High CV Tantalum Capacitors - Challenges and Limitations

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A B S T R A C T

The trend toward portable electronics is a major driving force in the need for miniaturisation of electronic components. Tantalum capacitors are becoming a product of first choice where high electrical and mechanical stability along with long service life   and volumetric efficiency are demanded. The latest generation of ultra-high surface area tantalum powders in combination with an efficient constructional and encapsulation system provides a new solution for the next generation of component downsizing.

This paper describes the main challenges and limitations in processes and materials that have been necessary to overcome for increased capacitance and voltage ratings. Comparison of materials and technologies and their potential development for the future are also discussed.

1. Introduction

The rise of the portable electronic appliance has changed the baseline requirements for all kinds of components. In particular it created a need for parts with high 'cost versus performance' value. The requirements on capacitors for example are not just the basic capacitance value but also mechanical robustness against shock, longevity and ability to withstand ever greater temperature extremes. At the same time, these parts have had to adapt to fit product developers aspirations for small, light and inexpensive systems.

One very key trend driven exclusively by IC technology is the maximum height that is acceptable for passive components. Thinner, smaller end-products with increasing functionality, intense focus on 'time-to-market' and cost pressures are the background to the development trend for ICs and ultimately drive the requirements for passives. Package proliferation continues at a pace but with a common constraint – height. Early low profile series of tantalum capacitors were defined as being less than 1.2mm and were driven by CABGA (Chip Array BGA) devices which are now giving way to requirements of less than 1mm driven by VFBGA (Very-thin fine pitch BGA). Additionally, less than 0.8mm for WFBGA (Very thin fine pitch BGA) packages and UFBGA (Ultra-thin fine pitch) at less than 0.65mm is finding increasing favour. This has driven the development of a new series of conventional moulded tantalum capacitors and has spurred the introduction of new styles and the reformatting of older ones.

Materials advances have offered improvements with respect to many aspects of capacitor performance. In the portable arena, a key priority is volumetric efficiency (the amount of capacitance that can be provided in a given volume), which is often addressed most effectively with tantalum parts. This property is frequently quantified in terms of 'CV' values (where C and V are the capacitance and voltage). Since the mid-80's, manufactured tantalum powders have exhibited around a ten-fold improvement in CV/g values (from approximately 20k to 200k) and this has permitted the level of capacitance available within a standard case size to be increased accordingly. *(Fig 1)*.
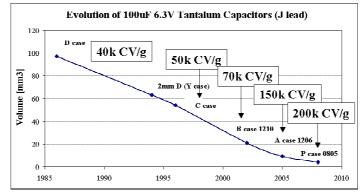

Fig.1. *Downsizing trend example for tantalum 100uF / 6.3V capacitors with typical powder used*
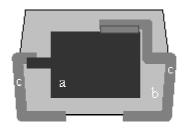
2. Ways towards higher CV

Electric capacitance of capacitors is based on formula 1:
Formula 1

$$C = \varepsilon_0 \times \varepsilon_R \times \frac{S}{d}$$

where ε_0 is permittivity of vacuum and ε_R is permittivity of the dielectric material (material constant)

S is active surface of anode (S_A) or cathode (S_c)
– lesser value is applied [m^2]

d is the thickness of dielectric material [m]

Traditional SMD solid tantalum capacitors are formed by the attachment of leads to an active zone and subsequent package encapsulation. The active zone contains the anode, dielectric and a cathode plate together with the terminating layers/contacts *(Fig.2)*.

Fig.2. Tantalum capacitor construction
(a – active zone, b – encapsulation case, c - leads)

Basically, there are two ways to achieve higher **CV (Capacitance x Voltage)** per given volume. It is possible to either increase the CV of the **active zone** itself or to improve **package internal utilisation** of the active zone i.e. to improve volumetric efficiency of the given case size.

1.1. Active Zone

The active zone CV increase will be discussed from the point of view of each basic component part, which is the anode, insulator (dielectric) and cathode.

1.1.1. Anode

Capacitance of the solid capacitor for the given forming voltage and dielectric thickness depends on the **sintered anode surface area (S_A) (*Formula 1*)**. This anode surface area comes from tantalum powder (surface area per gram of powder is represented by powder CV/g value) and powder sinter conditions combined. **Powder with higher CV/g is powder with smaller primary grains (Fig3).**

Fig 3 *: Schematic model of anodes from two differentCV/g powders showing significantly finer structure (sinter necks, pores, grains) for higher CV/g powder.*

High CV/g Powder Performance and Processing

Tantalum capacitor anodes are pressed using agglomerated tantalum powder. The powder is first mixed with a binder material to provide the right powder flow and lubrication properties during pressing. From sieve analyses a 70kCV/g agglomerated powder mixed together with a binder does not appear to have a significantly different particle size distribution in comparison to a 40kCV/g powder. However, 150kCV/g and greater powders show a significant shift in the particle size distribution to smaller diameters *(Fig.4)*.
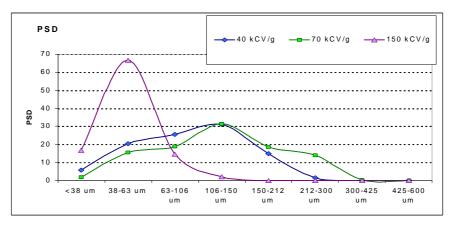
Fig.4*. Sieve analyses of different CV/g powders mixed with binder*

This creates a new challenge for press tooling accuracy and 'wear rate' lifetime to keep anode mechanical repeatability. Another challenge is presented by the powder agglomerate strength, which is again significantly lower in the higher CV/g powders. These weak agglomerates are crushed during the press cycle and the powder forms a dust around the pressing die causing additional pressing issues and powder losses. Indeed, using standard tooling can easily lead to as much as 50 % of the pressed powder being lost via this route. Therefore, improvements of press capability, tooling design and materials are required to order to manufacture quality high CV anodes.

High CV/g Powder Integrity

Another point of interest is the powder integrity post pressing. There is a significant 'drop off' in the crush strength of the powder mixed with binder as we go to higher CV's as can be seen in *Fig.5*. This poor pressed anode strength corresponds with the low powder agglomerate strength mentioned above. The pressed anode strength is critical during the subsequent anode processing, such as binder removal and sintering, where micro cracks can be easily generated inside the anode structure. These micro cracks represent the weakest anode points and thus are potential failure sites.
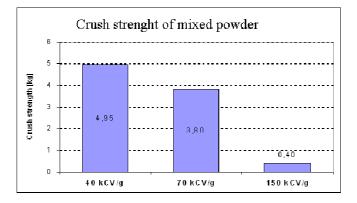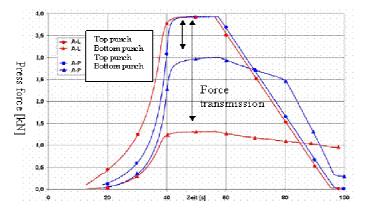

Fig.5. *Crush strength of powders mixed with binder*

Mixed binder system

Indeed the lubrication / binding requirements become increasingly critical for anode homogeneity and robustness with high CV/g powders. New binding / lubricating system are therefore required for high CV/g powders.

Finer grain powder has a much different sinter activity when compared to lower CV powders and the wire, by virtue of the greatly increased surface energy associated with the finer powder and higher surface area agglomerates. Therefore potential lower wire bond strength has to be compensated for through the use of higher press forces with these powders - low wire bond strength imparting similar issues for anode quality as the micro cracks. Though using just a binder, stronger anodes with potentially good wire bond strength could be achieved but the poor press force transmission in the press direction means there may be excessive density gradients inside the anode *(Fig. 6).*
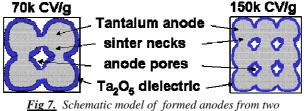

Fig 6. *Example of force transmission from top tobottom punch using two different binding systems*

This lower pressing force transmission might be of little importance for very small anodes but in larger anodes the influence into the next anode processing stage (dielectric quality and cathode creation) and reliability is much greater. The mentioned above post pressing density gradient can go from the top to bottom or from the sides to the middle of the anode depending on press methodology. High press density shells can thus be formed around the anode leading to an uneven electrical charge distribution inside some parts of the active zone which can cause overstressing and subsequent failure. Therefore the fine tuning of the mixed powder system and mixing methods are important challenges when dealing with high CV/g powders.

1.1.2. Dielectric

A Tantalum capacitor's insulating material (dielectric) is its own oxide - tantalum pentoxide. This oxide is formed by electrochemical isothermal oxidisation. The Capacitance is in inverse proportion to dielectric thickness - see **Formula 1,** where the dielectric thickness **d** is proportional to the applied forming voltage V_f at given conditions. The actual forming voltage used V_f is based on rated voltage V_r of the capacitor multiplied by F_r factor (forming ratio), so $d \approx V_f = V_r \times F_r$.

The Fr can be described as "safety factor" related mainly to the quality and electrical robustness of the dielectric, but it also reflects the state of tantalum technology, materials, capacitor application requirements etc . The F_r ranges typically from 3.5 to 2.0.

Using the simple model (**Fig 1**) it can be seen that all free surfaces of the anode are covered by dielectric - **Fig 7.**

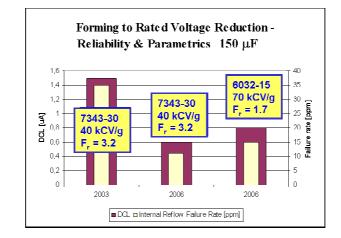***Fig 7.*** *Schematic model of formed anodes from two different CV/g powders*

During formation of Ta_2O_5 dielectric layer a portion of the original Tantalum grains or sintered necks are consumed. As it is apparent from **Fig 7** that the aim to keep sinter neck thickness under control as well as to not form them away causing disconnects or cracks in the anode structure which typically shows up in capacitor performance such as leakage current, capacitance loss, surge robustness etc. So this once more supports the afore mentioned need for homogenous powder and anode structures, but also chemical homogeneity and quality of the dielectric are more pronounced for high CV anodes. The dielectric thickness control and relative reduction is also needed to leave pores for later cathode material infiltration and lay down. Although this is positive in supporting the capacitance increase, it is also critical to overall dielectric quality.

Dielectric thickness reduction

A preferred lower dielectric thickness unfortunately gives a naturally higher DCL level and in combination with anode irregularities (density gradients – different stress/strains etc.). This appears to be one of the most challenging issues to resolve. An example of a successful dielectric property improvement may be seen in **Fig. 8**. The DCL value in the example went to the half of its original value. In the same way the in-house accelerated reflow failure rate is improved. This quality enhancement enabled a reduction in Fr for the next new capacitor with similar parametric (DCL) and its stability performance as the original proven part type.

Fig 8. *Example of forming to rated voltage ratio(FR) reduction (Miniaturization of 150μF from 7343-30 to 6032-15 case size)*
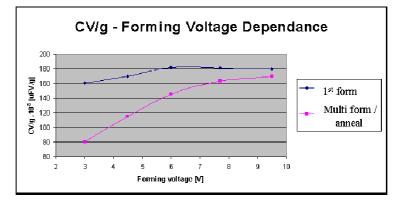
Shell formation

The study of failure modes of the older original range of capacitors clearly identified significant sensitivity to thermo-mechanical stresses of the dielectric on the slim outer part of

the anodes compared to dielectric inside of the anode. All the electrical current goes first through the outer anode surface when charging and discharging the capacitor. The current stream is divided into many smaller channels inside the anode and therefore the electrical load is minimised here. To reduce

the risk of the capacitor failure the outer anode surface is being equipped with a thicker dielectric layer i.e. dielectric shell. The impact of the shell formation is more pronounced with higher CV/g powder utilisation and with lower and lower dielectric general thickness adopted.

Native oxides

Tantalum capacitors with rated voltages of 4V and 6.3V are those most favoured in battery operated portable devices and these have been specifically targeted for dielectric thickness and quality enhancements. The native oxide that forms in air on tantalum at room temperature (i.e. post sinter and before dielectric formation) is equivalent in thickness to having used a 2 to 3V forming voltage. Therefore it is apparent that this thermo-oxide layer starts to play a very important role in the dielectric behavior as the forming voltage is decreased towards this value. In particular, a 6V formed oxide layer may not be sufficiently protective to the tantalum anode surface to prevent further oxidization as the component passes through subsequent process steps at elevated temperatures (*Fig. 9*) - CV losses might therefore be generated.

Fig.9 *CV/g dependence of high CV powder on the processing conditions*

Apparently, to maintain the CV/g attained at low formation voltages during both the process and application load is a matter of process adjustment.

1.1.3. Cathode

See the general *Formula 1.* The capacitance is proportional to S_c – cathode surface area. In the ideal state it is the same as anode surface S_A , i.e.100% dielectric coverage. One can understand that the smaller the pores of a formed anode structure *(see Fig 7)* the more issues of anode infiltration with the cathode materials becomes. Having successfully infiltrated the pores then the cathode materials are required to cover 100% of the total internal surface area. S_c being <100% means loss of the final capacitance.

Impregnation issues

Today tantalum capacitors either use manganese dioxide or conductive polymer as a cathode plate. MnO_2 is prepared in situ inside the anodes through the thermal decomposition of manganese nitrate. Similarly, monomer for conductive polymer is polymerised in situ. In both cases liquid has to penetrate fully all the agglomerate pores and subsequently to leave behind the reaction product. Look at the actual high CV powder structure example **(Fig.10).** It is apparent that the pore diameters are very small (in the range of 10's to 100's of nm) and the surface area is also typically up to four times that of low CV powders. Thus the ability to penetrate and coat through such pores is a significant challenge.
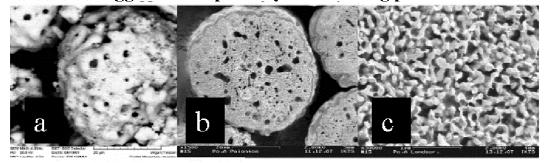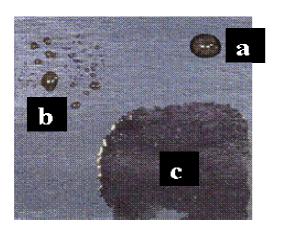

Fig10. *150 kCV/g powder porosity (**a**-agglomerate outside, **b**-agglomerate intersection, **c**- inside the agglomerate)*

Capillary forces and air/gas dissipation play a major role in the cathode plate production and the degree of coverage and surface conformity can have a large effect on the wet to dry solid state capacitance ratio. While the conductive polymer does not

have such big issue to recover wet capacitance with typically 92 to 99% of the wet value, the MnO_2 cathode is a rather different case. Here the common wet capacitance utilization is about 95 to 98 % for lower CV materials, however, it falls to only 75-90% typically for high CV/g powders which may cause unsatisfactory loss of capacitance and related capacitance fluctuations in products when exposed to atmosphere humidity.

MnO₂ Cathode

Modifications to existing manganising methods present a significant challenge to achieve improvements in surface coverage and pore penetration. Two major effects in final wet to dry performance are influenced by the manganese nitrate used for the MnO_2 cathode are it's surface tension/interfacial wetting and the decomposition speed. The pyrolysis process where manganese nitrate forms manganese dioxide is a vigorous reaction consisting of many intermediate steps which are sensitive to temperature, rate and atmosphere (humidity and the presence of other oxidising agents). The decomposition involves oxide crystals seeding and their subsequent growth with additional nitrate dips. During the decomposition there is an enormous nitrous gas evolution which takes place within a few seconds inside the very fine pore structure of the anode. The surface coverage can be significantly improved by modification of the manganising process - see **Fig.11**

A successful capacitance recovery in solid capacitor development over the past few years may be seen in **Fig 12**.

Fig.11 *Ta₂O₅ surface coverage by one equal volume drop of manganese nitrate prior to decomposition:*
a –1.3 g/cm3 of Mn(NO₃)₂
b – improved formulation of the same,
c – optimised formulation of the same

Fig12. *Wet capacitance recovery improvement over last 5 years for case 3216, 100 µF, 6.3 V (150 kCV/g)*

Polymeric Cathode

As it was mentioned above the conductive polymer cathode coating does not suffer the same wet to dry capacitance loss generally. Conductive polymer in a tantalum capacitor system is not a source of oxygen at elevated temperature and therefore the sensitivity of such parts to ignition is significantly reduced when they are electrically overloaded.

ESR related to fine anode structure and ways forward

The other significant feature of miniature case sizes is the increase of ESR related to the physically smaller anode surface area. Cathodes made from better conductive materials compared to MnO_2, such as conductive polymer, can provide improvement in ESR values that compensate for the smaller case size as it can be seen in **Tab.1**.

Capacitor rating	Ta Powder grade	ESR [mOhm]	DF [%]
Std. Ta B 100 uF / 4 V	50 kCV/g	150	2,8
Std Ta A 100 uF / 4 V	150 kCV/g	450	16,0
CP Ta A 100 uF / 4 V	150 kCV/g	110	3,8

Table. 1 *ESR and DF comparison of tantalum capacitors 100 µF, 4 V in different cases with different cathode*
Std = MnO₂, CP = Conductive Polymer

1.2. Volumetric efficiency by design

Another approach to improving the packaging efficiency and reducing the foot print area required for mounting is by capacitor design, whereby the 'J' leads are replaced by terminations that do not protrude outside of the outline of the case. The face down (under tab) design saves internal construction space by up to 60% but also permits the PCB pads to be little more than the outside dimensions of the part. This also allows for very close packing of similar parts and thus it represents a significant advantage in high density, high performance miniaturised boards. This packaging construction also has benefits in lower self inductance ESL and thus a better working frequency range. A limitation on the other hand, from a user point of view, could be visual inspection of the solder fillet on the terminations which is possible with conventional "J" lead technology. However, in practice this has not been a major issue as most of the high density board manufactures are already using BGA IC packaging technology with much smaller "underneath" terminations when compared to tantalum capacitors. Examples are in *Fig 13*.

It is not the primary subject of this paper to discuss face down or similar designs, but the volumetric efficiency of the active zone within the capacitor case is also a significant contributor to capacitance volumetric efficiency together with production cost considerations and customers needs.

Fig. 13 *Examples of different Volumetric Efficiency Constructions*

3. Reliability

Tantalum capacitors are considered as one of the most reliable and stable capacitor technologies. How are these features maintained with the trend towards higher CV and associated downsizing and miniaturisation?

Reliability of tantalum capacitors come from the high stability of the dielectric oxide and from the well known self healing mechanism with MnO_2, which even partially takes place with conductive polymer parts. The reliability relies on DCL stability and a model of the DCL mechanism can be seen in ***Fig. 14***.
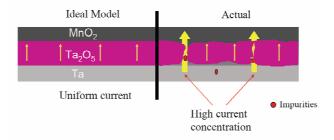

Fig. 14 *Model of DCL mechanism – impurities effect*

The level of purity of the tantalum powder is one of the most important parameters defining its reliability. Capacitance values increase with thinner dielectrics as mentioned earlier and this process of reduced forming ratios for higher capacitance is only possible with the existence of a new generation of tantalum powders with reduced levels of impurities. Significant improvement in the reduction of impurities in tantalum powder has been achieved over the past 5 years as shown in *Fig. 15*.
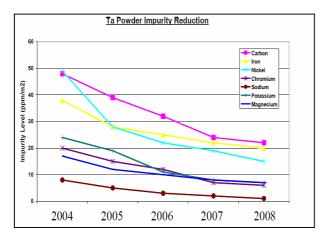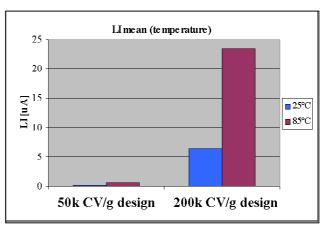
Fig. 15 *Typical Tantalum powder impurity reduction over the last 5 years*

Fig. 16 *DCL at different temperatures for 100 µF Tantalum capacitors using different powder CV's and different dielectric thicknesses*
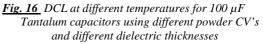
This reduction has enabled the stabilisation of the absolute DCL value. However, the thinning of the dielectric may also have an affect on the DCL at a given temperature and comparison of 50k CV/g powder (standard CV) and

200k CV/g (high CV) powder in 100µF, 6.3 V capacitors is shown in *Fig. 16*

Although the ratio of the DCL at 25 to 85 deg C remains similar, the original starting level indicates that the DC application of very high CV/g powder tantalum capacitors at elevated temperatures might be limited.

Lowering the dielectric thickness brings also some advantages, the most remarkable being the improvement of the parts robustness to current surge when compared to a part with thicker dielectric on the same design. As already mentioned, micro cracks or low wire bond strength as well as consumption of tantalum at inter-particle necks during the dielectric formation are the most likely cause of current surge failure mode. Lowering the dielectric formation voltage minimises such effects. Lower dielectric thickness also influences the part break down voltage (it goes to a lower value). Nevertheless, as can be concluded from *Fig. 17*, the break down voltage distribution remains very narrow and it is still about double the rated voltage.
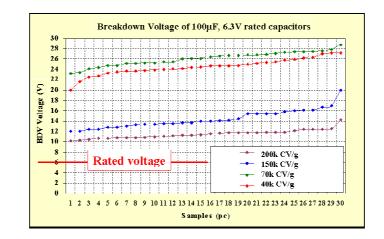

Fig. 17 *Break down voltage comparison according to Ta powder CV/g. (150 & 200k CV/g powder parts wereprepared with lower dielectric thickness)*

It might be concluded that high CV tantalum capacitors remain the original typical tantalum quality and reliability standard. The Leakage current level is higher although its stability can be maintained well throughout by actions as discussed. The parts remain robust against the current and voltage surge. Some limitation with increasing CV/cc however is in voltage range and need for higher temperature derating.

4. Summary and Future Focus

Table 2 summarizes the challenges and limitations of high CV tantalum capacitors.

	Today	Future
powder CV/order	+	-
anode pressing	+	+/-
dielectric	+	+/-
MnO2 cathode	+/-	-
CP cathode	+	+
package efficiency	+	+/-
Reliability	+	+

Tab. 2 *Challenges and limitations for futureTa capacitor development*
+ means O.K. or on the right track,- means a major issue, need for further
attention and development

The key question still comes back to the final anode surface area S_A increases opportunities. As it can be seen in ***Fig 18*** even the 200k CV/g sintered anode structure shows yet more significant anode volumetric efficiency potential. One can see that the space could be utilised better with improved anode structure. Mathematical models of the capacitor active zone were prepared in order to better understand the opportunities still available.
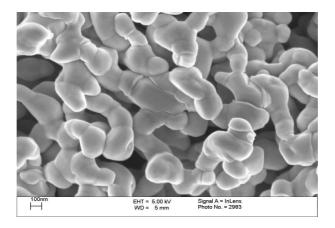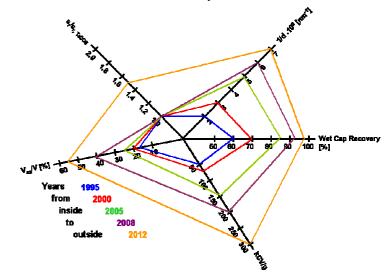

Fig. 18 *200kCV/g sintered anode structure*

The model concludes that, based on physical limits, the tantalum capacitor active zone's CV could at least triple in comparison to today's maximum. The model also reveals two very important challenges for future tantalum capacitor development: 1] To prepare powder and anodes with very compact order of the elemental tantalum grains and 2] to penetrate and cover the pores with a size less than 10nm.
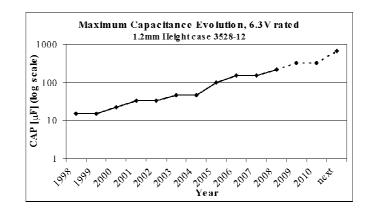
The other direction for further increase of CV is improvement of permittivity of the dielectric in the Tantalum capacitors. The advance study shows interim potential to increase it by 1,5 times.

Fig. 19 *Progress in*
Ta capacitor technology:
1/d is an inverse of dielectric thickness,
$\varepsilon_r/\varepsilon_{r, Ta2O5}$ is a Ta2O5 dielectric constant increase index,
V_{az}/V [%] is volume efficiency,
kCV/g is a powder charge per gram

The current and future progress may be visualized in ***Fig 19.*** The continuous progress in the five directions displayed has been driving the increase of the Tantalum capacitors CV.

Based on the current state of the art in the parameters, Tantalum capacitors are expected to **increase its CV 3 times by 2012.** For the practical impact of this **see *Fig 20*.**

Fig 20 *Progress in Capacitance example for case 3216-12, 6.3V rated Voltage*
(1,2 mm max height low profile A case)

5. Conclusion

With the continuing development of ever higher CV MLCC capacitors, new challenges are faced by the tantalum capacitor manufacturers. The need to maintain their volumetric and performance advantages but in ever smaller and lower profile cases becomes paramount. The general trend of reduction in rail voltages and demands from portable electronic devices provides opportunities whereby a new range of alternate materials and constructions have delivered major new advances. In addition, the trend towards the use of ever thinner IC packages below 1mm means passive components will be required to follow the same trend.

The discussions outlined in this paper suggest that there is good potential to increase CV of Tantalum capacitors about 3 times by 2012. Mathematical modeling of the ideal anode structure and recent studies of dielectric properties show also the further potentials for the CV increase to continue beyond 2012. Some limitation however might be expected in voltage range and higher temperature ratings, so the key also will be design the Tantalums by specific circuit applications

6. Acknowledgement

The authors would like to acknowledge the help and assistance in the development of this paper to Mr. W. Millman

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