TECHNICAL PAPER

New Tantalum Technologies Tantalum Polymer and Niobium Oxide Capacitors

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Abstract:

Tantalum has been a favored capacitor technology in space-limited designs and high reliability applications for a long time. Recent years have seen the emergence of one or two equivalent technologies offering many of the advantages of tantalum, such as volumetric efficiency and reliability. Two new technologies recently introduced into their commercialization phase are niobium oxide capacitors and tantalum capacitors with conductive polymer cathodes. A circuit designer trying to choose between these solid electrolyte capacitor systems has a number of trade-offs and subtleties of operation to consider. This paper reviews the main features of the two technologies, the latest electronic application needs and discusses the feasibility of the latest technology trends in tantalum, niobium oxide and polymer capacitors.



Introduction

Conventional tantalum capacitors with a MnO₂ second electrode system have proven to be a highly reliable solution with high volumetric efficiency for over 50 years. Continuous improvements have led to the development of higher CV (capacitance times voltage constant) powders that have enabled the creation of capacitors with higher capacitance in smaller case size dimensions. Three main features of tantalum capacitors have been the focus for a key development direction, i.e. the reduction of ESR (equivalent series resistance), the reduction of ignition risk and the flexibility of the supply chain. The evolution of DC/DC converters and power supplies has required a significant reduction of and major improvements in safety. Supply chain flexibility issues grew during the business upturn in 2000 where a slow response time from the tantalum metal supply chain resulted in a serious shortage of tantalum capacitors. Despite the fact that the supply chain has now brought in additional capacity to prevent a reoccurrence of year 2000 it has remain a significant issue in the minds of purchasing and design managers as a restriction to using and even a reason to remove tantalum capacitors from their boards.

Two new steps in technology have been successfully introduced to the market in order to meet the requirements from designers for the very latest electronic devices:

1] tantalum capacitors with polymer electrodes 2] niobium oxide capacitors

Major reductions in ESR are achievable by replacing the MnO_2 electrode by a conductive polymer. MnO_2 conductivity is 100 times less than that of metals and it represents a significant part of the total capacitor's ESR. Replacement of oxygen rich MnO_2 has also helped to reduce the potential for ignition of capacitors with a polymer cathode.

Niobium is a sister metal to tantalum in the periodic table and it has many similar features. AVX has been a pioneer in the development of niobium capacitors. This intial development was focused mainly on resolving issues with the supply chain & availability as niobium is much more abundant in nature. Niobium oxide has been identified as a niobium based material with the best features for capacitor production. It exhibits a metal like conductivity and can be produced with simpler and higher yielding powder manufacturing techniques. Niobium oxide also provides a high ignition resistance and safety through its efficient self-arresting failure mechanism. Additionally a capacitor made from NbO material improves steady state reliability. The NbO capacitor has been commercialized under the AVX trade name OxiCap^{™.}.

One limitation during the early stages of introduction of these new technologies, is a relatively lower CV in comparison to conventional tantalum capacitors with MnO_2 . However the process of high CV introduction

for these new technologies is much faster based on the knowledge already gained from "base" tantalum technology. Figure 1 shows the evolution of downsizing on a very popular rating 100μ F 6.3V.

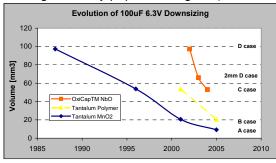


Fig.1. Time evolution of 100µF 6.3V downsizing

It is possible to see that even today conventional technology offers the highest CV solution in an A case (1206), however both polymer and NbO technologies are moving towards higher CV faster and will provide an equivalent solution in the near future. It should be also noted that higher derating (e.g. use of capacitor at a lower voltage than rated) is recommended for tantalum MnO₂ capacitors in low impedance circuits and from the application point of view the offering in polymer technology today is already equivalent. It suggests that the role of polymer and NbO technologies will grow in the future as a way to increase CV of capacitors.

Key Features

The following chapter will describe the key features of tantalum polymer and NbO capacitors. The scope of this paper is not to give a detailed overview of all the differences but to explain the key features that make these capacitors popular for some circuit applications. More detailed descriptions can be found in references 1] - 5].

Tantalum Capacitors with MnO₂ Electrode

The conventional technology with MnO₂ was introduced to the market 30-40 years ago as a major improvement over the existing wet tantalum electrolyte, electrode system. Since that time tantalum MnO₂ capacitors have established a strong position as a highly reliable, stable and high CV capacitor. Voltage range is typically from 2.5 to 50V and the case size offering has grown from basic four EIA case sizes (A,B,C,D) to more than fifteen in order to better meet specific height or space limited design requirements. The other case sizes includes larger cases to offer capacitance up to 1500µF, small case sizes with high CV in a minimum footprint and low profile packages with heights as low as 0.6mm. The unique flexibility of the powder technology to provide thin & flat capacitors is very important for applications where height is critical such as cellular phones and MicroHardDrives. The strength of the conventional MnO₂ technology is in the robustness against thermomechanical load, temperature and DC Bias stability, voltage range up to 50V and very good steady state reliability. That is why the most popular applications of tantalum MnO₂ capacitors today include automotive (up to 175°C operation temperature), military, aerospace, medical and high end applications such as servers.

The key process that defines the behavior of tantalum MnO_2 capacitors is the very efficient self-healing process. The self-healing reaction is based on thermally induced oxidization of the conductive MnO_2 counter-electrode and converting into Mn_2O_3 – a higher resistivity form of manganese oxide. The complete reaction is:

$$MnO_2 \xrightarrow{+heat} Mn_2O_3 + O^*$$
 [1]

If there is an area on the tantalum anode's dielectric surface that has thinner dielectric than the surrounding area, then the larger proportion of the capacitor's current (charging, leakage, etc.) will flow through that site (see Figure 2), causing localized heating. As the temperature at the fault site increases, the above reaction [1] takes place converting conductive manganese dioxide (MnO₂), which has a resistivity of between 1 - 10 Ohm/cm², to a less conductive form (Mn₂O₃) having a resistivity between $(10^6 - 10^7)$ Ohm/ cm². Thus the conduction site is effectively "plugged" or "capped", as shown in Figure 3, and the fault current clears.

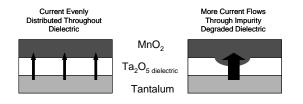


Fig.2. Current flow through dielectric fault side

The oxygen produced is absorbed by any lower order tantalum oxides other than tantalum pentoxide (Ta_2O_5) present in the dielectric layer, such as TaO_2 , or any MnO in the counter-electrode layer. See reference 6] for more details about the self-healing system.

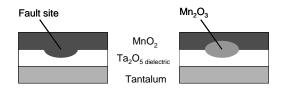


Fig.3. The fault site in dielectric after MnO₂ selfhealing process

The self-healing reaction [1] applies to situations where current availability is limited. In the case of high surge currents in low impedance applications, the breakdown of the dielectric can progress faster than the healing mechanism, and it can result in a hard short circuit and complete thermal breakdown. Thus it is of importance to protect tantalum capacitors against any surges that can exceed their design capabilities. Further information related to surge current and derating rules on tantalum MnO_2 capacitors can be found in 7].

Tantalum Capacitors with Polymer Electrode

One of the major contributors to ESR in a capacitor is the second electrode. The conventional tantalum capacitor uses MnO_2 as the 2nd electrode with a relatively high resistivity which, in tantalum polymer capacitors, is replaced by an organic material – conductive polymer. This replacement leads to a significant reduction of ESR, especially at frequencies above 100kHz. Typically the ESR value is reduced in polymer technology by about a quarter compared to the MnO_2 electrode.

Based on the fact that MnO_2 is not present in the structure the MnO_2 self-healing reaction [1] will not be working in the capacitor as would be the case in conventional tantalum capacitors. This brings an additional advantage in reduced ignition of these capacitors as oxygen is not in the structure. On the other side the efficient MnO_2 self-healing system does not operate in the capacitor. Conductive polymer shows a different kind of self healing process. The failure site is insulated by evaporation/peeling off of the polymer layer (disconnecting of CP) in the defect site – a hot spot that stops further current flow through the failure site. See figure 4. and reference 5] for more details.

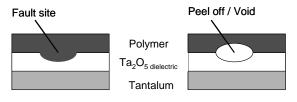


Fig.4. The self-healing process in polymer

In practice the polymer self-healing process has been found not to be as effective as the MnO₂ self-healing in conventional tantalum capacitors. Together with the other features, there are some limitations of polymers in voltage range, sensitivity to thermoelectrical load and humidity. This is reflected in the specifications of some manufacturers which offer 105°C maximum temperature range, limited lead-free reflow capability (one time 255C peak) and MSL level 3 (Moisture Sensitive Level 3 = storage in dry pack). The basic leakage current specification is also ten times higher compared to tantalum MnO₂ capacitors. These negatives may currently limit the use of polymer capacitor in some high-end, military, medical and aerospace applications. However, tantalum polymer capacitors will fully meet the requirements of the majority mass volume consumer applications. The recent improvement of tantalum polymer by some manufacturers has also significantly improved the features and specifications have been upgraded to 125°C max temperature range and full

compatibility to lead-free reflow (3x260C 10s reflow). See reference 8]. Polymer technology has found a strong market in the latest consumer designs mainly due to its low ESR and reduced ignition features.

Niobium Oxide Capacitors

Technology niobium oxide for (NbO) OxiCap[™] Capacitors is based on conventional tantalum capacitors with MnO₂ electrode. The first electrode, originally made from tantalum powder, is replaced by niobium oxide powder (NbO). The MnO₂ self-healing process as per equation [1] also works efficiently in the case of the NbO capacitor. However, there are some differences based on the origin of the NbO powder. NbO as a material has a very high ignition energy compared to tantalum due to the oxygen content in the base material (however NbO has a much lower risk of combustion). There is one more additional and very effective self-arresting mechanism which makes these capacitors safer compared to the other technologies. Should a dielectric breakdown occur the high resistance NbO sub-oxide NbO₂ is thermally formed on the junction between NbO (first electrode) and Nb₂O₅ (dielectric). The transformation temperature is lower than the MnO₂ self-healing process per [1] and thus it is effective and complimentary to this reaction. See fig.5.

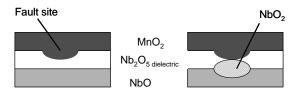


Fig.5. The NbO2 self-arresting process

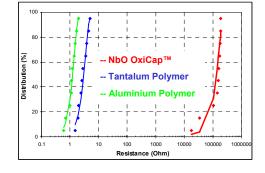


Fig.6. Resistance after breakdown on NbO, Tantalum polymer and Aluminum polymer capacitors

As a result the capacitor is not likely to create a short circuit after the main Nb_2O_5 dielectric breakdown, but keeps a high resistance around 34kOhms typically – see Fig.6 with comparison of resistance after breakdown on tantalum polymer, aluminum polymer and NbO capacitors. It can be noted externally as just a slight increase of leakage current, and otherwise the capacitor keeps working.

Thus within its rated voltage the NbO OxiCapTM capacitor is not likely to fail as a short circuit in applications. The capacitor can be thermally damaged only when used outside the specifications

such as over-voltage breakdown (> ~ 4 times rated voltage), reverse voltage, excessive ripple current and high acceleration of temperature with voltage. NbO capacitors, as well as tantalum MnO₂, are very robust against thermo-mechanical load and comply with 3x260C 10s lead-free reflow requirements. The limited oxygen flow at operating temperatures together with the self-healing and self-arresting processes are the main contributors to excellent steady state reliability typically ten times better compared to the conventional tantalum capacitors. The superiority in safety ("non-burn") of NbO capacitors has been verified in mass production. Over 500 million NbO ($OxiCap^{TM}$) capacitors to date (03/06) have been manufactured and sold without a single recorded incidence of burning in the field. The manufacturing and test programmes for both tantalum and oxide capacitors involve very low impedance ageing and high current surge and while low level burning exists with tantalum, none has ever been experienced with oxide capacitors. This is strong, statistically founded proof of the safety of NbO capacitors in applications in the field.

There are currently some limitations of NbO technology namely voltage range (10V maximum), lower CV compared to tantalum capacitors and higher temperature derating over 85° C. Leakage current specification is twice that of conventional Ta MnO₂ capacitors. For more details see 1], 2].

Key Features Summary

Conventional MnO_2 tantalum capacitors are the ideal choice for applications with requirements for high temperatures (currently up to 175C), high voltage (up to 50V) and established reliability. The technology offers highest CV in a small package. It's possible to use them up to 80% of rated voltage, but in low impedance circuits further derating needs to be applied - see 7].

Tantalum Polymer Capacitors are the best choice for consumer applications with low ESR requirements such as DC/DC converters in notebooks, PDA, telecom and other applications. The parts can be used up to 80% of rated voltage. Manufacturer's specifications of lead-free reflow process capability, temperature range ratings, leakage current and appropriate storage/handling in accordance to the MSL level should be verified for specific application needs.

NbO OxiCap[™] Capacitors offer the safest, available alternative among the various capacitor technologies with good cost-versus-performance value. The parts can be used up to 80% of rated voltage and are compatible with lead-free reflow requirements. The excellent steady state reliability makes these parts a favorite choice not only for consumer applications but also for high end, automotive, computer and professional designs. Appropriate temperature derating needs to be applied for temperatures over 85°C.

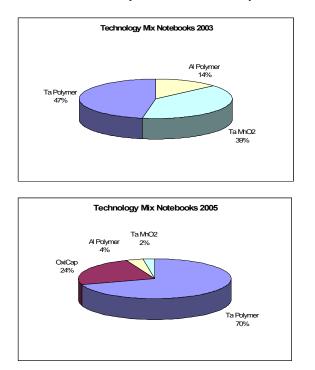
Usage Trends in Applications

Notebooks

PC notebooks have been selected as the application example to demonstrate trends in the of tantalum and the new usage capacitor technologies within the past two years. The following chapter compares usage of capacitors in notebooks designed and manufactured in 2003 and 2005. The notebook industry represents a good example of transition from high-end business to consumer type of applications in past two years. The growth of usage for notebooks in consumer market has significantly increased the importance of flexibility in design and manufacturing. One of the key capabilities that had to be achieved was to select the right high-tech components with the best performance versus cost performance.

The analysis presented in this paper is based on inhouse AVX detail analysis (teardown) of four notebooks from different manufacturers made in 2003 and six notebooks made in 2005. The analysis includes statistics on the following capacitor technologies: Tantalum MnO₂, Tantalum Polymer, Niobium Oxide and Aluminum Polymer. MLCC capacitors have not been included in this report as these are not body coded and it is difficult to easily recognize the capacitance and voltage on the board without a detailed destructive analysis. In two cases Aluminum Electrolytic Can type capacitors were used (one each in two different notebooks), but as they were so few statistically these were excluded from the report.

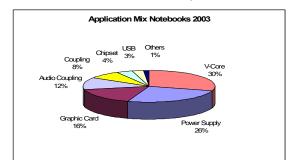
The figures 7 and 8 demonstrate how the capacitor technology usage has changed in just two years. At the same time, the total typical count of Tantalum MnO_2 , Tantalum Polymer, Aluminum Polymer and

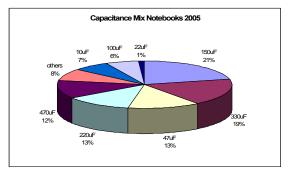


NbO capacitors (in further text noted as "capacitors" only) moved from 19 in 2003 to 28 in 2005.

Fig.7 and 8. Technology Mix in Notebooks 03-05

The share of the conventional tantalum MnO_2 capacitors has dropped significantly from 40% in 2003 to just only 2% in 2005. The shortage of tantalum capacitors in year 2000 and surge issues in low impedance applications has led to a "no-tantalum" policy by some manufacturers. Around 50% of the share of Ta MnO_2 capacitors has moved





to Tantalum Polymers and the other 50% to NbO $(OxiCap^{TM})$ as these new technologies became available in the marketplave from 2003.

Aluminum polymer capacitors remained in position in V-core applications as the main processor bulk capacitors. The total count of capacitors per notebook has fallen; the share of aluminum polymers has also dropped.

The next comparison in figures 9 and 10 shows the change of usage for various applications.

Fig. 9. and 10. Application Mix Change 03 – 05

The main application of these capacitors in notebooks in 2003 was V-core processor filtering with tantalum and aluminum polymer capacitors. The V-core application has moved to a minor application in 2005 as a result of 1] improvement in device capacitance and reduction of ESR resulting in lower unit count per processor, 2] usage of capacitors in other applications has grown.

A major increase is seen mainly in USB port applications, where advanced USB 2.0 standard and USB port count per notebook has moved the USB capacitor usage to among the top three in 2005.

The other trend is a reduction of share in coupling applications. A 2003 notebook shows 20% of

capacitors in coupling or audio coupling applications. The coupling application in 2005 has reduced to just 4%. This can be explained by the transition of small capacitance ~ 10uF and below from tantalum to MLCC technology. MLCC capacitors are not an ideal substitution of tantalum capacitors in audio applications due to their piezo effect that downgrades signal clarity and added noise. That is why some portion of the low capacitance parts continue to utilize tantalum/niobium oxide technology.

The trends seen in these applications are confirmed with the following figure Fig.11 and Fig.12 showing share of capacitance value.

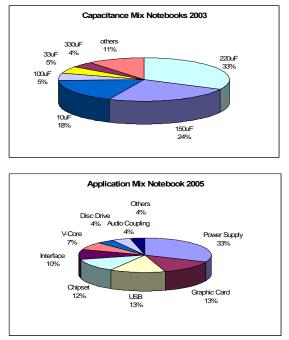
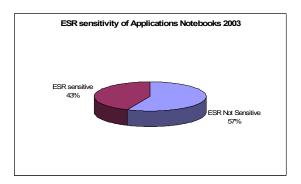


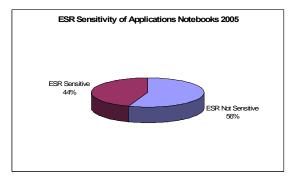
Fig.11 and Fig.12. Capacitance Mix Change 03-05

220 μ F capacitors were popular choices for V-core applications in 2003 and were replaced by 470 μ F and 330 μ F in 2005 with reduced component counts. A majority of USB ports use 150 μ F capacitors and together with some other applications 150 μ F have become the most popular capacitance value in 2005. Low capacitance parts (10 μ F) have dropped from third best position with 18% share to just 7%, which can be explained by the migration to MLCC technology.

By analyzing the of share between "ESR sensitive" and "Non ESR sensitive" applications an interesting finding can be observed. Figures 13 and 14 show that an "ESR sensitive" application means that the board position or application needs a low ESR part e.g. today only tantalum polymer or aluminum polymer can be used. The "ESR non sensitive" application is the application where it is not necessary to use capacitors with low ESR. This has been found experimentally based on oscilloscope measurements of parts with high (MnO₂ electrode) and low ESR (polymer).

Fig. 13 and Fig.14 ESR sensitivity of Applications 2003-2005





The interesting conclusion is that despite all the significant changes in applications and new circuit functionalities the ratio between ESR sensitive and ESR non sensitive circuits is the same in 2003 and 2005 with 60% of all application as "non ESR sensitive". This suggests that actually the fundamental functional blocks of notebooks have not changed within the two years. Hence, the major performance improvements and cost reductions have been achieved through implementation of new technologies into the existing functional blocks.

Note: The application analysis is an approximation based on experimental evaluation. Generalization of the presented conclusions needs to be considered according to the relatively small sample size of tested notebooks.

Desktop PC

The previous analysis was performed on notebooks; however there is an opportunity for the adoption of NbO technology also in desktop PCs e.g. the product that has already been in the consumer product area for a long time. Recent reliability issues with Aluminum capacitors in PC desktops have again raised questions on the true cost of ownership of aluminum capacitors in processor filtering. Leaking electrolyte has resulted in CAP, ESR and leakage instability that has stopped operation of many desktop computers in the hands of end users. The warranty claims and cost to brand image can easily eliminate the very thin margins that many desk top manufacturers struggle to achieve. The reliability level of aluminum electrolytic capacitors is typically between 1000 to 5000 hrs at 85°C. This may be a considerable limitation for many applications such as LCD displays, LCD and Plasma Screens, Televisions and PC computers.

NbO OxiCap[™] capacitors have no wear-out mechanism and due to its self-healing and selfarresting mechanisms it provides the highest level of safety and reliability within family of the capacitor technologies. The MTBF (Mean Time Between Failures) is in the range of 200 000 to 500 000 hrs i.e. up to 100 times better in comparison to Aluminum capacitors. NbO can operate at temperatures ranging from -55°C to 105°C (generic series) / 125°C (higher grade series) with little degradation of capacitance with time as very often seen in case of Aluminum capacitors where the electrolyte dries out especially at continuous operating temperature of 40°C to 85°C which is typical in a PC environment. Often designers have to include a redundant level of capacitance, adding to it's the cost and bulk.

<u>Automotive</u>

Usage of the two technologies tantalum polymer and niobium oxide in automotive designs has grown significantly in 2005 despite the relatively conservative nature of the automotive industry. The very positive features of NbO OxiCapTM capacitors in safety, high reliability, cost saving and lead-free process capability have resulted in very fast adoption in cabin electronics such as telematics, infotainment, electronic mirrors, seat electronics etc. NbO capacitors are replacing the traditional positions taken by aluminum capacitors in critical applications like airbag controllers and dashboard control circuits providing an increase in safety and long lifetime performance.

LCD and PDP(Plasma) TVs

One of the latest technological development creating major interest in past two years are LCD and PDP (Plasma) TVs. More than 15 milion LCD TVs were sold in 2005 and the forecast for 2006 is as high as 24 milion and it is still in its early market growth phase. There are more than 200 aluminum capacitors used in each LCD and PDP TV. Major manufacturers of these devices are facing two major issues - 1] how to secure a component supply chain which can react to fast production expansion - 2] increase customer trust in a new and expensive technology by extending guaranteed lifetime from the current 1-3 years to 5-10 years. Aluminum electrolytic capacitors are of concern in both cases as one of the most popular parts on the board together with the limited lifetime. NbO capacitors can replace up to 80% of Aluminum Electrolytic capacitors on the board and they are one of the best alternatives to increase reliability and lifetime of these equipments.

Summary

Two new technologies have been developed based on conventional tantalum MnO_2 technology to which answer the requirements for reduced ESR and improved safety. Tantalum polymer technology has reduced ESR by a factor of four compared with conventional MnO_2 tantalums. Niobium oxide – OxiCapTM capacitors offer a new technology with no

dependence o the narrow tantalum supply chain and with a unique non short circuit failure mode providing new, higher levels of safety & reliability.

The notebook consumer market has shown a great level of flexibility in the adoption of these new technologies in order to provide the best performance versus cost value to their customers. The six notebook models introduced into production during 2005 used 94% of these higher capacitance devices with these two technologies: tantalum polymer (70%) and niobium oxide – OxiCapTM (24%). NbO capacitors can also represent a significant step up in safety and reliability for critical applications such as airbag computers or extend guaranteed operational time in LCD and PDP TVs.

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