REPLACING MnO$_2$ WITH CONDUCTIVE POLYMER IN SOLID TANTALUM CAPACITORS

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Abstract

The solid tantalum capacitor was born at the same time as the invention of the transistor, in the same Bell Laboratories in 1948. It has grown in piece volume as applications have increased because of surface mount demands and performance improvements. The performance improvements have been pushed by the increased demands of newer applications as well as continuing process and materials development throughout the years. The proposed change in materials to the conductive polymer constitutes the first deviation from the solid state materials of composition going all the way back to the Bell Laboratories. The conductive polymer that we are now incorporating in this capacitor, in place of the manganese dioxide (MnO$_2$), represents an enormous shift in material performance. The MnO$_2$ presented the tantalum with a capability of becoming a solid state device, but it also carried some undesirable traits as a cathode plate contact.

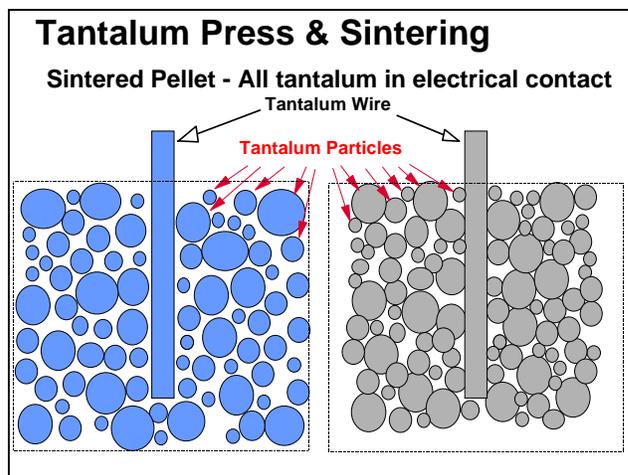## Construction - Form & Dielectric

The tantalum capacitor is known as such because the tantalum metal forms the basis of the dielectric. In both the tantalum and aluminum capacitors, the dielectric is actually an oxide layer of the base metal.
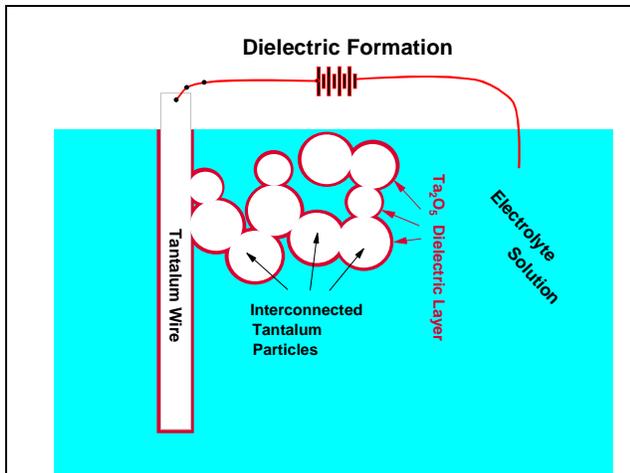
The construction of the tantalum capacitor begins with tantalum powder. At first this powder was granular, and more recent developments have presented this metal in the form of flakes. The flake represents an optimization of surface area to volume over that of the grain, and this relates directly to volumetric efficiency of capacitance per unit of volume. Unlike the aluminum capacitor that uses the metal in a foil or plate form, the metal for the tantalum capacitor is formed into a pellet. This pellet is a compacted collection of tantalum particles pressed together; but there is within the volume of this pellet, an enormous amount of open or void volume. These voids exist as the geometry of the particles create point contacts of the particles to each other in random fashion, leaving large gaps between most of the particles. These voids run around the particle, and create channels or tunnels that are interconnected throughout the pellet, extending to the outside surfaces. In many cases, this void channeling within the pellet is compared to the structure of a sponge, both having enormous void volume within their structures.

A tantalum riser wire is connected to the tantalum pellets to allow a commonality of electrical contact for all of the tantalum. These pressed pellets are then sintered in a vacuum at temperatures approaching 2,000°C, to expand the bond areas of the contact points. It is also during this sintering process that contaminants are pulled out of the tantalum particles that may have been introduced during the pressing process. The volume of the pressed pellet decreases slightly because of this sintering process.

The next step in the process is the formation of the dielectric on all "exposed" surfaces of the tantalum metal. This is accomplished by immersing the pellet into an electrolyte solution and passing a current through the system. Where the electrolyte has filled the channels and is in

Tantalum Press & Sintering

Sintered Pellet - All tantalum in electrical contact

Tantalum Wire

Tantalum Particles

Dielectric Formation

Tantalum Wire · Interconnected Tantalum Particles · Ta_2O_5 Dielectric Layer · Electrolyte Solution

Interconnected Tantalum Particles · Tantalum Wire · MnO_2 Penetration into Channels · Ta_2O_5 Dielectric Layer

contact with the tantalum particles and the wire, oxygen from the electrolyte combines with the tantalum to form an oxide. The desired oxide is tantalum pentoxide (Ta_2O_5) and this is created by proper selection of the electrolyte. The depth and consistency of the Ta_2O_5 layer is usually determined by the time, current, and voltage of the process. As the dielectric is created and supports a voltage, the thickness of the dielectric is in the range of 18 angstroms per volt (18Å/v).

At this point in the construction, the electrolytic capacitor exists as the dielectric (Ta_2O_5) now separates the pure tantalum metal on one side and the electrolyte solution on the other. The voltage developed during construction actually creates charge along the opposing surfaces of the oxide material. The construction of a wet tantalum capacitor would replace the forming electrolyte solution with one more favorable in performing the task as cathode plate contact. One favorable characteristic of the electrolyte would include a capability of reformation. In this mode, the dielectric can collapse or fail at a point along the surface, but the polarization of the capacitor and the electrolyte solution act in a manner that recreates a new dielectric in place of the failed point. This reformation process is required in electrolytic capacitors because the formed oxide layer can have deficiencies of formation due to impurities in the base metal, slightly below its surface, or within the electrolyte solution. In aluminum capacitors, there is a time dependent deterioration of the oxide layer, when the capacitor is kept in an "unbiased" state. To overcome this deterioration, a DC voltage is slowly ramped up across the capacitor to "reform" the dielectric.
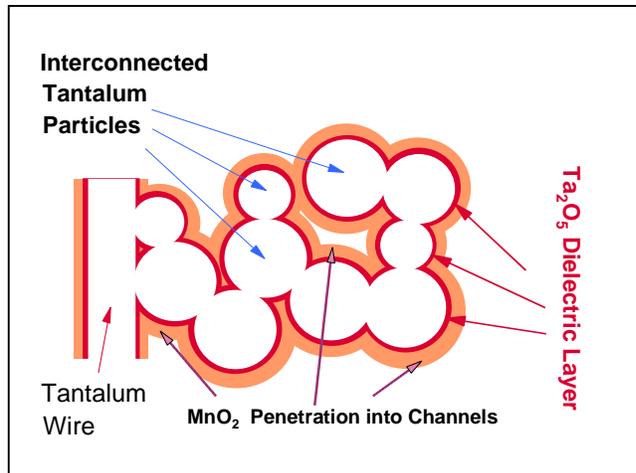
Construction — Cathode Plate

Defects that exist within the oxide dielectric are there regardless of what type of construction is next followed. Using an electrolyte without reformation properties or depositing a conductive material along the internal surfaces of the tantalum pentoxide will create a capacitor with high initial leakage that will deteriorate until a short is created, and the capacitor cannot function. The semiconductor material manganese dioxide (MnO_2) is a solid state material with a unique property. The highest oxide form (MnO_2) is the most conductive of all possible states. Conversion from this high oxide state to a lower one (e.g., Mn_2O_3), increases the resistivity of the material dramatically. Typically this conversion process takes place at a temperature range of 400°C to 480°C.

The cathode plate in a solid tantalum capacitor is created by a successive series if dip and dry processes that result in a coating of MnO_2 along all exposed surface of Ta_2O_5, within and around the tantalum pellet. This process has been refined over the many years to the point where we believe we have reached an optimum in this material capability. We have created special low ESR versions of capacitors that utilize special particle size requirements of the tantalum as well as an elongated and multiple process for depositing thick and consistent layers of MnO_2 throughout the tantalum pellet.

The MnO_2 now extends into the pellet and covers the outside surface of the pellet. The pellet is then dipped in a carbon solution, and then in silver paints and cured. The silver paint surface is connected to a lead-frame element with a conductive epoxy and the tantalum riser wire is

Tantalum Construction
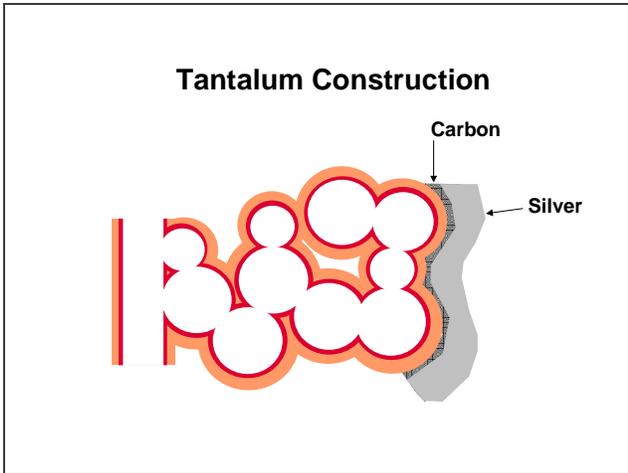
welded to another lead-frame element. The entire unit is molded with the lead-frame extending out through the plastic.

MnO_2 — the angelic protector.

The MnO_2 is in contact with a point in the dielectric layer that fails or draws high currents focused to that point. This in turn also creates a current that is focused to that point within the MnO_2. This localized current eventually creates enough heat localized to this point within the MnO_2 layer, to cause a conversion of the manganese oxide to a lower oxide level such as Mn_2O_3. This conversion causes a restriction of current to the fault site, effectively shutting the site off, or removing it from the capacitor. We refer to this as "self-healing," although in fact, no defect sites are healed — they are merely removed from the circuit. Every capacitor built is exercised in this manner as we apply a voltage through a restricting resistance to activate the healing mechanism. In our process we refer to

Electrical Conditioning

Healing Effect of MnO_2 Layer
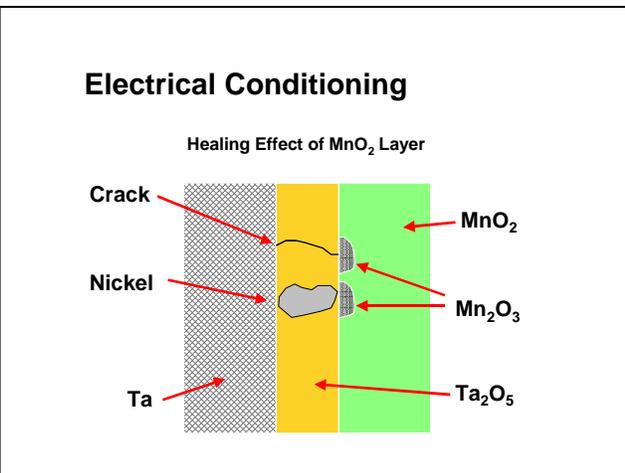
this event as aging the capacitor.

This healing mechanism causes the decreasing leakage apparent in solid tantalum capacitors as application life increases. More sites within the dielectric are healed and removed causing the leakage to decrease with time as the voltage is applied.

This healing mechanism is extremely important because although there is a great deal of care exercised in the process of creating the oxide layer on the exposed surfaces of the anode material, there are always a finite number of faults associated with the enormous surface area required for the electrolytic capacitors. Contamination on the PPM level as well as stresses created within the structure during the process, instigate sites within the dielectric that are weakened or undeveloped. These sites when exposed to a specific voltage stress, collapse and allow current to flow through what is supposed to be, an insulative layer.

The momentary reductions of voltage during these healing activities are sometimes referred to as scintillations. The collapse is initiated by the voltage stress across the dielectric reaching a level high enough to cause the leakage current to accelerate dramatically. If the current feeding the mechanism is limited, then the time necessary for the conversion to take place is guaranteed and the effect is a scintillation, or momentary and partial collapse of the energy required for healing or conversion. Because this process is triggered by the current and requires heat generation, there is a time element involved. The time to activate the healing mechanism and shut the current down has been measured in milliseconds. The heat conversion required heat generation and energy expenditure — this energy is supplied by external current as well as by the stored energy of the capacitor.

MnO_2 — the evil fuel.

The key to "healing" is the allowance of time for the conversion to take place through the restriction of current. If this time is not allotted for, then the region of Ta_2O_5 dielectric involved with the leakage site can initiate another failure mechanism. The Ta_2O_5 material is capable of existing in multiple states. As the created dielectric oxide material on the surface of the anode material, it is

amorphous — very much like glass. It has properties of glass in that it is translucent. This property allows a quick evaluation of the thickness of the oxide layer, which created different colored appearances for different thickness.

The Ta_2O_5 can also reside in a crystalline state, but this state is not insulative, and the conversion from the amorphous state to crystalline occurs at temperatures just above those for the MnO_2 conversion. This crystalline conversion moves radially out from the point of inception, involving more cross sectional area, spreading the currents across ever increasing areas of MnO_2, thereby diminishing the healing effect created with focused current into a singular site.

The temperature rise continues and then the tantalum metal starts to absorb oxygen. This failure may now reach a an exothermic reactive state if the tantalum can feed on a readily available source of oxygen. The MnO_2 acts as that source of oxygen. The MnO_2, which was once a savior for the tantalum capacitor, is now the villain as it feeds the consuming tantalum.

Performance Issue - need for replacement.

The problems associated with the failure of tantalum capacitors were under constant attack and improvement through process modification as well as material changes. The application field for these devices has spread from protected circuits into power applications with direct contact to the bus. An understanding of the difference between an apparent current related failures and voltage induced failures establishes this device as a viable component for this application. The tantalum is the preferred solution to this application because its effective series resistance (ESR) is much lower than similar aluminum electrolytics, and the SMD capability has no equivalent capacitive competition.
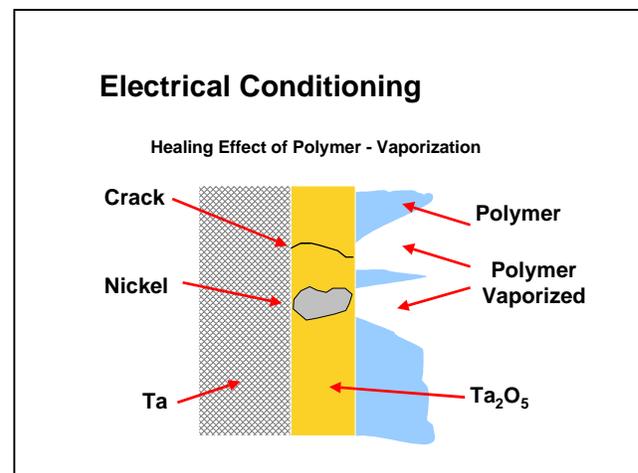
Yet for the improvement in ESR over other types, there is still the requirement to continue to target reductions in this parasitic element. Modifications in assembly techniques (low ESR product built specifically for low ESR), material refinements, and structural changes (multiple anode) have allowed great leaps to be made in the reduction of ESR, but the major contributor to this

parasite remains the MnO_2. As I stated before, this is a semiconductor material - a "poor" conductor. It has resistivity in the range of 2 to 6 ohm-cm. As long as we were using this material for the cathode plate contact, were saddled with its poor conduction. Until recently, we had never found a material that could offer better conductivity, offer a feasible manufacturing process, and still exhibit the self-healing capabilities of the MnO_2. The breakthrough came with investigations of conductive polymers.

There is a broad range of conductive polymers, and the choice of which one to use weighed many options. There were obvious characteristics such as conductivity and an ability to be deposited in the pellet structure as easily as the MnO_2. Most polymers have a low vaporization point (most between +85°C and +135°C) that would prohibit their use in IR reflow or conduction solder reflow processes. We needed a polymer with higher vaporization temperatures to also withstand the exposure to these temperatures in a life test environment. Finally, though this could have stopped all implementation, were cost factors.

The conductive polymer cathode

The healing mechanism of the polymer is one of two possible scenarios: the possible change of oxygen levels in the polymer causing a higher resistivity as with the MnO_2, or an evaporation process whereby heat causes the film to vacate the fault area. Either case establishes a fault correction mechanism in the polymer that allows this material to replace the MnO_2.

Electrical Conditioning

Healing Effect of Polymer - Vaporization

Crack — Nickel — Ta — Polymer — Polymer Vaporized — Ta_2O_5

The changing oxygen level in the polymer is theorized to begin as the Ta_2O_5 dielectric heats both the dielectric and the polymer film in the vicinity of the fault. The oxygen from the dielectric is released into the polymer film, thereby causing an increase of resistivity of the polymer film. This mechanism mirrors that of the healing action of the MnO_2 cathode material.

With the evaporation process, the method is that the heat is localized at the fault site, causing the heat to rise to a point greater than the vaporization temperature of the polymer, thereby vacating the conduction into the fault site.

In either case, the healing mechanism works, allowing a full production change of materials starting after the dielectric formation. The process of depositing the polymer is close to that of the MnO_2, both being a dip and dry process. The monomer is suspended in solution, and when dipped and dry, a polymerization on the surface of the anode takes place.

The conductivity of the polymer is much more than the MnO_2 — in the range of 20 to 100 times better. This difference does allow us to build capacitors with lower ESR, but the ESRs are not in the same ratio as the conductivity ratios of the polymer to MnO_2. The tradeoff is that we have 35 years of experience with depositing the MnO_2 in the anode structure, while we do not achieve the same laydown thickness of polymer as we do in MnO_2.

Performance and Models

We have tested the performance of the polymer

MnO₂ in RC-Ladder
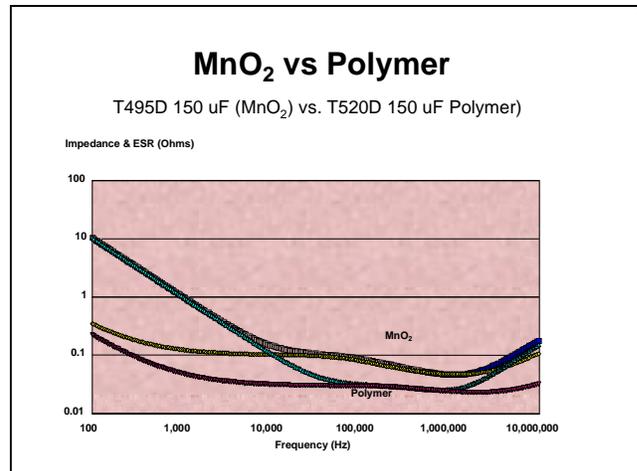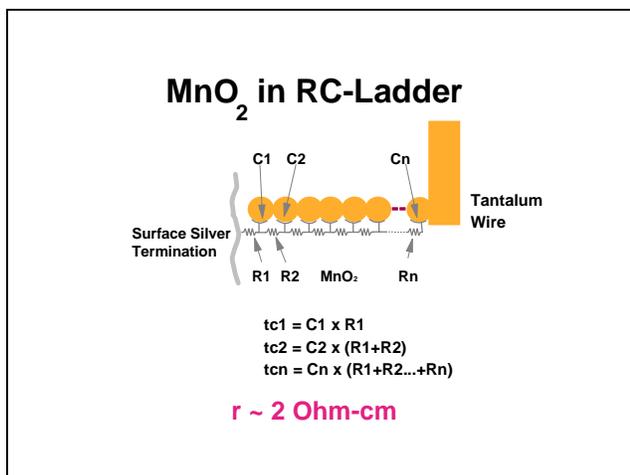
cathode over frequency and temperature, and we find that the models that we established for the MnO_2 cathode devices can be quickly adapted to the polymer devices.

Comparison of MnO_2 versus the polymer looking at impedance and ESR versus frequency in the figure below shows the improvement with the polymer. Across the entire frequency spectrum, the polymer consistently outperforms the MnO_2.

The electrical package is the same for both with the only difference being the material in the cathode connection. The *RC-Ladder* effect of capacitance roll-off remains, but the materials have caused the resistive elements in the *RC-Ladder* to be smaller. This in turn reduces the time constants for all capacitive elements, thereby causing these capacitances to respond to higher frequencies.

With the polymer, we are achieving ESRs that are so much lower that they cause the capacitance roll-off to occur at much higher frequencies. The graph of capacitance roll-off versus frequency at 25°C for the MnO_2 versus the polymer demonstrates how the resistive elements of the cathode connection, factor the available capacitance for these devices. This change also impacts the self-resonance of the capacitor, as more capacitance remains causing the self-resonance frequency to decrease.

From the data collected for the performance graphs, the polymer achieves self-resonance at ~480 kHz, whereas the MnO_2 device doesn't go into self-resonance until ~2 MHz. The capacitance at 480 kHz for the polymer is still 45 uF, while the other has only 20 uF remaining of the initial 150 uF. It is important to remember that the energy

delivery to the circuit (this is the primary purpose that a capacitor is used for), is proportional to the capacitance of the device — the larger the capacitance the greater the energy deliverable.

Capacitance Roll-Off

T495D 150 uF (MnO_2) vs. T520D 150 uF (Polymer)
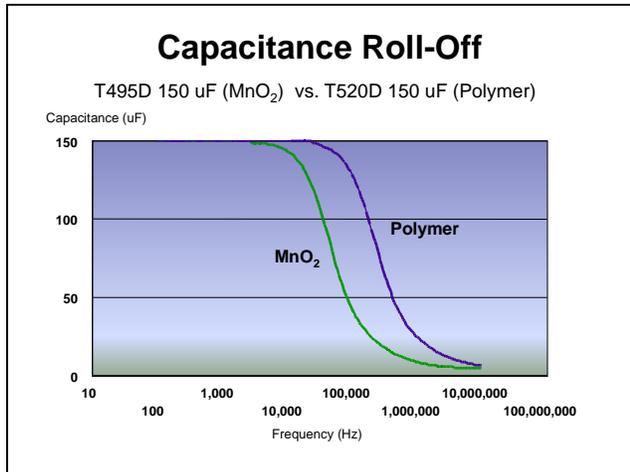
Because the ESR for the polymer is so much lower than the MnO_2 equivalent, the KEMET Spice model was changed to allow an external element of ESR not factored by temperature, and the low frequency ESR temperature variation is lower. There is no crossover of ESR versus frequency.

Additional Observations

Leakage

Lower ESR of the material might be a contributing factor to the higher leakage rates apparent when we replace the MnO_2 with the polymer. The leakage may have to be higher in order to generate the heat required for conversion. This would allow more individual "low current" sites to exist well below a current threshold level, thereby giving the appearance of higher overall leakage for the devices.

No Ignitions

The greatest saving grace of the polymer may reside in what it does not bring to the capacitor — an abundant source of oxygen that can sustain an exothermic reaction. The failure mechanism of the polymer devices is still short, but without the source of oxygen for the tantalum to feed on, there is no significant thermal event.

Now if 100 vdc with an available current of 100 amperes was applied to a 6-volt capacitor, yes this may cause it to burn, but the same effect could occur for any type of capacitor, including film and ceramic. If the voltage and current are large enough, they can create a plasma effect of the shorted device and ignite *anything* into an apparent welding arc.

Costlier

The polymer materials are quite a bit more expensive than the MnO_2 materials, but the deposition is considerably less. When one considers the history of the MnO_2 cathode and the time and development compared to the polymer, we are still in the infancy stage of this product. The cost curves should follow the historical time and piece improvements with cost.

The system costs should still show improvements even with higher piece price, because the piece counts should decrease with lower ESR, higher efficiency of capacitance, and lower capacitance roll-off.

Reliability

Early indications are that the polymer device appears to improve the performance over long term life testing, above that of similar MnO_2 devices. One theory is that the elasticity of the polymer compared to the rigidity of the MnO_2, could eliminate some forces within the pellet structure. These develop because of mismatches in thermal coefficients of expansion of the various materials. These forces may also be responsible for the creation of new faults in the tantalum capacitors when they are thermally exercised in the application solder processes.

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