

High Voltage Tantalum Powder – Challenges and Opportunities for new Powder Generation

Marcel Hagymási

H.C. Starck GmbH, Im Schleeke 78-91, 38642 Goslar, Germany
Tel.: +49 5321 751 3160, Fax +49 5321 751 4160, e-mail: marcel.hagymasi@hccstarck.com

Helmut Haas

Tel.: +49 5321 751 3937, Fax +49 5321 751 4937, e-mail: helmut.haas@hccstarck.com

Christoph Schnitter

H.C. Starck GmbH, Im Schleeke 78-91, 38642 Goslar, Germany
Tel.: +49 5321 751 3939, Fax +49 5321 751 4939, e-mail: christoph.schnitter@hccstarck.com

Holger Brumm

H.C. Starck GmbH, Im Schleeke 78-91, 38642 Goslar, Germany
Tel.: +49 5321 751 3294, Fax +49 5321 751 4294, e-mail: holger.brumm@hccstarck.com

Introduction

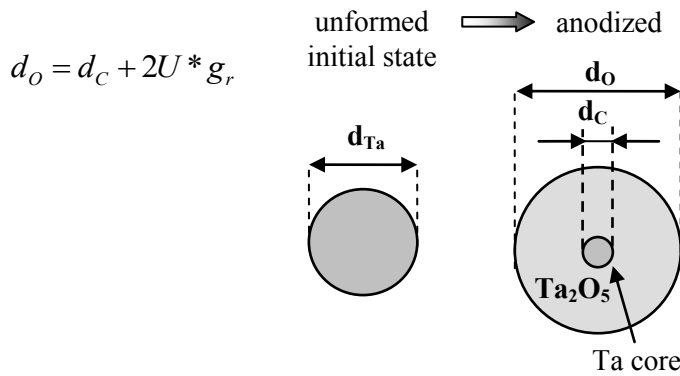
As a leading tantalum producer, H.C. Starck notes an increasing demand for high voltage (HV) powders for different new application fields like flat panel display, automotive as well as medicine devices with high reliability. Any discussion of HV applications must begin with the fundamental question, “what is high voltage for tantalum capacitors”. This is not an easy question to answer and depends on the application as well as the consumer. In past, many tantalum makers would answer: capacitors with rated voltages of 50 or 63 V. However, this limit has been already pushed since new techniques of anode production like improved polymer cathodes have been developed. AVX for example recently reported the development of new tantalum polymer capacitors with a voltage rating of 125 V, which means a doubling, compared to capacitors available before. Another limit, too high ESR values, could be solved by using special anode shape¹. To enhance the HV ability of tantalum capacitors it is essential to provide not only new polymer cathode materials or changed anode designs but also new powders with an adapted microstructure. Improved HV powders could also allow decreasing the forming to rated voltage ratio, which would lead to an additional capacitance increase². This paper gives an overview about different requirements for such new powders and presents also a new anode characterization method for fast capacitance evaluation. Finally, new improved tantalum powders for high voltage applications will be shown and discussed.

Demands on Microstructure

To meet the market needs, H.C. Starck is developing new tantalum powders with focus on high formation voltages ≥ 100 V. A good high voltage powder requires a different microstructure than does a low voltage powder. The requirements for good high voltage performance include:

1. Suitable big primary particle size
2. Sufficiently strong sinter necks: between primary particles as well as between different agglomerates
3. Sufficient large pore size diameter
4. Good homogeneity of 1. – 3.
5. High purity

HV powders need a proper primary particle size in order to provide enough tantalum that can be converted into Ta₂O₅ during anodization. Moreover, remaining tantalum core has to be big enough to ensure a good conductivity within the anode structure which is also responsible for the resulting capacitance. By using a simple model, the required tantalum primary particle size can be estimated. Therefore, the tantalum structure can be described as a cylinder with the diameter d_{Ta} . The outer diameter d_O after formation can be calculated by the remaining tantalum core diameter d_C and oxide thickness which depends on formation voltage U and growth rate (g_r 2.3 nm/V)³:



By using the different densities of tantalum (16.6 g/cm³) and amorphous Ta₂O₅ (8.0 g/cm³)⁴ it is easy to calculate back the original tantalum diameter d_{Ta} of such a cylinder structure before anodization. Result is the minimal necessary tantalum primary particle size for a given formation voltage and remaining tantalum core diameter (fig. 1).

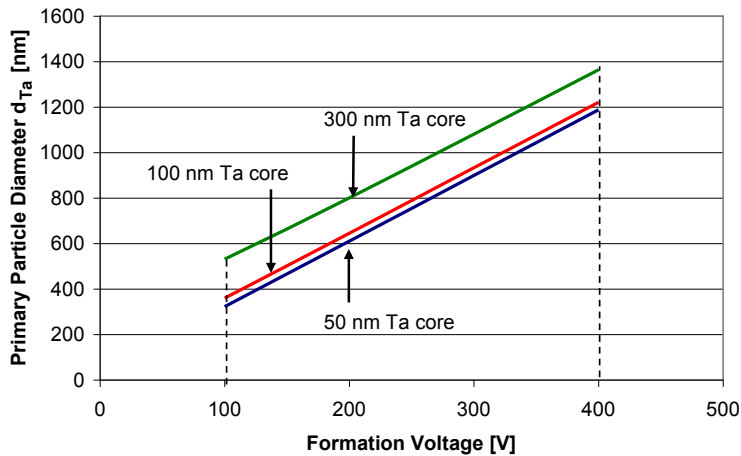


fig. 1 Particle diameter d_{Ta} for different formation voltages and tantalum core diameters for a cylindrical microstructure.

Smaller particles will be totally converted to oxides without remaining tantalum core which is equal to a total loss for the capacitor. For a 100 V formation with a Ta core diameter of 50 nm for example it is necessary to have a cylinder diameter of 322 nm before formation, which has to be increased for a 400 V formation to 1188 nm. Even if the real tantalum microstructure has a mono- or bimodal particle size distribution and consists not of uniform cylinder structure, this simple model gives a good hint of the required particle dimension.

Beside primary particle size the size of the sinter necks is one of the most important parameter. A “sinter neck” is defined as the smallest connection between two adjacent particles which ensure the electrical path through the tantalum structure (fig. 2).

Sinter necks can be distinguished between

- sinter necks within one and the same powder agglomerate
- sinter necks as interconnection between different agglomerates which are formed during pressing and sintering.

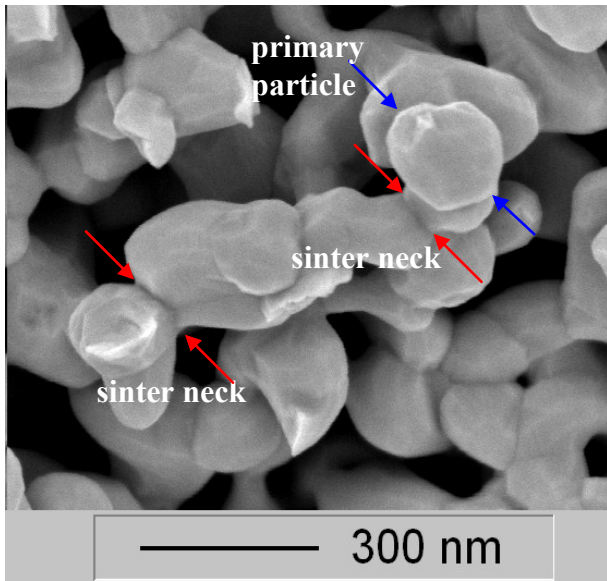


fig. 2 Sinter necks and primary particle within the tantalum structure (150k μ FV/g powder).

The latter kind of necks can be improved during pressing the powder to the anodes: higher press densities increase the cross sectional areas between agglomerates. All sinter necks will then be increased and strengthened during the anode sintering process. Main driving force for sintering is the reduction of free surface energy⁵⁻⁷ which is caused by particle curvature: the smaller the particle, the higher the surface energy. This means in case of sinter necks: the smaller the sinter necks, the higher the radius of curvature and therefore the higher the sinter activity. Material flow by surface diffusion from region with low radius of curvature to necks with high curvature leads to a neck growth. It was already presented⁸ that anode surface area and sinter neck size oppose each other. Increasing sinter neck size caused by shrinkage reduces simultaneously the surface area and therefore the capacitance of the anode. Similar to primary particles, the sinter necks will be decreased with ongoing anodic oxidation. That's why the calculated minimal diameter seen in fig.1 is not only valid for the "primary particle size" but also for sinter necks: too small neck sizes will be completely formed to oxides without any conductive connections which mean an additional loss of active capacitor surface.

For every given voltage exist an optimum particle size that ensures the highest capacitance. Too big particles have low surface area and therefore low capacitance. Too small particles have high initial specific surface but capacitance will be low due to surface area lost during high voltage formation. Using the simple cylinder model allows also estimating the maximum capacitance and the correlated unformed surface area for a given voltage. Therefore, the cylinder capacitor equation was used (l: cylinder length):

$$C = 2\pi\epsilon_o\epsilon_r \frac{l}{\ln \frac{d_o}{d_c}}$$

In case of a 100 V formation, oxide thickness is constant with 230 nm (g, 2.3 nm/V) while the inner tantalum core diameter is variable. Resulting capacitance and initial surface area can be seen in fig. 3. The highest possible capacitance was determined with 51.7 k μ FV/g from this model and would be reached for a tantalum core of 125 nm respectively an initial unformed surface area of 0.67 m²/g. According to calculation in fig. 1, this is correlated to an initial tantalum cylinder diameter of 380 nm. Please note, that this model did not include the influence of pores respectively sinter density.

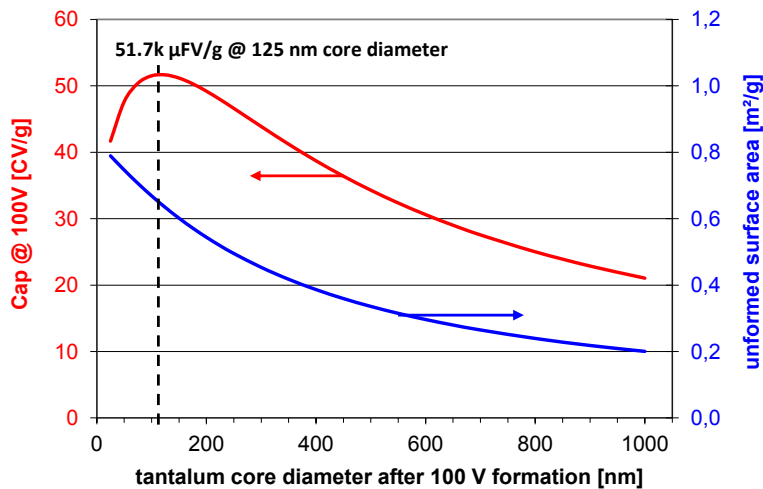


fig. 3 Theoretical capacitance and surface area of 100 V formed tantalum cylinder depending on remaining tantalum core.

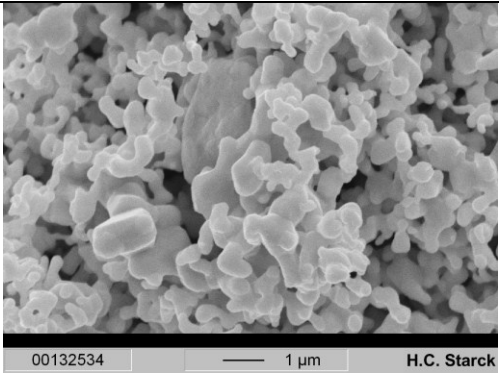
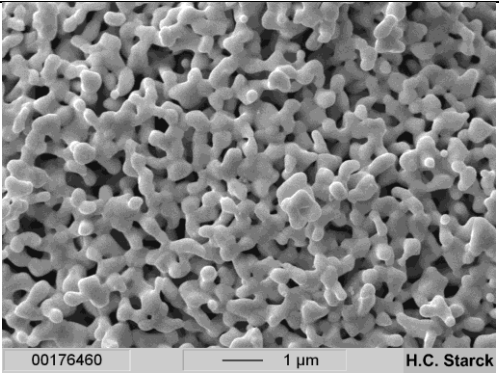
Next important parameter is the pore size distribution. The higher the final formation voltage the higher the required pore size in which the Ta_2O_5 can grow. The initial (unformed) pore size distribution affects the pore size distribution after anodization; too small initial pore size will hinder the impregnation after anodization and can lead to additional capacitance losses. In worst case, the pores will be totally closed and filled with Ta_2O_5 so that additional oxide growth can not occur and no coverage with cathode material will be possible. On the other hand too big remaining pores can also result in capacitance dissipation since these pores can be regarded as unused space for tantalum surface area. However, currently it is not known which remaining pore size is sufficient for a good impregnation with cathode material or low ESR values. Moreover, beside the pure powder properties also pressing and sintering have a big impact on anode pore size distribution which depends on producer and their process.

High microstructural homogeneity as well as inter-agglomerate strength are two important but difficult to determine parameters. Small particles have a higher specific surface area than large particles, but show an increasing surface area and therefore capacitance loss with increasing formation voltage⁹. That's why it can be assumed that powders with a more uniform primary particle size will show a lower capacitance loss during formation than a heterogeneous powder with comparable initial specific surface.

Impurities like many metallic elements or carbon are often discussed to have a negative impact on wet or solid leakage as well as breakdown behaviour^{4,10,11}. This effect can be magnified as the formation voltage increases¹². Table 1 illustrates the microstructural advantages and disadvantages with respect to HV applications of current tantalum powders obtained from different production routes, namely from sodium reduction of K_2TaF_7 and from magnesium reduction of Ta_2O_5 .

The powder from sodium reduction process reveals large pores with diameters up to 2 μm as well as big primary particles with sizes of several μm . The large primary particles provide enough tantalum that can be converted to thick oxide film and the open pore structure ensures enough space for the growing oxide film. Main disadvantage of this powder is the heterogeneous microstructure: the powder contains not only the desired large primary particles but also much smaller particles which will be totally converted in tantalum oxide at higher voltages. This causes two drawbacks: first additional capacitance loss at high voltages and second the "dead" tantalum oxide will reduce the remaining pore size which will decrease impregnation efficiency.

table 1 Comparison of HV capability of tantalum powders from sodium respectively magnesium reduction process

	Na Reduced Powder	Mg Reduced Powder
Advantages	Big pore size: up to several μm	Very homogenous primary particle structure high purity
Disadvantages	Heterogeneous primary particle structure higher impurity level	Small pores (<400 nm)
Main Focus (Past)	Low CV, high voltage (>50 V)	High CV, low voltage (<50 V)
Microstructure (showcase)		

In contrast, the tantalum powder from magnesium reduction process provides a very homogenous microstructure with very uniform primary particle size. Main disadvantage here is the comparably small pore size (<400 nm) which is the main reason why this powder is not capable for formation at 100 V because all pores will be closed. Due to this limitation, tantalum powders from magnesium reduction process were mainly used in the past for high CV applications where small pores and primary particles are necessary.

The simple illustration in table 1 gives the main direction for new developments in HV tantalum powder capabilities by combination of best properties of both kinds of powders. In case of powder from magnesium reduction process, the pore size as well as primary particle size has to be increased by keeping its high microstructural homogeneity and chemical purity. Therefore, a new production process was developed that allows to open the pore structure and simultaneously increase the primary particle size, so that high capacitances at formation voltages of 100 V -150 V can be realised.

In contrast, the powder produced by sodium reduction process has to be optimised with the focus on improved homogeneity, so that maximum capacitance at formation voltages up to 250 V can be reached.

New fast electrical test for anode characterisation: constant rate formation (CR formation)

Improvement of tantalum powders for HV applications requires a comprehensive evaluation of many anodes for electrical properties like e.g. capacitance. In the course of this evaluation, formation of anodes needs to be done at different voltages and shrinkages as well as press densities in order to get detailed information about the capacitance behaviour of the powder. Subsequently, all anodes have to be washed, dried and measured. Results are the well-known capacitance vs. voltage curves shown in fig. 4 for different powder types. After reaching a maximum in the range of 12-30 V, the capacitance of all powders drops down due to surface loss during anodization. As a rule of thumb: the higher the capacitance the higher the capacitance loss with increasing formation voltage.

This procedure enables a precise capacitance characterization but requires many anodes and measurements. To ease the powder evaluation, a fast anode characterisation test that provides similar capacitance vs. voltage information but with less effort was developed. Main focus was not a very precise capacitance determination but a faster and more easy comparison method for different powders and anode conditions with the goal to find out which powder / anode condition would show the highest capacitance at a given formation voltage.

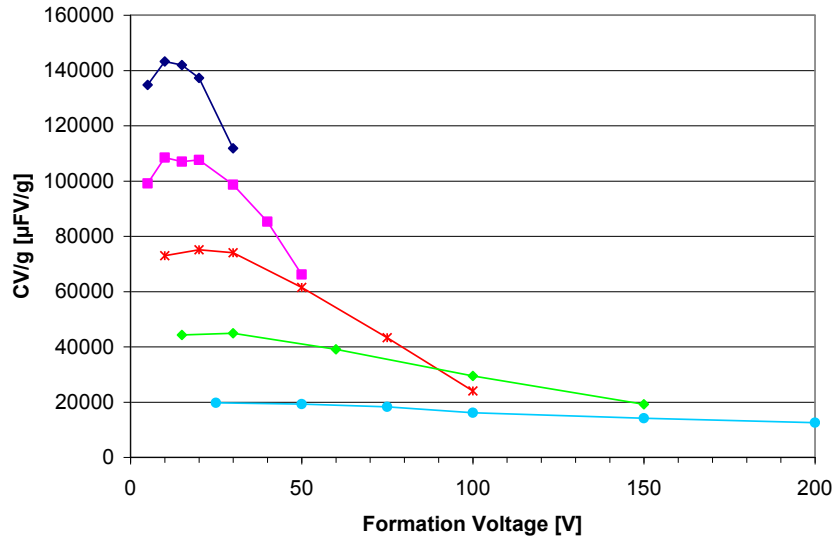


fig. 4 Capacitance vs. formation voltage for different tantalum powders.

The new electrical test method is called “constant rate formation” since the main idea is to keep the formation rate F_{rate} (V/min) constant which means a constant tantalum oxide growth (nm/min) during anodization independent from surface loss during anodization. The formation rate F_{rate} depends on anode surface area A and applied current I :

$$F_{rate} = \frac{I}{A} \quad (1)$$

For a constant anode surface area it can be concluded that the higher the current, the higher is the formation rate. If equation (1) is transposed it is obvious that for a constant F_{rate} the current has to be increased when the anodes surface area is increased and vice versa. This means: to provide the same formation rate for a high CV anode like a low CV anode the current has to be increased in the same ratio like the surface ratio of both anodes.

$$A = \frac{I}{F_{rate}} \quad (2)$$

The general capacitance equation of a plate capacitor (3)

$$C = \epsilon_0 \epsilon_r \frac{A}{d} \quad (3)$$

is mainly depending on anodes surface area since dielectric constant of Ta_2O_5 ϵ_r (~27) as well as the thickness growth d (~1.8-2.3 nm/V)^{3,4} is nearly constant for all tantalum anodes. If the surface A in (3) is replaced by equation (2) and both terms are multiplied with U/m (voltage per gram) we get finally equation (4)

$$C * \frac{U}{m} = \epsilon_0 \epsilon_r \frac{I}{d F_{rate}} * \frac{U}{m} \quad (4)$$

From (4) it follows that in case of a constant rate formation the capacitance “CV/g” can be directly correlated with the applied current density “mA/g”. That means also that a surface reduction during formation, which is responsible for the decreasing capacitance with increasing formation voltage (see fig. 4), can be directly correlated with the current density. As a result, a current-voltage curve is obtained which is comparable to the capacitance-voltage curve in fig. 4. To measure this current-voltage behaviour, a power supply with an intelligent control unit is used which adjusts the required current for a given constant formation rate independent of anode type. The recorded current is always normalised to the used anode weight (mA/g). The adjusted current depends on different parameter that has been taken into account:

- Formation rate
- Powder type
- Pressing and sintering conditions
- Formation temperature
- Electrolyte conductivity

The mechanism of the CR formation test will be demonstrated with two standard powders: A 150 $\mu\text{FV/g}$ powder from Mg reduction process and a 40 $\mu\text{FV/g}$ powder from Na reduction process. The anodes made from 150 $\mu\text{FV/g}$ powder were formed @ 60°C up to 50 V with three different formation rates: 0.15 V/min, 0.25 V/min and 0.77 V/min; the corresponding current voltage curve can be seen in fig. 5a. According to equation (1), the current at a given voltage is increased with increasing formation rate. The first section of all curves, starting at zero voltage, shows a steep slope which is caused by the native oxide film and can not be correlated with capacitance behaviour while the subsequent curve ranges characterize the capacitance progress. For a better comparison of the different rates all curves have been normalized to the maximum current values (see fig. 5b). Evaluation of all three curves revealed that the high rate of 0.77 V/min lead to a curve “deformation” and shift to higher voltages, while 0.25 and 0.15 V/min curve are comparable. The high formation rate increases the differences of the oxide thicknesses between the outer and the inner part of the anode; the oxide thickness in the anode centre will be smaller than on the outer anode surface area. This heterogeneous oxide thickness distribution will be increased with increasing anode size and decreasing pore size. For anodes made from 150 $\mu\text{FV/g}$ powder, the 0.77 V/min rate can be regarded as too fast, slower rates of 0.25 or 0.15 V/min are more reliable. The comparison of measured capacitance (displayed as single points) to the normalised CR current in fig. 5b over the range of 16-50 V shows a good agreement with the low F_{rate} curves 0.15 and 0.25 V/min. Using the low rate of 0.15 V/min, the native oxide layer was determined with ~ 4 V which is equal to 8 nm oxide thickness in case of a growth rate of 2 nm/V^4 .

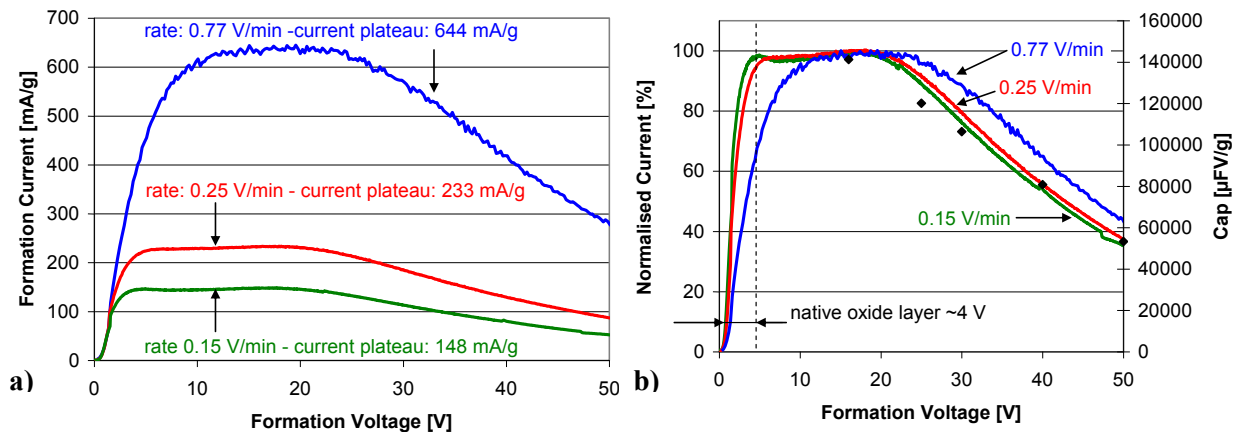


fig. 5 CR formation of anodes made from 150 $\mu\text{FV/g}$ powder @ 60°C (sinter density: 6.1 g/cm^3) with different rates a) formation current vs. voltage b) normalized current curves in comparison to capacitance (single points).

However, for anodes made from lower capacitance powders with larger pores 0.77 V/min has been proven as a proper formation rate that provides a good correlation between CR current and real capacitance curves. The CR formation curve of an anode made from a 40 $\mu\text{FV/g}$ powder, displayed in fig. 6, differs clearly from those described above and has only two different stages. The first stage is similar to those described above: a steep slope caused by native oxide film. A plateau region can not be observed, so that the second section is characterised by a continuous slope drop caused by continuous surface area loss. The measured capacitance shows a good correlation to the CR formation curve over the whole investigated range up to 150 V which means that one CR formation can replace 7 single formations including the capacitance measurements.

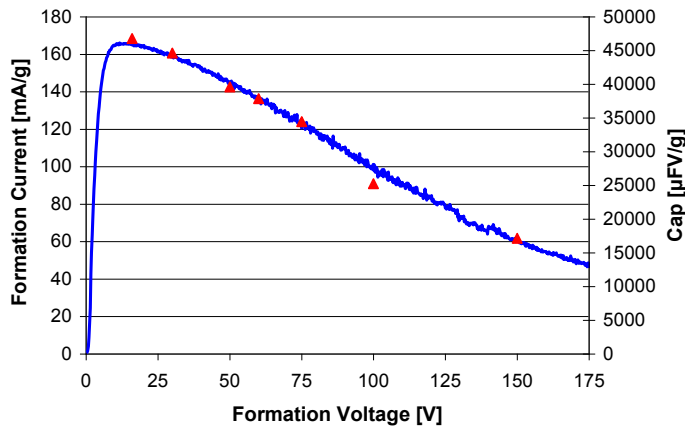


fig. 6 CR formation curve of a 40 kµFV/g anode (sinter density 5.7 g/cm³) and corresponding capacitance values.

New improved tantalum powders for high voltage applications

As described above, the smaller primary particle size and especially smaller pore sizes were the main reasons why tantalum powders from Mg reduction process couldn't be used for high voltage application up to now. To overcome this limit, new powder types were developed by introducing major process changes allowing to achieve a simultaneous increase of pore size and particle size. This allows combining the high structural homogeneity and high purity of powder produced by Mg reduction with desired high voltage capability. The pore size distributions of new tantalum powders HV1-HV4 in comparison to standard 150 kµFV/g powder is illustrated in fig. 7a. The standard 150 kµFV/g powder exhibit a pore size peak at 144 nm while the pore peak of the newly developed HV powders can be adjusted between 400-870 nm. Using mercury porosimetry allows also calculating the pore area of the pores size distribution (fig. 7b). Corresponding to the pore size, the surface area of the HV1 powder which shows the largest pore size maximum at 870 nm, was determined with 0.64 m²/g while HV4 (pore maximum at 400 nm) has a surface area of 1.13 m²/g.

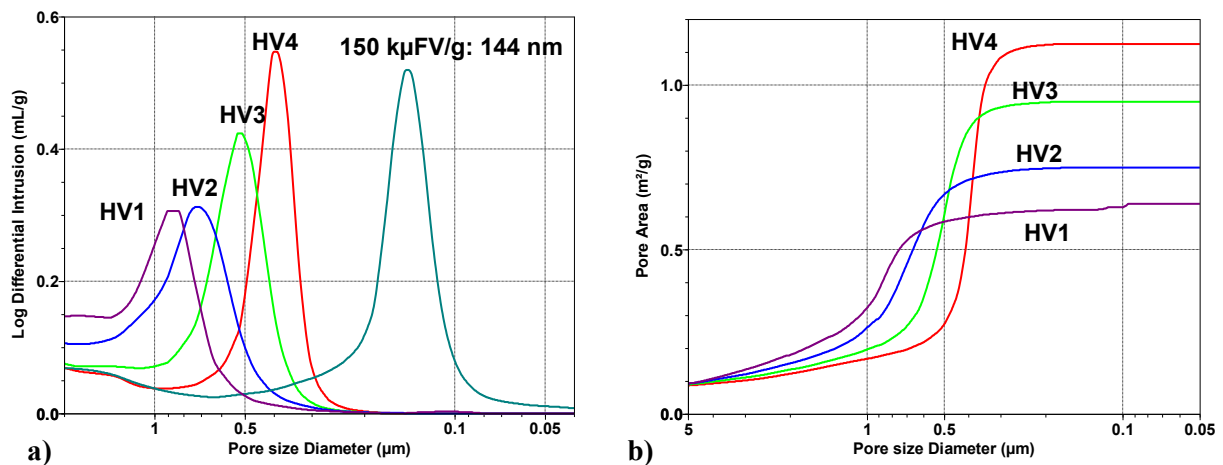


fig. 7 Properties of new improved tantalum HV powders: a) Pore size distribution of different HV powders in comparison to a standard 150 kµFV/g powder b) Pores area of new HV powder.

According to the presented simple cylinder model it was estimated that for a 100 V formation the unformed particle size should be at least 320 nm in order to provide enough tantalum for anodization, the maximum capacitance value was calculated for 380 nm particles. SEM investigations reveal that that new powder provides primary particle structures >350 nm which can also be adjusted over a wide range.

The new CR formation described above was applied for an extensive anode characterization in order to evaluate the capacitance capability of the new HV1-HV3 powders in comparison to standard 20 kμFV/g and 40 kμFV/g powders from Na reduction process up to 200 V (fig. 8). Again, the recorded current curve correlates to the capacitance – the higher the current at a given voltage the higher the capacitance. The anode made from 20 kμFV/g powder has the lowest capacitance up to 165 V. The anode made from 40 kμFV/g powder is comparable with that made from the HV1 powder up to 75 V. However, at higher voltages the capacitance performance of the HV1 powder is slightly better since the current curve of the anode made from HV1 powder is above those of the anode made from the 40 kμFV/g powder. The capacitances of the anodes made from HV2 and HV3 powders are distinctly higher than that of the anode made from 40 kμFV/g powder for a wide formation range; in case of HV2 the current curve is higher up to 180 V, while the HV3 will perform better up to 140 V.

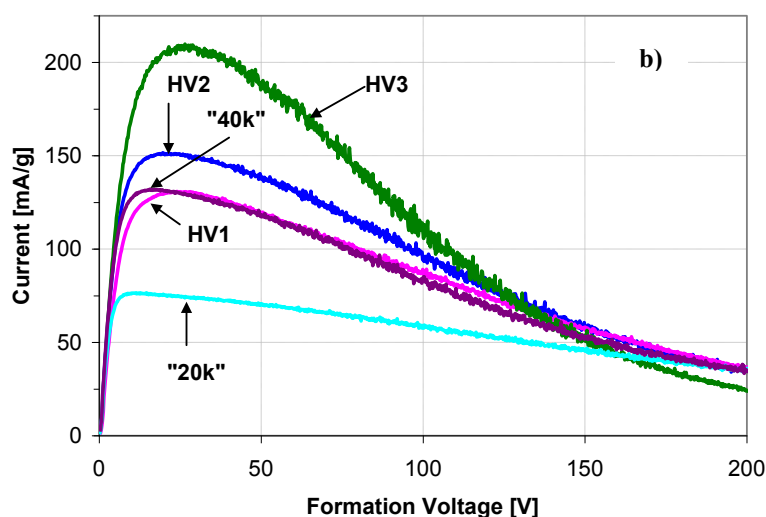


fig. 8 CR formation curves of new HV powder in comparison to conventional 20 kμFV/g and 40 kμFV/g anodes (formation rate 0.77 V/min, sinter density 7.0 g/cm³).

Using the CR curves allows estimating the capacitance sequence at a given voltage. For a 100 V formation the sequence, in which the capacitance is increasing from left to right, is:

$$20k < 40k < HV1 < HV2 < HV3.$$

A 100 V standard formation using anodes made from these powders have been carried out in order to check the validity of the CR based sequence with standard measured capacitance. It is already known that the wet capacitance of high CV anodes is significantly influenced by the measuring frequency due to limited electrolyte conductivity and small pore sizes^{13,14}. Anodes with small pores require low measuring frequencies (<120 Hz) in order to allow measurement of the total capacitance. A comparable behaviour was also observed for high voltage anodes when pores are getting smaller due to increasing oxide film growth. That's why a measuring frequency of 20 Hz was used instead of 120 Hz. The determined capacitance is in total agreement to the CR based sequence and demonstrated that this method is a powerful tool for powder evaluation (Table 2)

table 2 Capacitance of standard and new high voltage anodes HV1-HV3

Powder Type	20 kμFV/g	40 kμFV/g	HV1	HV2	HV3
Capacitance @ 100 V [μFV/g]	18.385	28.087	29.672	31.127	36.010

According to the CR formation test, the HV3 powder will provide the highest capacitance up to 120 V while the HV1 and HV2 powders should be used for higher voltages up to 150 V. The lower initial current of anodes made from HV1 powder in comparison to those made from HV2 powder indicates that the HV1 anodes have higher porosity which should have a positive impact on impregnation and ESR. That's why the HV1 powder should be the better choice of a 150 V formation even if the CR current curve, and therefore capacitance, is comparable at this voltage.

The HV powder shows not only higher capacitance but also improved microstructural homogeneity. Fig. 9 compares the cross section of 100 V formed anodes of a standard 40 $\mu\text{FV/g}$ powder and new HV2. The brighter shining tantalum cores are surrounded by the darker Ta_2O_5 layer. The standard anode structure is more heterogeneous concerning particle size and pore distribution: apart from open pore regions contains the anode very dense regions which will be difficult to impregnate. In contrast, HV2 anodes have a more uniform pore size distribution which allows a better impregnation. Furthermore, also the tantalum particle structure is more homogeneous concerning particle size and shape. This is the main reason why the HV2 anode capacitance is in comparisons to 40 $\mu\text{FV/g}$ anode more than 10 % higher.

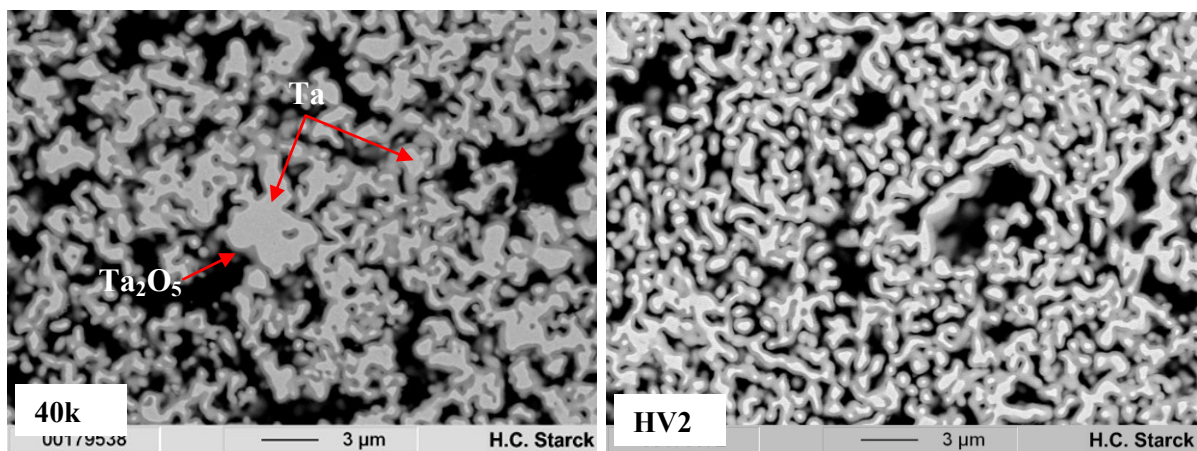


fig. 9 SEM polished cross section of 100 V formed anodes (sinter density 7.0 g/cm^3): The unformed tantalum core appears bright while the Ta_2O_5 film is darker, pores are black.

Summary

It was shown that high voltage tantalum capacitors have special requirement on microstructure that has to be taken into account like sufficiently big primary particle size, neck size as well as pore size. For each formation voltage exist an optimum particle size that provides the highest possible capacitance. By using a simple cylinder model it was calculated that a 100 V formed anode can provide a capacitance of maximum 51.7 $\mu\text{FV/g}$ when the unformed tantalum cylinder has a diameter of 380 nm.

To find best anode conditions, like pressing and sintering, but also to ease the evaluation of different powders, a new characterization method was presented. It could be shown that the constant rate formation provides current-voltage curves that can be directly correlated to the capacitance-voltage behaviour with only one single formation.

Finally, new developments allows to extend the capability of the Mg reduction process to produce excellent tantalum powders for HV applications which show comparable or even better capacitance behaviour than standard sodium reduced powders up to 150 V. Not only capacitance but also the pore structure was improved which will be an addition benefit for impregnation. The process allowing control of the pore size over a remarkable range is still under development and its limit is not reached. An additional pore expansion $> 1 \mu\text{m}$ should allow to extent this range up to 200 V by keeping its high homogeneity and improved capacitance.

- 1 J. Petrzílek, T. Zedníček, M. Uher, I. Horáček, J. Tomáško, L. Djebara “Next Generation of High Voltage, Low ESR Tantalum Conductive Polymer Capacitors”, CARTS Europe, Munich 2010.
- 2 I. Horáček, T. Zedníček, S. Zedníček, T. Karník, J. Petrzílek, P. Jacisko, P. Gregorova, I. Pinwill “High CV Tantalum Capacitor – challenges and limitations” CARTS USA, Jacksonville, 2009.
- 3 L. Young “Anodic Oxide Films” Academic Press, New York, 1961.
- 4 W.D. Westwood, N. Waterhouse, P. S. Wilcox “Tantalum Thin Films” Academic Press, London, 1975
- 5 R.M. German, G.L. Messing and R.G. Cornwall, “Sintering Theory and Practice. Sintering Science and Technology”, ed. T.P.S. University, John Wiley & Sons, New York, USA (2000)
- 6 M. N. Rahaman, „Ceramic Processing and Sintering“, Marcel Dekker, Inc., New York (1995)
- 7 Yet-Ming Chiang, Dunbar Birnie, W. David Kingery, „Physical Ceramics – Principles for Ceramic Science and Engineering“, John Wiley & Son, Inc., 1997
- 8 Leah F. Simkins, Michael J. Albarelli, Kathleen B. Doyle „Tantalum Powders for High Voltage Applications“ CARTS US 2002.
- 9 H. Haas, M. Hagymasi “Tantalum capacitor anodes providing highest capacitances: Where are the limits?” Carts Europe, Nizza 2011.
- 10 G.C. Wood, C. Pearson “Dielectric breakdown of anodic oxide films on valve metals” Corrosion Science, Vol. 7 issue 2, pp 119-125, 1967
- 11 C. J.B. Fincham “Properties of Tantalum Oxide in Electrolytic Capacitors” Proceedings of the fourth Electrical Insulation Conference, Washington, 1962
- 12 Y. Pozdeev-Freeman, A. Gladkikh “The Effects of Thermal Treatment on the Dielectric Properties of Anodic Films on Tantalum and Niobium: Crystallization” CARTS 2003.
- 13 H. Haas, C. Schnitter, N. Sato, H. Karabulut, Y. Fujimori, O. Thomas „Challenge: Highest Capacitance Tantalum Powders” CARTS USA, Jacksonville, 2009
- 14 Stephen E. Hluchan “Powder Geometry and Structural Design of the High Volumetric Efficiency Tantalum Electrolytic Capacitor” IEEE Transactions on Parts, Hybrids and Packaging, Vol. PHP- 9, No. 3, September 1973, pp. 148-155.