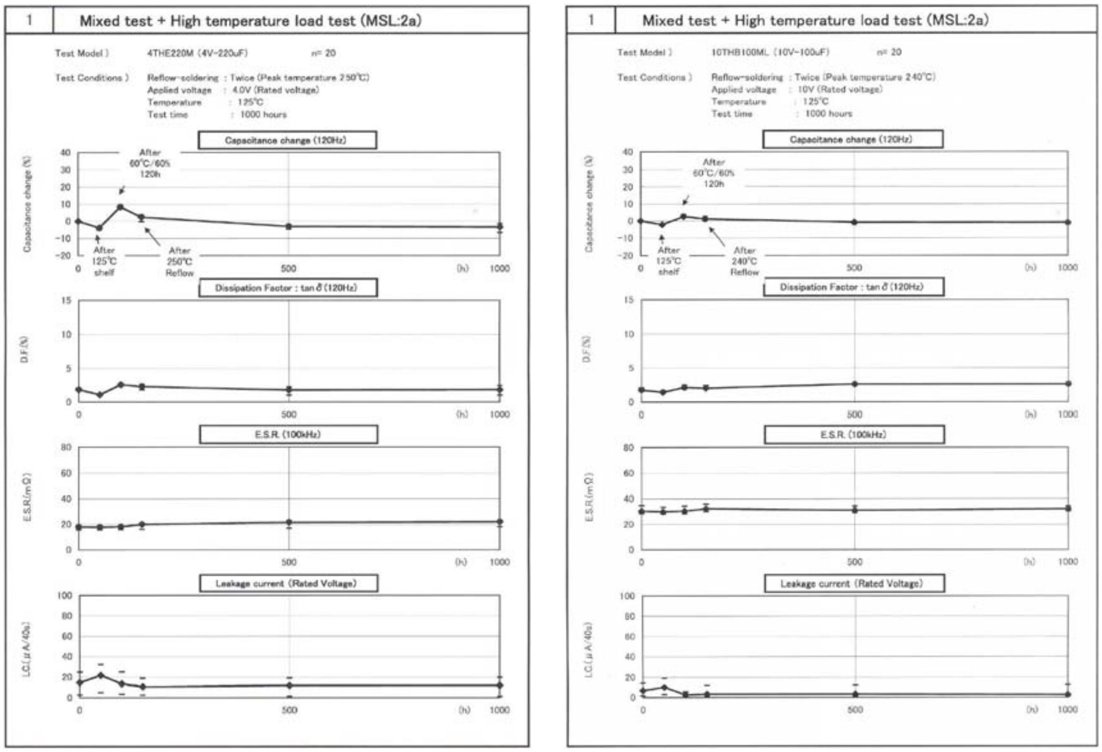


Figure 23. Typical Time-to-Failure Performance of 100μF, 6V B-Case Tantalum Polymer Capacitors during Highly Accelerated Lifetesting (Data from KEMET; CARTS 2004, pg. 120).

There is something else important about the data of Figure 23. The failure distributions are very tightly distributed in time. If these data were plotted on a Weibull scale, the β parameter would be significantly greater than one, indicating a rapidly increasing failure rate. This means that the dielectric is wearing out under the applied stress. There is so little dielectric damage done during manufacturing that we can actually observe and model the wearout of tantalum pentoxide, and we see very little difference between the best and worst performers in the sample.   This is in direct contrast with the times-to-failure presented in Figure 22 for MnO_2-based capacitors where the failures are distributed over many orders of magnitude in time. Such wide distribution of times-to-failure indicates an equally-wide range of dielectric damage inflicted during the manufacturing process.

Typical Environmental Stability

Other manufacturer-supplied test data shed light on the typical behavior of tantalum polymer capacitors after exposure to various environmental stresses. Sanyo provided data that describe the typical response of their capacitors to dry heat, moisture, solder reflow conditions, and DC lifetest at rated voltage and 125°C. Data for two device types appear in Figure 24.


1 Mixed test + High temperature load test (MSL:2a)

Test Model) 4THE220M (4V-220uF) n= 20

Test Conditions) Reflow-soldering : Twice (Peak temperature 250°C)
Applied voltage : 4.0V (Rated voltage)
Temperature : 125°C
Test time : 1000 hours

1 Mixed test + High temperature load test (MSL:2a)

Test Model) 10THB100ML (10V-100uF) n= 20

Test Conditions) Reflow-soldering : Twice (Peak temperature 240°C)
Applied voltage : 10V (Rated voltage)
Temperature : 125°C
Test time : 1000 hours

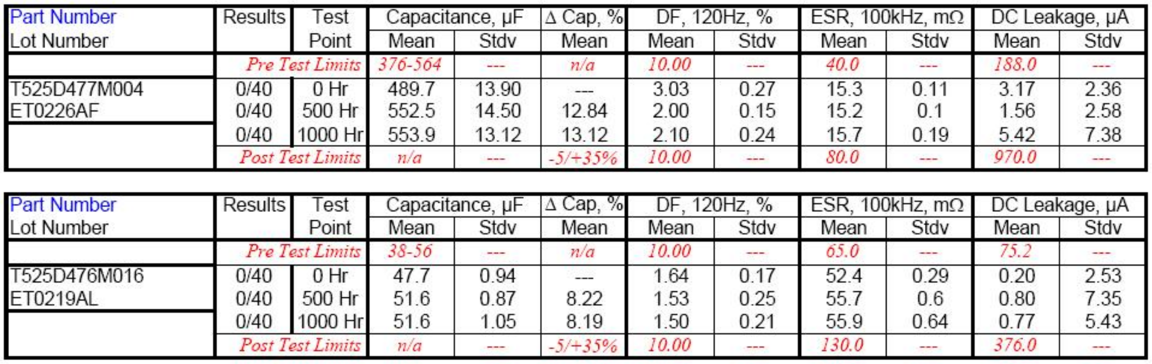
Figure 24. Typical Moisture Sensitivity and 125°C Lifetest Performance of 220μF, 4V and 100μF, 10V Tantalum Polymer Capacitors (Charts Courtesy of Sanyo).

The data of Figure 24 demonstrate that tantalum polymer capacitors absorb some moisture from the ambient environment and this moisture affects the capacitors' electrical behavior. Moisture absorption is also common MnO_2-based tantalum capacitors that have plastic-encapsulation. The effect of the moisture is inferred by detecting parametric electrical shifts after drying the capacitors at 125°C for an unspecified period. Removing the moisture by drying at 125°C causes the capacitance and dissipation factor to drop slightly and causes the DC leakage current to increases moderately. ESR is largely unaffected.

After this dry-out step, the capacitors are exposed to 60°C, 60%RH moisture conditions for 120 hours to simulate controlled exposure to atmospheric moisture. Not surprisingly, this moisture exposure increases the capacitance and dissipation factor while reducing the DC leakage current. Again, ESR remains stable. It is significant to note that DC leakage current typically decreases with moderate exposure to moisture and increases as the capacitor dries out. The precise cause of this DC leakage current behavior is unknown and is typically opposite of the response for MnO_2-based tantalum capacitors. However, the effect on capacitance, DF, and ESR is similar to what is expected for MnO_2-based tantalum capacitors.

After moisture exposure, the capacitors are exposed to two reflow profiles having peak temperature of 250°C. The high peak temperature is sufficient to drive off substantial internal moisture as is reflected in the reduction of capacitance and dissipation factor to levels similar to those observed in the pre-test state. DC leakage current appears to decline slightly or stay the same. ESR increases slightly, almost certainly due to thermo-mechanical stresses on the interfaces among the cathode layers. These preliminary stresses are followed by a steady-state DC lifetest at full rated voltage and 125°C. All parameters remain substantially stable for 1000 hours.

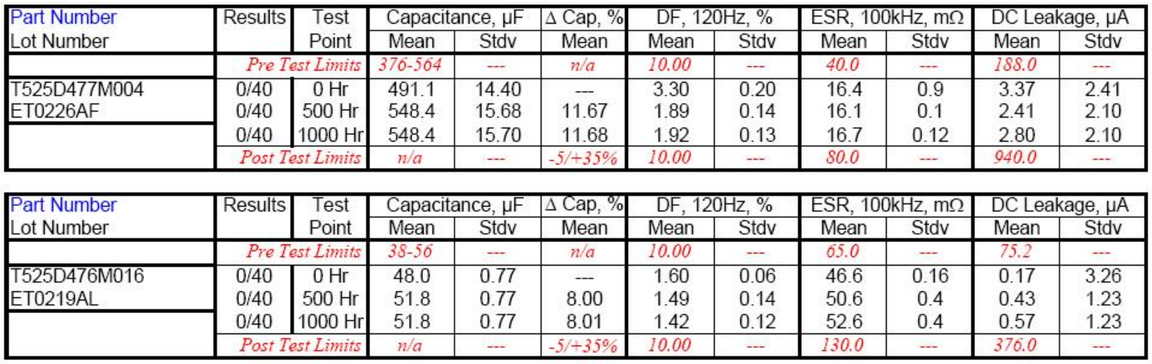
KEMET provided 0, 500, and 1000 hour data for two tantalum polymer part types that were exposed to 85°C, 85%RH humidity conditions with and without rated voltage applied. The part were 470µF, 4V and 47µF, 16V capacitors. Data for the humidity test with rated voltage applied appear in Table 1 while the passive humidity data appear in Table 2.



Part Number Lot Number	Results	Test Point	Capacitance, µF		Δ Cap, %	DF, 120Hz, %		ESR, 100kHz, mΩ		DC Leakage, µA	
			Mean	Stdv	Mean	Mean	Stdv	Mean	Stdv	Mean	Stdv
		Pre Test Limits	*376-564*	---	*n/a*	*10.00*	---	*40.0*	---	*188.0*	---
T525D477M004 ET0226AF	0/40	0 Hr	489.7	13.90	---	3.03	0.27	15.3	0.11	3.17	2.36
	0/40	500 Hr	552.5	14.50	12.84	2.00	0.15	15.2	0.1	1.56	2.58
	0/40	1000 Hr	553.9	13.12	13.12	2.10	0.24	15.7	0.19	5.42	7.38
		Post Test Limits	*n/a*	---	*-5/+35%*	*10.00*	---	*80.0*	---	*970.0*	---

Part Number Lot Number	Results	Test Point	Capacitance, µF		Δ Cap, %	DF, 120Hz, %		ESR, 100kHz, mΩ		DC Leakage, µA	
			Mean	Stdv	Mean	Mean	Stdv	Mean	Stdv	Mean	Stdv
		Pre Test Limits	*38-56*	---	*n/a*	*10.00*	---	*65.0*	---	*75.2*	---
T525D476M016 ET0219AL	0/40	0 Hr	47.7	0.94	---	1.64	0.17	52.4	0.29	0.20	2.53
	0/40	500 Hr	51.6	0.87	8.22	1.53	0.25	55.7	0.6	0.80	7.35
	0/40	1000 Hr	51.6	1.05	8.19	1.50	0.21	55.9	0.64	0.77	5.43
		Post Test Limits	*n/a*	---	*-5/+35%*	*10.00*	---	*130.0*	---	*376.0*	---

Table 1. Typical 85°C, 85%RH Rated Voltage Humidity Performance of 470µF, 4V and 47µF, 16V Tantalum Polymer Capacitors (Table Courtesy of KEMET).



Part Number Lot Number	Results	Test Point	Capacitance, µF		Δ Cap, %	DF, 120Hz, %		ESR, 100kHz, mΩ		DC Leakage, µA	
			Mean	Stdv	Mean	Mean	Stdv	Mean	Stdv	Mean	Stdv
		Pre Test Limits	*376-564*	---	*n/a*	*10.00*	---	*40.0*	---	*188.0*	---
T525D477M004 ET0226AF	0/40	0 Hr	491.1	14.40	---	3.30	0.20	16.4	0.9	3.37	2.41
	0/40	500 Hr	548.4	15.68	11.67	1.89	0.14	16.1	0.1	2.41	2.10
	0/40	1000 Hr	548.4	15.70	11.68	1.92	0.13	16.7	0.12	2.80	2.10
		Post Test Limits	*n/a*	---	*-5/+35%*	*10.00*	---	*80.0*	---	*940.0*	---

Part Number Lot Number	Results	Test Point	Capacitance, µF		Δ Cap, %	DF, 120Hz, %		ESR, 100kHz, mΩ		DC Leakage, µA	
			Mean	Stdv	Mean	Mean	Stdv	Mean	Stdv	Mean	Stdv
		Pre Test Limits	*38-56*	---	*n/a*	*10.00*	---	*65.0*	---	*75.2*	---
T525D476M016 ET0219AL	0/40	0 Hr	48.0	0.77	---	1.60	0.06	46.6	0.16	0.17	3.26
	0/40	500 Hr	51.8	0.77	8.00	1.49	0.14	50.6	0.4	0.43	1.23
	0/40	1000 Hr	51.8	0.77	8.01	1.42	0.12	52.6	0.4	0.57	1.23
		Post Test Limits	*n/a*	---	*-5/+35%*	*10.00*	---	*130.0*	---	*376.0*	---

Table 2. Typical 85°C, 85%RH Passive Humidity Performance of 470µF, 4V and 47µF, 16V Tantalum Polymer Capacitors (Table Courtesy of KEMET).

Performance for both humidity tests (with and without voltage applied) is comparable. As was observed in the Sanyo data, capacitance increased with exposure to humidity. For the 4V parts the increase was 12-13%, similar to the dry-to-wet capacitance change for the 4V Sanyo parts in Figure 24. The capacitance of the 16V KEMET parts increased about 8%.

Dissipation factor fell slightly after the initial measurements and then remained substantially stable. This is different from the increased DF for the Sanyo capacitors after moisture exposure. The reason for this discrepancy is unknown and may represent a measurement error during the zero-hour measurements. ESR was substantially stable for the 4V parts and increased slightly for the 16V parts. DC leakage was substantially stable. Although the test conditions were somewhat different for the Sanyo and KEMET tests, overall performance was comparable.

An important point must be made regarding the passive humidity test data of Table 2. The data indicate little degradation of performance after 1000 hours of exposure to 85^{o}C, 85%RH. It must be noted that these data represent substantially *superior* performance of tantalum polymer capacitors versus MnO_2-based tantalum capacitors. MnO_2-based tantalum capacitors typically perform poorly on passive humidity tests and suffer substantially increased DC leakage after 1000 hours at 85^{o}C, 85%RH. This DC leakage current increase is typically blamed on the migration of silver ions to the surface of the dielectric through porosity in the MnO_2 cathode layer.

The reasons for the superior performance of tantalum polymer capacitors on this test are not known with certainty. Some speculate that the polymer cathode coating is less porous than the MnO_2 layer and physically blocks migration of silver ions to the dielectric's surface. Others think that the effective surface charge of the dielectric is altered by the polymerization process such that silver ions are repelled from the dielectric.

Summary, Suitability for Space Applications, and Path Forward

The primary objective of this FY05 task is to introduce the tantalum polymer capacitor technology and contrast it with the well-established MnO_2-based technology. As a foundation for this introduction, the origins of the solid tantalum capacitor are reviewed and the basics of its internal construction are described.

The case for lower ESR is made and the original MnO_2 cathode material of the solid tantalum capacitor is identified as a major contributor to total device ESR. Various candidate materials are identified as potential replacements for MnO_2, and the conductive polymer PEDT is identified as the material of first choice, while PPY is identified as a strong competitor. Processing options for creation of the conductive polymer are identified and typical assembly steps for the resulting capacitors are photographically documented.

Typical electrical characteristics of tantalum polymer capacitors are then presented. It is emphasized that the only significant electrical performance differences versus MnO_2–based capacitors are the desired 2 to 3 times reduction in ESR and an undesired, but manageable increase in DC leakage current. In spite of the higher DC leakage current, the general robustness of the dielectric of lower-voltage tantalum polymer capacitors is demonstrated to be significantly superior to that of MnO_2-based capacitors and this robustness reflects itself in superior long-term reliability on DC lifetests. This advantage does not hold for higher-voltage devices. Finally, tantalum polymer capacitors are shown to react to environmental stresses in a generally predictable fashion, but appear to be more robust than MnO_2-based capacitors to passive humidity exposure.

Suitability for Space Applications

Some observations are in order regarding the suitability of tantalum polymer capacitors for use in spacecraft. The pertinent environmental factors are radiation and vacuum.

In comparison with semiconductor devices, MnO_2-based tantalum capacitors are generally considered to be insensitive to radiation. Small shifts of roughly 10 mV/krad (Si) are observed in the open-circuit voltage of previously discharged capacitors, but this effect is transient and generally only of interest in high-impedance, small-signal circuits. However, tantalum capacitors are rarely used in such circuits, even when radiation is not of concern. Moreover, radiation-generated oxide defect concentrations for doses in excess of 10 Mrad (Si) are estimated to be orders of magnitude lower than intrinsic defect levels and are not thought to significantly impact long-term performance or reliability. Since the same dielectric and dielectric thickness are employed in tantalum polymer capacitors, these devices are expected to be similarly insensitive to radiation effects.

Vacuum impacts tantalum polymer capacitors in two ways. Convection is eliminated as a cooling mechanism and all internal moisture will be lost via diffusion through the plastic case.

Because a significant cooling mechanism is lost, higher device temperatures are expected in vacuum for similar levels of power dissipation. This is equally true for capacitors with MnO_2 and conductive polymer cathodes. However as previously discussed, the conductivity of the polymer cathode begins to degrade at lower temperatures than are true for MnO_2. Thus, careful attention must be paid to thermal design to avoid chronically exceeding peak temperature ratings, a condition which can increase ESR and capacitance roll-off.

The second impact of vacuum is that all internal moisture will eventually be lost via diffusion through the plastic case. As previously discussed, it is expected that the DC leakage current of tantalum polymer capacitors will rise somewhat as the moisture level falls. However, no clear connection has been made between this effect and loss of long-term reliability, so it appears that this effect is only of concern when proper circuit operation depends on very low and stable DC leakage current. However, almost all tantalum polymer capacitors are used in power circuits where increases in leakage current that remain below specification limits are not generally of significant concern.

Path Forward

The FY06 task will involve competitive testing of representative tantalum polymer capacitors. Direct comparisons will be made of similar part types from multiple vendors, and appropriate contrasts will be drawn against MnO_2-based capacitors of similar capacitance and voltage ratings. Results of this competitive evaluation will be published in FY06 as the phase-two NEPP task deliverable for this project.