

Highest Capacitance at higher voltages: Pushing the limits of tantalum high voltage capacitors

2nd Space Passive Component Days (SPCD), International Symposium

Marcel Hagymási¹, Christoph Schnitter², Rich Reifenheiser³, Oliver Thomas⁴

(1) Tel.: +49 5321 751 53160, e-mail: marcel.hagymasi@hcstarck.com

(2) Tel.: +49 5321 751 53939, e-mail: christoph.schnitter@hcstarck.com

(3) Tel. +1 617 678 8497, e-mail: rich.reifenheiser@hcstarck.com

(4) Tel.: +49 5321 751 5955, e-mail: oliver.thomas@hcstarck.com

H.C. Starck GmbH, Im Schleeke 78-91, 38642 Goslar, Germany

There is an increasing demand for electronic applications using tantalum capacitors operating at high voltages. This demand is driven by automotive (e.g. driving assistance systems and infotainment systems), medical devices and aviation, as well as data storage (SSD). This will require new improved tantalum powders that can meet the specifications of high dielectric strength, improved energy density and excellent reliability at voltages >100V. These applications must also follow the trend of miniaturization and therefore cannot be satisfied by existing powders since their volumetric efficiency is simply too low.

Therefore H.C. Starck has developed a class of new tantalum powders with a tailored microstructure that can provide higher capacitances than any other tantalum powder and high reliability for anodization voltages from 75 V to 350 V. In this paper it will be shown that microstructural homogeneity of primary particles as well as pore size distributions are the key factors for increasing capacitance. Beside superior material properties of these new powders the anode manufacturing process has to be taken into account in order to achieve capacitors with highest energy density. Therefore it will be discussed how pressing and sintering conditions influence the performance of anodes made from these powders. For anodization of these powders, new organic based electrolytes have to be utilized to prevent breakdown of the oxide layer at higher voltages > 100 V.

Introduction

As a technology leading company H.C. Starck made considerable efforts to develop new tantalum powders to follow the trend of miniaturization. In general for tantalum capacitors two different trends can be observed. For lower application voltages up to 6.3 V HC Starck continues to increase the capacitance of the powder up to 250k $\mu\text{FV/g}$ and even higher – these powders are often designated as “high CV”. The increase of capacitance ability of such powders is achieved by decreasing the primary particle size so that the total surface area is increased.

The second trend which shows a significant growth is to increase the application voltage of tantalum capacitors to higher values from 25 V to 100 V and even higher. The definition of high voltage range depends on the market and

application. As a result of intensive research H.C. Starck has recently developed a new class of high voltage powders – called HVMC (high voltage medium capacitance) that can be anodized over wide range from 75 V up to 350 V. These powders provide the highest capacitance and energy density at such high anodization voltages that cannot be achieved by other available tantalum powder. The HVMC powders enable the capacitor producers to make new capacitor types with highest energy densities for new applications that could not be achieved in the past. They are designed for different applications such as data storage (solid state drives), battery charger for faster charging as well as a specific focus on high reliability applications:

- Automotive: Assisted driving systems, the change of the board net system of cars to higher voltages and electromobility
- Transportation and railroad applications
- Medical application such as implantable defibrillators
- Aviation and aerospace, e.g. for satellites
- Defense

These powders are used for both solid (MnO₂ and Polymer) and wet type capacitors. The anode weight can vary over a wide range up to several grams and also the shape is very different from large flat anode (round, “half moon”, rectangular) as well as cylindrical ones.

First we will have a look at the microstructure of such a powder in order to explain what makes these powders so unique and why they are so superior compared to standard powders. Afterwards it will be shown that it is simply not enough to have an excellent high voltage powder – it is also essential to use the right pressing and sintering conditions to gain the maximum capacitance and good leakage current.

HVMC – new high voltage powder class

High voltage powders must have a different microstructure than a “high CV” powder used for lower voltages. Tantalum primary particles require larger sizes so that enough tantalum remains after anodization: too small tantalum particles will completely converted to Ta₂O₅. On the other hand too large particles will have a lower surface area which corresponds to a lower capacitance as well. Also pores has to be large enough so that the formed oxide film has sufficient space for its growth otherwise they will be closed resulting in lower capacitance. Too large pores can be regarded as a waste of space and therefore capacitance. Moreover sufficient strong neck sizes as smallest connection between two adjacent particles are required otherwise the current path will be discontinued. It was already shown by calculations that each anodization voltage has its own optimum concerning primary particle and pore size distribution [1]. The real structure of tantalum consists not of a single pore or particle but a distribution. The unique capacitance properties of the HVMC powders are based on the higher homogeneity of both primary particle size and its pore size distributions. In contrast to other powders also the naming of the special powder class was changed – it is not correlated with the expected capacitance (mostly measured at lower voltages) but for the designated forming voltage! “HV100” means that this is an HVMC powder with a target formation voltage of 100 V. Through minimal adjustments to the pressing, sintering and forming condition this powder can also be used for lower or higher voltages. The comparison of the cross section of anodes in fig. 1 shows differences in microstructure

between a standard 12k $\mu\text{FV/g}$ powder and an HV300 powder, both formed at 300 V. Note that this is an SEM in back scattering mode where the level of brightness is correlated to the average atomic weight: heavy elements/compounds will be bright while lighter elements/compounds are darker.

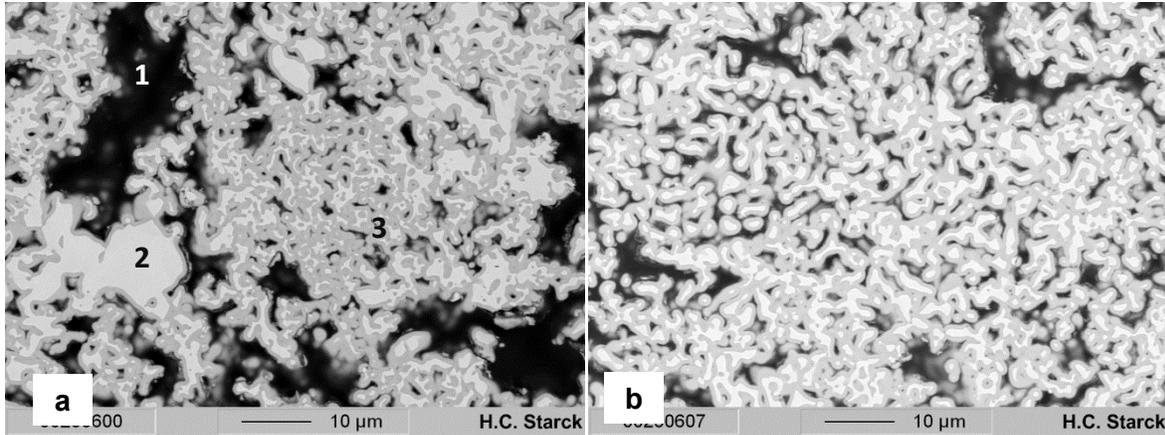


fig. 1 Microstructure of 300 V formed anode made of a) 12k $\mu\text{FV/g}$ standard powder that has (1) too large pores, too large primary particles and (3) too small primary particle with closing pores b) new HV300 with significantly improved homogeneity.

The standard powder has a wide primary particle and pore size distribution: beside very large particles (2) that consist of sufficient tantalum to be formed to even higher capacitance but having low contribution to capacitance also too small tantalum particles (3) can be found which are nearly totally converted to oxide while the remaining pores are already closed. This surface area will also give no contribution to capacitance. Finally too large pores (1) can be regarded as a waste of space that reduces the achievable volumetric capacitance. In contrast to that the HV300 clearly shows the superior microstructure with improved homogeneity: tantalum particles as well as pore size variation are much smaller so that the provided capacitance is significantly higher due to improved utilization of tantalum. This is the main reason why the HVMC powders can always provide a higher capacitance than any other current powder. Through our research we have determined the optimum primary particle and pore size distribution at a given anodization voltage therefore we have developed a different powder for each anodization range that will provide the highest capacitance [2]. For a range of 100 to 350 V anodization voltage in fig. 2 it is illustrated that over the entire anodization range HVMC powders are offered providing higher capacitances than the corresponding “best in class” standard powder available today. To provide a fair competition all anodes have the same press density (6.0 g/cm^3) and shrinkage ($\sim 10 \text{ vol.-%}$) conditions.

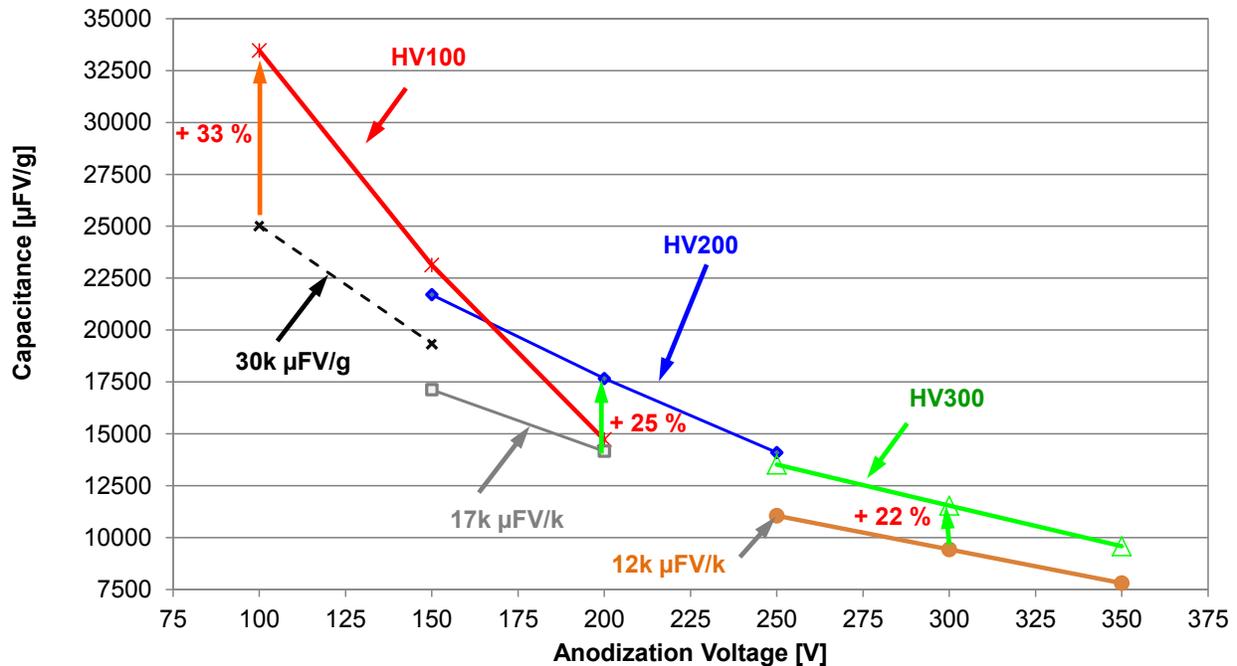


fig. 2 Capacitance vs. anodization voltages: HVMC HV100-HV300 vs. standard (Na reduced) powders.

For 100 V the HV100 offer 33 % more capacitance than the 30k µFV/g powder, the HV200 offers more than 25 % capacitance increase at 200 V while the HV300 can provide more than 22 % additional capacitance at 300 V. These findings have been confirmed by capacitor manufactures as well. However to gain the highest capacitance it is not enough to use the right HVMC powder, proper pressing and sintering conditions are required. Next it will be shown how to find the best anode conditions.

Finding the optimum: Impact of pressing on sintering

As a leading tantalum powder producer it is not enough for H.C. Starck to develop a powder – it has first to be tested internally to ensure it meets the development requirements such as improve efficiency, increased capacitance or higher voltage capability. It will also be compared to other new or already existing powder that serves as benchmark. Based on these results the proper powder will be developed.

While chemical and physical powder properties are only depending on powder production most of the important capacitor properties like capacitance, leakage current and breakdown behavior are also strongly influenced by the processing parameters. Pressing and sintering as well as anodization have a significant impact on such properties and cannot be neglected. It can be compared with fuel consumption of a car: driving mostly high speed with high acceleration will lead to high consumption while a fuel-conversing driving style (lower speed, slower acceleration) with the same car will lead to totally different result. Let's transfer this picture to tantalum capacitors: Even a perfect

high voltage powder can provide less than desired results or even fail if the wrong conditions are applied. Moreover which process parameters are required to find the maximum capacitance and simultaneously an acceptable leakage current?

Each anodization voltage has its own capacitance optimum – which depends on the powder microstructure. It was already shown that the HVMC microstructure is unique when compared to existing standard powders [2,3]. Therefore the optimum pressing and sintering conditions can be different from standard powders and has to be determined.

Experimental Part

Anodes have to be pressed and sintered before anodization. Both steps have an impact on the final anodes. For a given target sinter density (SD) of e.g. 6.3 g/cm³ different paths are possible to achieve it: a low press density (PD) of 5.0 g/cm³ requires shrinkage of 20.6 vol.-% while a higher press density of 6.0 g/cm³ needs only 4.8 vol.-%. In both cases the same sinter density will be achieved but the different procedures have a significant impact on the final capacitance, leakage current, breakdown behavior as well as anode pore structure. We will use HV300 that provides currently the highest capacitance at 300 V for an extensive investigation to find optimum pressing and sintering condition. We will look at both weight correlated (“CV/g”) and volume correlated (“CV/cm³”) capacitance, but which is the “right” capacitance that should be used to decide which pressing and sintering conditions are ideal? Finally volume is given for each capacitor type. Powder weight of this volume can be changed by using different sinter densities which is not included in weight correlated “CV/g” – only the volume correlated capacitance “CV/cm³” takes this into account. This means that a condition that results in lower “CV/g” can provide in the end a higher “CV/cm³” because more powder is included in the same volume due to higher sinter density that compensate the lower CV/g.

Round anodes (Ø 3.0 mm) were used with press densities from 5.0 up to 6.5 g/cm³ in 0.5 g/cm³ steps. All anodes were sintered for 20 min at three different temperatures (1380°C, 1435°C, 1490°C). This corresponds to 3 shrinkage ranges (low, medium and high) of ~5, 10 and 16 vol.-% (Δ1.5 %) that are illustrated in fig. 3. Sinter density varies over a wide range from 5.2 to 8.0 g/cm³. As described before we achieved comparable SD by different steps: e.g we achieved ~6.0 g/cm³ by applying a PD of 5.5 g/cm³ and low shrinkage of ~6 vol. %- or a PD of 5.0 g/cm³ and high shrinkage of ~16 vol.-%.

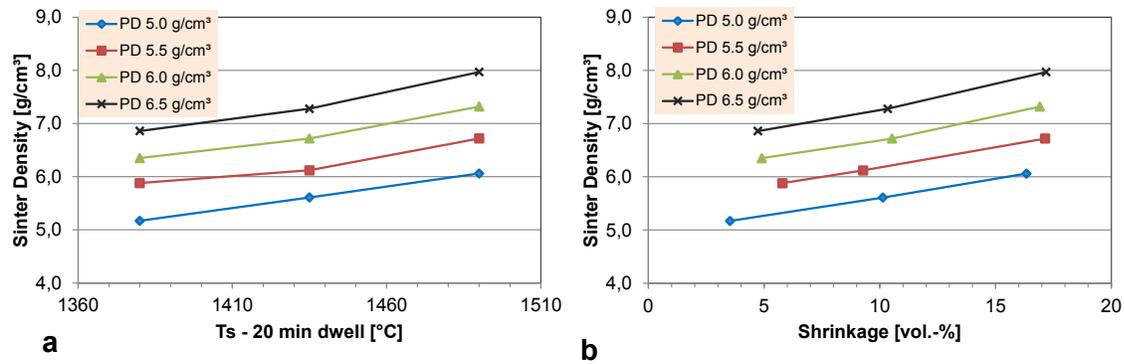


fig. 3 Sinter density of HV300 anodes for all applied press densities against: a) sinter temperature b) corresponding shrinkage

All anodes were formed at 60°C in a water/glycol based phosphoric acid electrolyte – it has been shown that glycol based electrolytes are recommended for high voltage formation >100 V [4-6]. Even if the whole mechanism is not scientifically understood it was observed that such electrolytes reduce the breakdown tendencies and improved the leakage current. It is known that anode size and shape have an impact on forming condition and capacitance behavior. However, to minimize the effort it was decided that this will be investigated separately. Moreover it is assumed that the general tendencies are comparable.

For all anodes we applied the same constant rate (potentiodynamic) formation program with stepwise decreased rates until we reached the final voltage (fig. 4). Current is always automatically adapted to provide exactly the required forming rate (V/min) independent from anode type, amount or even powder type. Standard formation with galvanostatic formation (current is fixed) has the disadvantage that the area decrease during anodization leads to an increase of current density (current per area) and therefore to an increase of anodization rate (V/min). Too high forming rate will lead to the increased generation of oxygen [7], increases the breakdown ability and can finally crack the oxide film. Moreover, if defects such as breakdowns or other structural oxide flaws are generated during anodization the current will mainly flow over these anodes while the remaining anodes will get much less current thereby effecting the anodization of good anodes. Using constant rate formation prevents this interaction between “good” and “bad” anodes – in the case of local defects in single anodes the current will be increased to provide the same oxide growth for all anodes: each anode will get exactly the current that is required! According to many anodization trials it was found that anodes are much more stable at lower voltages when most of the tantalum is not yet converted to oxide. With increased voltage the remaining tantalum core is getting smaller while the oxide film is growing and closes more and more the pores. As a result the tantalum anode gets weaker and anodization rate has to be decreased. That’s why our anodization profile starts with a fast anodization rate (V/min) when the anode is very strong and is stepwise decreased when it’s getting weaker. In total our program has 3 different ramp rates until we reach 300 V, in each step the required current is automatically adjusted.

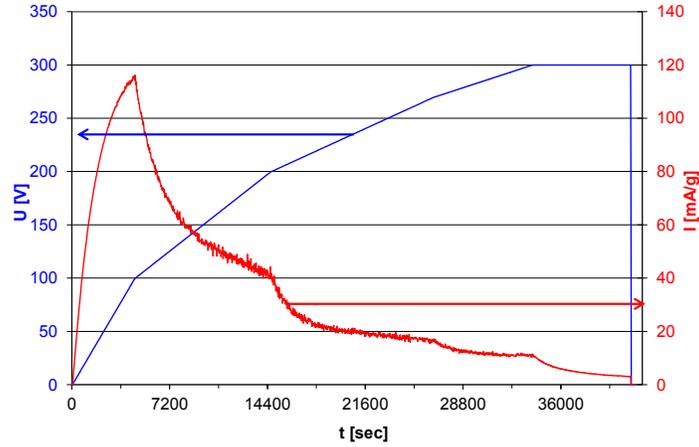


fig. 4 Potentiodynamic anodization program used for HV300 forming.

Weight correlated capacitance “CV/g”

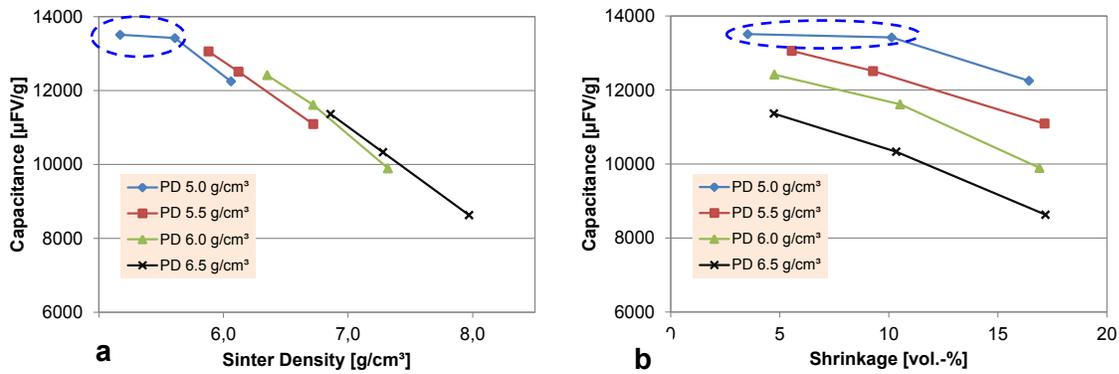


fig. 5 Capacitance of HV300 @ 300 V for different press densities: a) cap vs. sinter density b) cap vs. shrinkage for same anodes. Apparent cap maximum is encircled with blue dashed line.

Let's first have a look at weight correlated capacitance. To illustrate the effect of sintering, capacitance is plotted against final sinter density as well as to the corresponding shrinkage for all press densities. It is obvious in fig. 5 that the combination of the lowest press density of 5.0 g/cm³ and lowest shrinkage of 4 % provides the highest CV/g of ~13510 μFV/g. For the lowest PD of 5.0 g/cm³ when increasing shrinkage from 5% to 10 vol.-% had a nominal impact on capacitance (drops to 13420 μFV/g). At all higher press densities show the same tendency: increasing shrinkage will decrease weight correlated capacitance. It has to be noticed that the powder has always the highest surface area and therefore the highest capacitance. Densification of tantalum anodes occurs via solid state sintering with the driving force of reducing free surface energy by reducing the power surface area [8]. With increasing shrinkage surface area is reduced by particle size growth, pore size and volume will also be reduced ultimately reducing the anode capacitance.

Moreover, increasing press density also results in a decrease of the anode capacitance. Mercury porosity (Micromeritics Instrument) was carried out with all sintered anodes to determine pore size distribution from low shrinkage anodes. Pore distribution in fig. 6 reveals that with increasing press density the entire pore distribution is shifted to smaller sizes. In general the HV300 and all HVMC powders have two kinds of pores: primary pores are the smaller pores within the agglomerate structure formed by primary particle structure. They are responsible for the majority of the total surface area and therefore the capacitance. The larger secondary pores are a result of the empty space between larger adjacent agglomerates, the contribution to capacitance is negligible but they are important for impregnation of the cathode material and some electrical properties such as ESR. However, since tantalum itself cannot be compressed – it has always the same density of 16.6 g/cm^3 - only the total pore volume will be decreased with increasing press density which can be observed in the pore size shift to a smaller size: secondary pore peak decreases from $2.63 \text{ }\mu\text{m}$ (PD 5.0 g/cm^3) to $1.44 \text{ }\mu\text{m}$ (PD 6.5 g/cm^3) while primary pore peaks are shifted from $1.31 \text{ }\mu\text{m}$ to $1.12 \text{ }\mu\text{m}$.

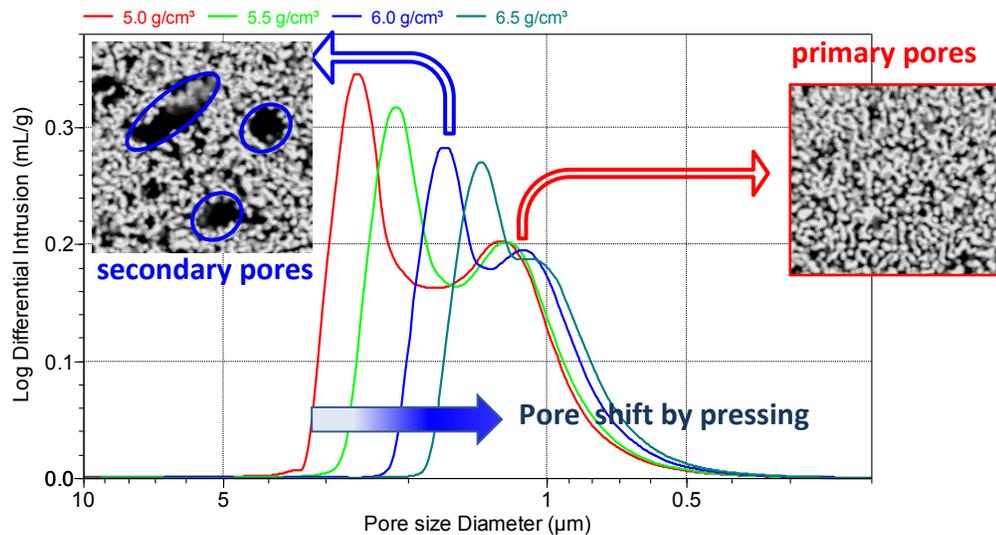


fig. 6 Sintered anode pore distribution for all investigated press densities ($\sim 5\%$ shrinkage) – please not the inverse logarithmic scale; smaller pores are at the right sight.

In addition higher press density increases the contact areas between adjacent tantalum agglomerates; the remaining surface area is decreased. Mercury porosimetry can also be used to calculate the pore area which correlates to the anode area and therefore with the capacitance. The weight correlated anode pore area distribution for all press densities in fig. 7 confirmed that increased press density not only shifts the pore sizes to lower values but also the pore area is decreased: the total pore area is decreased from $0.325 \text{ m}^2/\text{g}$ (PD 5.0) to $0.296 \text{ m}^2/\text{g}$ (PD 6.5) which corresponds to an 8.9% reduction. The observed capacitance drop with increased press density can be explained by the changed pore structure and decreased pore area. The observed capacitance decrease with increased press density for the low shrinkage anodes from $13510 \text{ }\mu\text{FV/g}$ (PD 5.0 g/cm^3) to $11370 \text{ }\mu\text{FV/g}$ (PD 6.5 g/cm^3) correlates with 8.4% pore area reduction in fig. 7!

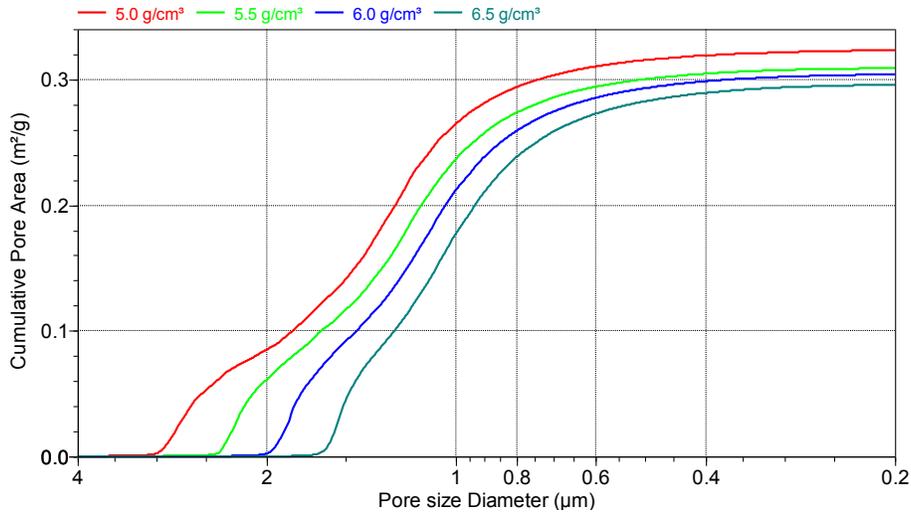


fig. 7 Sintered anode pore area distribution of all press densities (~5 % shrinkage).

Looking only at the weight correlated capacitance, a press density of 5.0 g/cm³ and low shrinkage of 4 % (or even 10 %) would provide the highest values of 13511 µFV/g at 300 V – this “apparent” cap maximum is marked in fig. 5 with a blue dashed circle. In contrast to that, anodes with the highest sinter density of 8.0 g/cm³ (PD 6.5 g/cm³) have the lowest capacitance value of only 8632 µFV/g. Too high pressing and shrinkage conditions leads to smaller pores that are closed during anodization resulting in additional capacitance loss. The general effect of closing pores and decreasing pore (and therefore anode) area which is valid for all anode conditions can be seen in fig. 8 for an anode with PD 6.0 g/cm³ and 10 % shrinkage. The pore peak is shifted to smaller sizes while the total intrusion (pore volume) is also reduced since the formed oxide film closes the remaining pore. The formed pore area is significantly reduced from 0.28 to 0.16 m²/g.

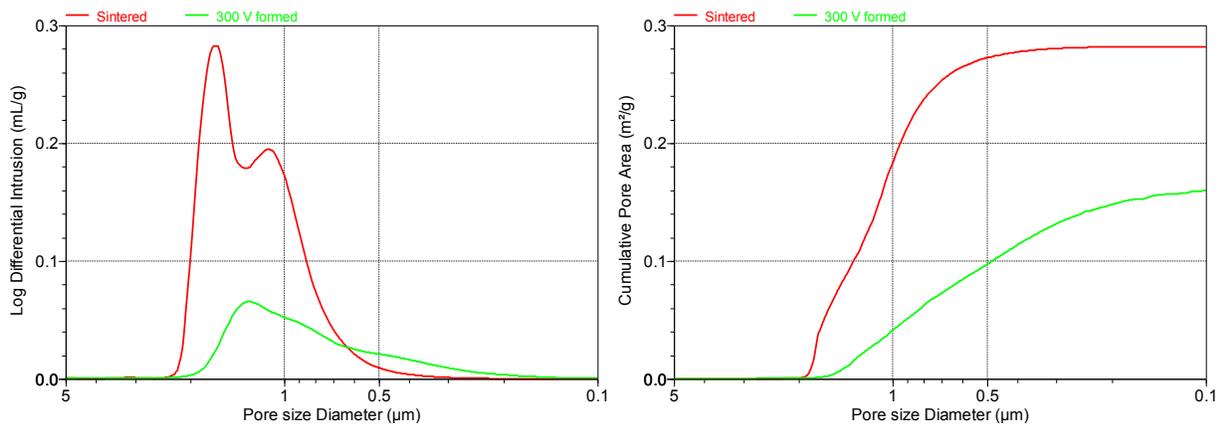


fig. 8 Anode pore size and pore area distribution of an HV300 (PD 6.0 g/cm³, 10 % shrinkage) after sintering and 300 V forming.

As already mentioned increasing shrinkage also leads to decreased pore volume as well as pore area that ultimately reduces the final capacitance. Since all press densities show the same trend we will use anodes with a PD of 5.5

g/cm³ in the following discussion (see fig. 9): Increased sintering temperature and therefore shrinkage reduces mainly the pore volume (“intrusion”), note how the primary and secondary pore peaks are shifted to smaller sizes. Finally the weight correlated pore area is reduced which is consistent with the capacitance drop.

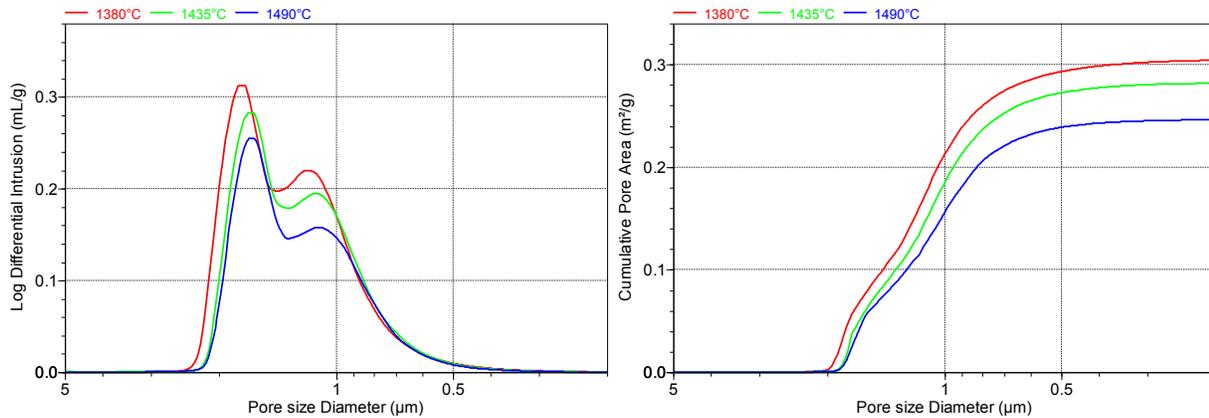


fig. 9 Effect of sintering on anode pore size and pore area distribution (PD 5.5 g/cm³).

Influence on breakdown stability and leakage current

Beside capacitance the structural strength of the anode has to be taken into account! Anodes with the lowest press density and shrinkage were very susceptible to oxide breakdown due to the weak connection between adjacent agglomerates and also smaller neck sizes within the agglomerates. Higher shrinkage improves the anode strength and therefore breakdown probability is reduced. The anode condition that provides the highest “CV/g” (lowest PD of 5.0, lowest shrinkage of 4%) could not be formed without breakdown (fig. 10) – before the final voltage was reached (~297 V) current was significantly increased which indicates side reaction and local oxide breakdown - affected damaged anodes were recognizable by strong gas evolution. The current drop during the final potentiostatic stage at 300 V was very limited, in comparison to a good anodization behavior the final current that was reached when forming is finished was very high (20 mA/g final current instead of 4 mA/g at the end of the anodization, compare fig. 4)

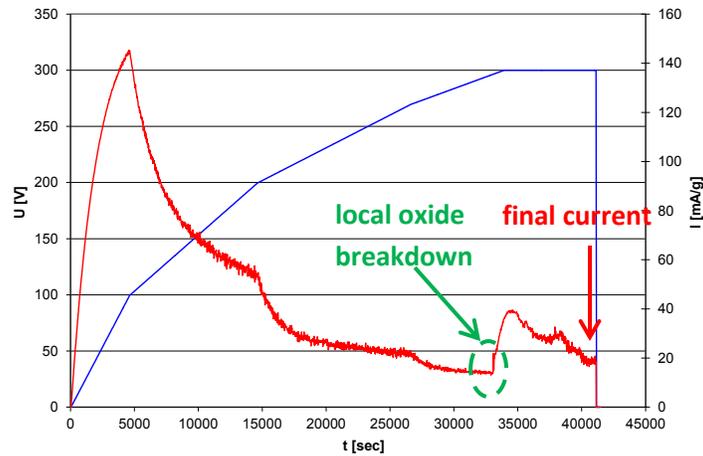


fig. 10 Constant rate formation curve of low pressed and sintered anode (PD 5.0 g/cm³, 4% shrinkage): Local oxide breakdown at 298 V causes rapid current increase.

Also the leakage current behavior confirmed that independent from press density the low shrinkage anodes are susceptible to anode damages that leads to high leakage current values (see fig. 11). For all press densities, increasing the anode shrinkage from 5 to 10 % results in much lower values due to the stronger anode structure. However, additional shrinkage leads only to an insignificant improvement. That's why it is recommended to use no more than ~10 vol.-% shrinkage for HV300 anodes formed at 300 V. Even though the capacitance seems to be better for lower shrinkage anodes, the anode integrity will be jeopardized resulting in higher leakage values. Second tendency that can be recognized is that with increased press density (same shrinkage) the leakage current is improved. Similar to shrinkage higher press density improves the structural strength of the anode by improving the contact area between adjacent agglomerates and particles so that after sintering a stronger connection is realized. The Impact of press density on leakage current for very high sintered/shrunken anodes is very limited since the anode strength is already very high at such conditions.

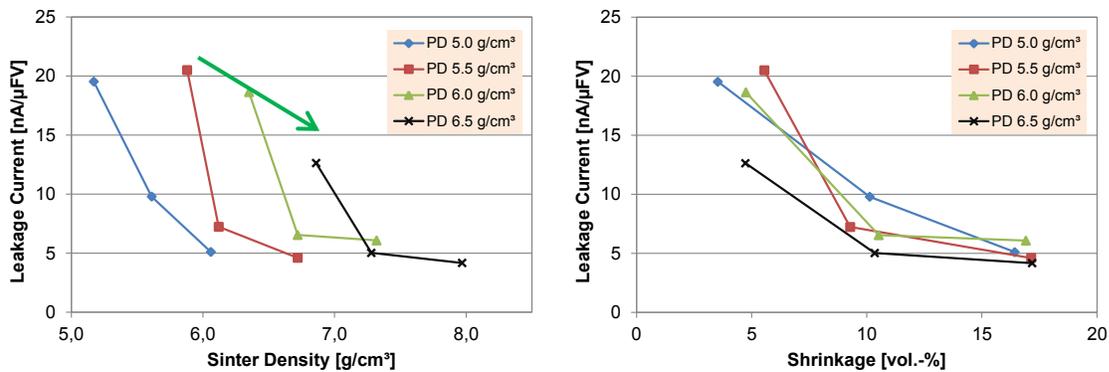


fig. 11 Leakage current of HV300 at 300 V for all press densities and shrinkages/sinter densities.

Volume correlated capacitance “CV/cm³”

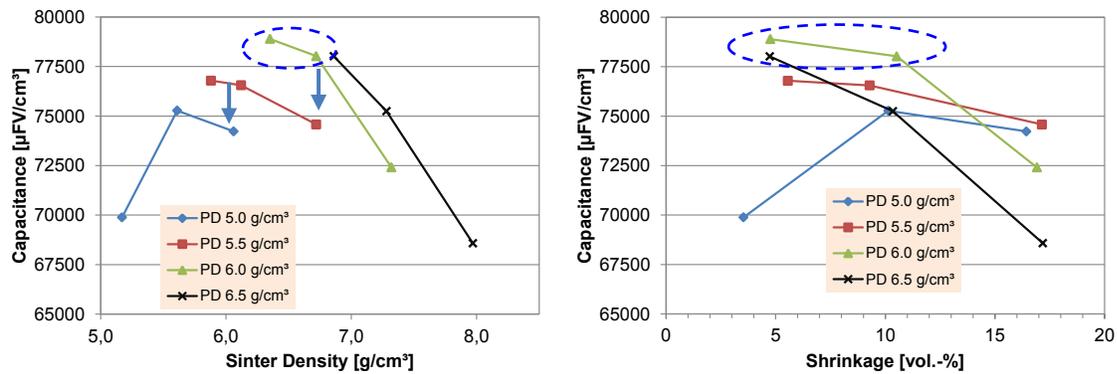


fig. 12 Volume correlated capacitance of HV300 @ 300 V as a function of press density and shrinkage/sinter density. Maximum is encircled with blue dashed ellipse.

Only the volume correlated capacitance takes the sinter density into account and therefore it is recommended to use it to determine the best volumetric pressing and sintering conditions that provides a capacitance maximum. The appearance of the volume correlated capacitance curves vs. sinter density and shrinkage in fig. 12 differs strongly from weight correlated capacitance in fig. 5. Using a PD of 6.0 and shrinkage of 5 % provides the highest capacitance of 78900 µFV/cm³. Increasing shrinkage to 10 % results in very high capacitance values of 78029 µFV/cm³ which is in the same range of higher pressed but lower shrunken anodes (78024 µFV/cm³, @ PD 6.5 g/cm³, 5 %). This area is regarded as the real maximum capacitance area of HV300. When leakage current behavior (fig. 11) is taken into consideration only one condition is left: PD 6.0 g/cm³ and 10 % shrinkage since the other low shrinkage anode conditions will lead to significantly worse leakage current. The formerly designated “apparent” CV maximum anode condition of PD 5.0 g/cm³ and shrinkage 4-10 % has distinctly lower volume correlated capacitance. In fact: the higher press density of 6.0 g/cm³ leads to lower “CV/g” but the increased powder amount could compensate for this. Higher press density has even more powder but due to the smaller pore sizes and pore volumes they are closed or filled very quickly at higher voltages that results in a significant capacitance drop.

Conclusion

Due to its structurally superior homogeneity the HVMC power class provides the highest capacitance over a wide anodization range up to 350 V. Pore size and primary particle size distribution is narrower compared to available standard high voltage powder. This narrow distribution results in a more efficient use of the Tantalum volume within the anode resulting in significantly higher capacitance with HVMC powders. It was shown for a 300 V anodization of HV300 that capacitance, leakage current, and also breakdown behavior is not a pure powder property, pressing and sintering has a strong impact on the final anode behavior and cannot be neglected. Increasing the press density

improves the anode strength and decreases the leakage current, this does have a limit as too high of a press density leads to smaller pores that are closed during anodization, reducing capacitance. Higher shrinkage improves leakage current but decreases the capacitance due to the reduction in surface area. If only the weight correlated capacitance is considered the lowest press density of 5.0 g/cm³ with low shrinkage of 4 % will provides the highest capacitance of 13511 μFV/g. However this condition will also result in higher leakage values due to the poor contact between agglomerates and the smaller necks and sinter bonds within and between the particles. Therefore this condition cannot be recommended. It was revealed that only the volume correlated capacitance has to be used to define the optimum conditions because it takes the increased powder amount of higher press densities into account. Using a press density of 6.0 g/cm³ and shrinkage of 10 % provides the maximum capacitance of 78029 μFV/cm³ and ensures low leakage current and high breakdown strength. Pressing and sintering conditions must be optimized in order to maximize the benefits of higher capacitance and lower leakage of the HVMC powders.

- [1] M. Hagymási, H. Haas, C. Schnitter, H. Brumm, "High Voltage Tantalum Powder – Challenges and Opportunities for new Powder Generation", CARTS Europe, Nice, France 2011
- [2] M. Hagymasi, K.P. Rataij, H. Haas, C. Schnitter, H. Brum, "Tailoring the microstructure: Optimization of Tantalum powders for highest voltage applications up to 350 V", QARTS US, Mesa 2015
- [3] M. Hagymási, H. Haas, C. Schnitter, H. Brumm, "Novel High Voltage Tantalum for New Applications", T.I.C. 2013, York, England 2013
- [4] M. Croset, E. Petreanu, D. Samuel, G. Amsel, J.P. Nadai, "An O¹⁸ Study of the Source of Oxygen in the Anodic Oxidation of Silicon and Tantalum in Some Organic Solvents", J. Electrochem. Soc.-1971-Croset-717-27
- [5] N. F. Jackson, "Field crystallization of anodic films on tantalum", J. Appl. Electrochem. 3 (1973), 91-98
- [6] Donald H. Stephenson, Martin D. Cymerman, Barry C. Muffoletto, "Using aqueous electrolyte containing ethylene glycol or polyoxyethylene glycol and phosphoric acid", US6231993 B1, 29. Sept. 1999
- [7] K. P. Rataj, C. Hammer, B. Walther, M. M. Lohrengel "Quantified oxygen evolution at microelectrodes", Electrochim. Acta, 90 (2012), p. 12-16
- [8] R.M. German, G.L. Messing, R.G. Cornwall, "Sintering Theory and Practice Sintering Science Technology", ed. T.P.S. University, John Wiley Sons, Ltd., New York (2000)