

**Pushing Tantalum capacitors to the limit: A powder manufacturers view to 300 V
anodizations and beyond.**

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Ta capacitors are the best choice when applications require highest capacitance (energy density) on miniature scale combined with high reliability, low ESR, and excellent stability over wide ranges of time and application temperature.

Recently, the demand of high reliability capacitors withstanding harsher conditions especially with respect to higher application voltage has been increased. Main driver for such applications are besides aviation and aerospace also automotive (driver assistance systems, e-vehicles) and transportation, medicine (defibrillators), defense but also consumer electronics like for data storage (solid state drive-SSD).

H.C. Starck continuously improves its portfolio of high voltage powders allowing to expand the tantalum capacitor technology to new fields of application. The “High Voltage Medium Capacitance” (HVMC) powders have a unique combination of structural homogeneity, high purity and tailored pore structure to provide the highest capacitance of Ta powder for the formation voltage (V_f) range $>80 V_f$. We will show the latest status of new developed powders that extend the range of forming voltage to 300 V and even up to 400 V.

Moreover, new options to further improve the pore structure resulting in increased capacitance at a given forming voltage will be presented as well. Beyond powder design, the tremendous impact of anode processing to master such high anodization voltages is highlighted.

Introduction

Moore’s law predicts that the number of transistors in a dense integrated circuit doubles about every two years [1]. This law describes the impressive speed of miniaturization but also the performance increase of electronic parts that has until

now never stopped. Likewise, the performance of tantalum capacitors is continuously improved but with a slower pace. For high voltage applications an unceasing and increasing demand for powders optimized for applications voltages >35 V is observed. They are used for different fields of application, often connected with high reliability: consumer electronics (SSD, charging devices, etc.), transportation and automotive, signal transmission for railway, medical devices (e.g. implantable cardioverter defibrillators), defense and aerospace (planes, satellites). There are in general different trends that we have realized in recent years: 1. Demand for more stored charge in a given volume at a given voltage, e.g. more capacitance at 150 V forming voltage not reachable with standard Ta powders to create new capacitor types for new applications. 2. Demand to further increase the forming voltage above 300 V since the energy W that can be stored by a capacitor is correlated with the voltage U squared:

$$W = C \int_0^U u \, du = \frac{CU^2}{2} \quad (1)$$

HVMC powders provide the required capacitance at forming voltages in the range of 100-350 V and are compared to standard tantalum capacitor powders, as shown in fig.1. At any voltage in this range, there is at least one powder type that has more capacitance and energy density than comparable standard powder types. It was already shown that the key for the excellent high voltage ability of HVMC powders is the improved microstructural homogeneity with respect to pore and primary particle sizes [2, 3]. The tighter primary particle distribution allowing higher capacitance is the result of extensive research to optimize the parameters of our production processes. We have developed different HVMC powder types, since each anodization voltage has its own optimum concerning primary particle and pore size distribution. To simplify the powder naming we have decided to put the classification (“HV” = High Voltage) and the recommended optimum forming voltage in its name (like HV200 – developed for 200 V_f) in contrast to the conventional naming where the capacitance (mostly measured at lower voltages) is included.

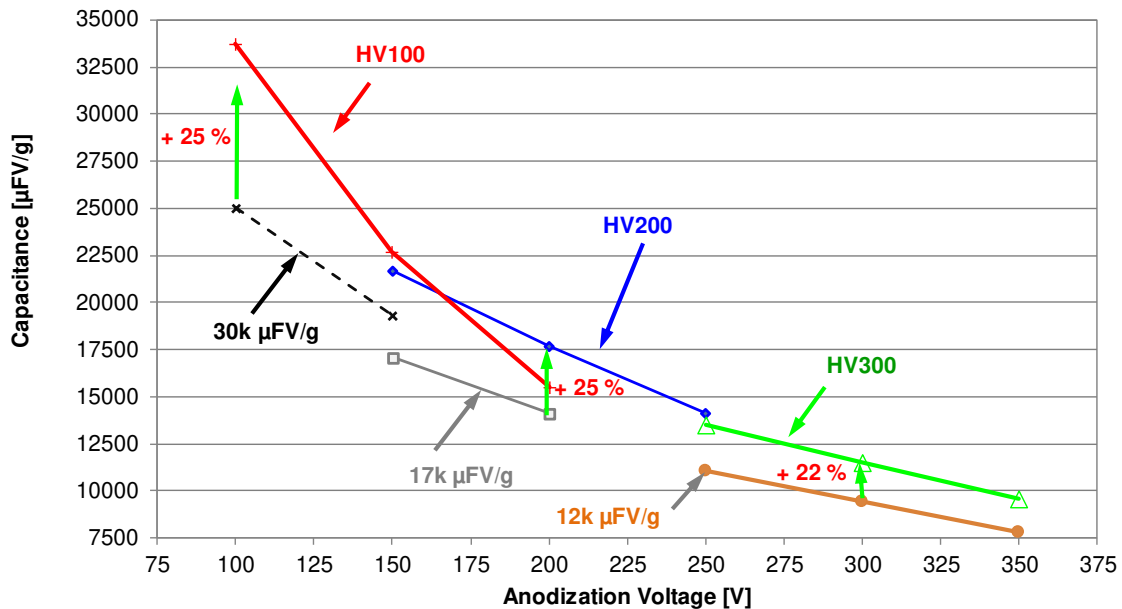


Fig.1 Capacitance as a function of forming voltage of HV100-HV300 in comparison to standard Na reduced powders.

The purpose of this paper is to show our general approach how to improve the microstructure regarding higher capacitance at a given formation voltage exemplified by our newly developed HV150 powder and how to extend the range of anodization up to 400 V by referring to our latest development, the HV400 powder. The impact of the anodization technique when reaching 400 V is significant and has, like the powder itself, to be optimized to realize new types of capacitors in the future.

How to provide more capacitance by tailoring the microstructure?

The microstructure of the tantalum powder is the key for realization of higher volumetric capacitances and must be tailored for each anodization voltage range to its optimum [2]. Currently, new capacitors with anodization voltage of ~ 150 V_f are highly requested. At 150 V anodization our products HV100 and HV200 show nearly comparable capacitance in electrical wet tests (see fig.2). However, due to its smaller pores as shown in fig. 3, capacitors made from HV100 will show worse impregnation and ESR behavior compared to those made from HV200 having larger pores. That's why HV200 would have been the powder of choice for 150V_f in the past.

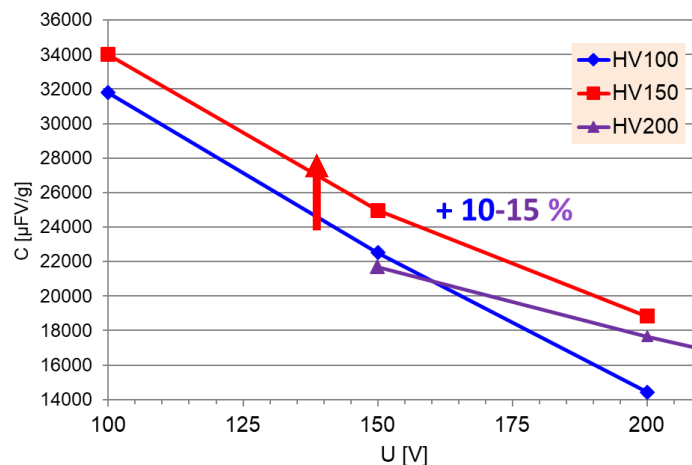


Fig. 2 Capacitance of different HV powder for the anodization voltage range of 100-200 V (@60°C forming bath temperature).

Our task was to develop a powder with distinctly higher capacitance than the HV100 and HV200 products in the range $V_f=100-200$ V by improving the particle and pore size distribution of the powders. To achieve this the Mg reduction process, proprietary to H.C. Starck and key step of the HVMC powder production route, needed to be enhanced. The pore size distribution of sintered anodes is considered as a suitable evaluation method because it demonstrates the influence of the pressing and sintering step on the powder structure.

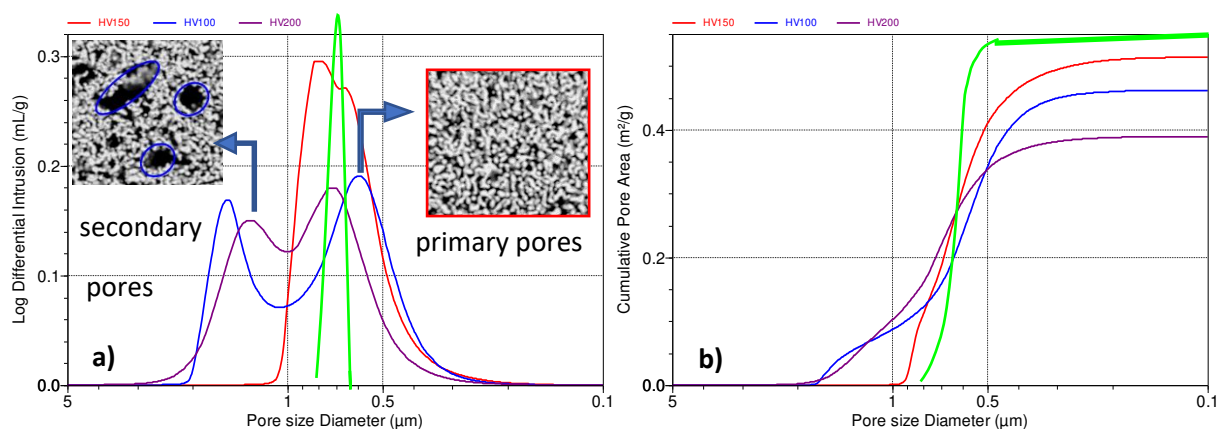


Fig. 3 Microstructure of sintered anodes made from HVMC powders (press density 6.0 g/cm³, 10 % shrinkage) a) pore size distribution b) pore area distribution (determined via Hg porosimetry).

Anodes made from HV100 and HV200 have both a bimodal pore size distribution. The smaller “primary” pores (maxima at 580 nm for HV100 and at ~720 nm for HV200) are responsible for the surface area of the porous anode body and therefore correlating to the capacitance. The larger “secondary” pores (maxima at 1540 nm for HV100 and at 1310 nm for HV200) representing the empty space between adjacent agglomerates. By adjustments in our processes it was possible to modify the pore size distribution for the new HV150 powder significantly. Anodes made from this new powder show a nearly monomodal pore size distribution and the maximum of the primary pore size is adjusted to 660 nm, i.e. between those of the maxima for HV100 and HV200 anodes. Moreover, the pore peak height (differential intrusion) is significantly higher than those for anodes made from HV100 and HV200 powders. This is caused by the more homogenous microstructure of the new HV150 powder which is intrinsically connected to a more uniform pore size distribution. As a result, the total pore area of HV150 anodes is even higher than that of HV100 anodes having smaller primary pore and particles.

The improved microstructure has a direct impact on the capacitance behavior (see fig. 2)! At 150 V_f this powder provides 10 % more cap than the HV100 powder and 15 % more cap than HV200 powder. It is interesting that also at 100 V_f and even 200 V_f this powder resulting in the highest capacitance – this reflects its enhanced uniformity that causes such stable capacitance slope. This is supported by the fact that the slope of the capacitance as a function of formation voltage for the HV150 anodes is not steeper than that for the HV100 anodes, but it is parallel.

This shows the general approach how to tailor capacitor powders to higher and higher capacitances in the future! To provide even more capacitance at 150 V_f the pores of future powders and anodes have to be as narrow as possible. In fig. 3 this is suggested by the green curve – the smaller and higher the pore peak the higher the feasible capacitance at a given voltage! It was already shown by a simple mathematical calculation [2] that for a perfect homogeneous anode structure consisting of uniform cylinders of the same size a maximum capacitance of 52 kμFV/g @ 100 V and 34 kμFV/g @ 150 V can be achieved. This is still far away from today’s available capacitors and shows the potential that could be realized with a powder having an even more improved microstructure in the future.

The next generation of high(est) voltage powder: HV400

Our HV300 product is mainly used for anodization voltages in the range of 250-300 V_f and is approved as a powder for highest reliability applications like medical and aerospace. It was proven by capacitor manufacturers that this is the tantalum powder enabling capacitors with the highest energy density currently available. The target of further increasing the energy density according to equation (1) was the driving force for the development of an HV400 that can be anodized up to 400 V. Therefore, again the powder microstructure must be adapted: both, primary particle size as well as the medium pore size must be increased. The higher anodization voltage will “consume” more tantalum that is converted to Ta₂O₅ film which in turn needs more space than a film formed at 300 V_f. A direct comparison of the pore structure of anodes made from HV300 and HV400 powders with identical pressing and shrinkage conditions can be seen in fig 4. The maximum of the primary pore peak has been shifted from 1200 nm to 1600 nm while the secondary pore peak position has no significantly change. Main difference is that the pore size distribution of anodes made from the new HV400 powder is narrower than that of anodes made from HV300 powder – primary and secondary peak position are closer, the distribution is “less” bimodal.

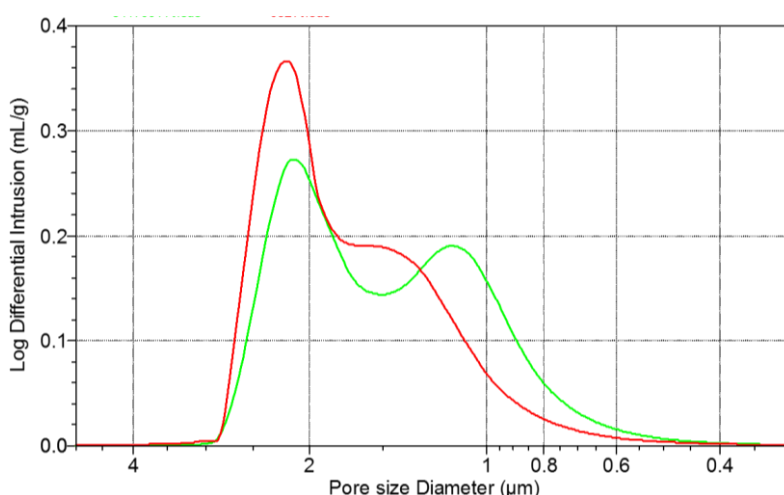


Fig. 4 Pore size distributions of anodes made from HV300 (green) and HV400 (red) powder (Press density 5,5 g/cm³, 10 % shrinkage)

Anodes of both HVMC powders were used for anodization from 250 to 400 V with the same formation program. At 250 V_f, the HV300 powder has a slightly higher capacitance, but for voltages above 260 V the HV400 has a higher capacitance (fig. 5). At 400 V_f anodes made from HV400 powder show 9550 CV/g, an increase by 20 % when compared to those made from HV300 powder. The slope of the HV400 capacitance curve is less steep than that of the HV300 – meaning it is more stable and could be used for even higher anodization voltages.

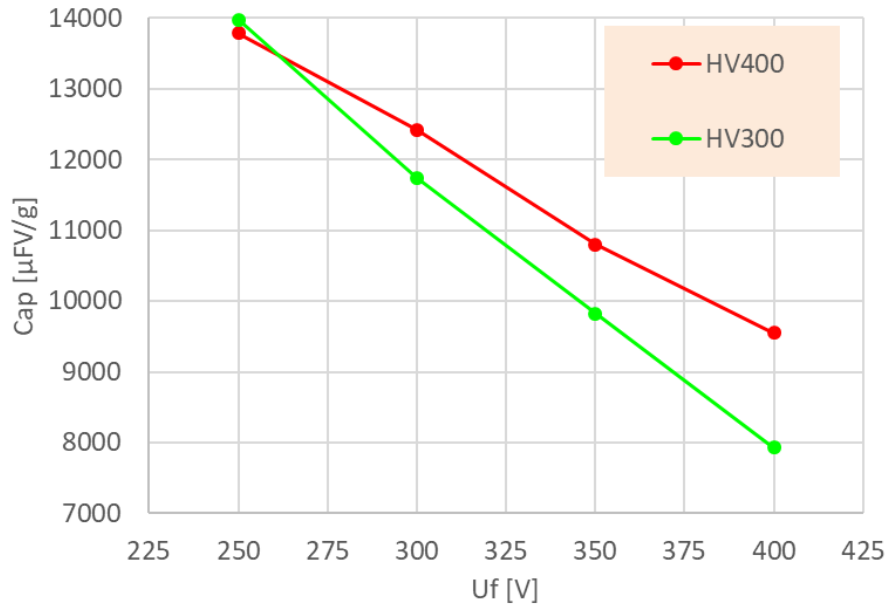


Fig. 5 Capacitance of new HV400 vs. HV300 anodes (Press density 5,5 g/cm³, shrinkage 10 %)

The microstructure of an HV400 anode formed at 400 V still show open pores, and an oxide film with an impressive thickness of ~760 nm suggesting that such a powder could be capable to reach even higher voltages (fig. 6). However, an increase of the leakage current to values >10 nA/μC at higher voltages limits a further anodization to 450 V due to the occurrence of oxide film breakdown. Since we could not find any breakdowns or oxide defects after 400 V anodization by intensive SEM investigations, it is assumed that the quality of the oxide film anodized in our current standard electrolyte recipe (glycol/water/H₃PO₄) is not good enough to withstand such high voltages. Therefore, we also have started to investigate the anodization process more deeper and its influence on the oxide structure.

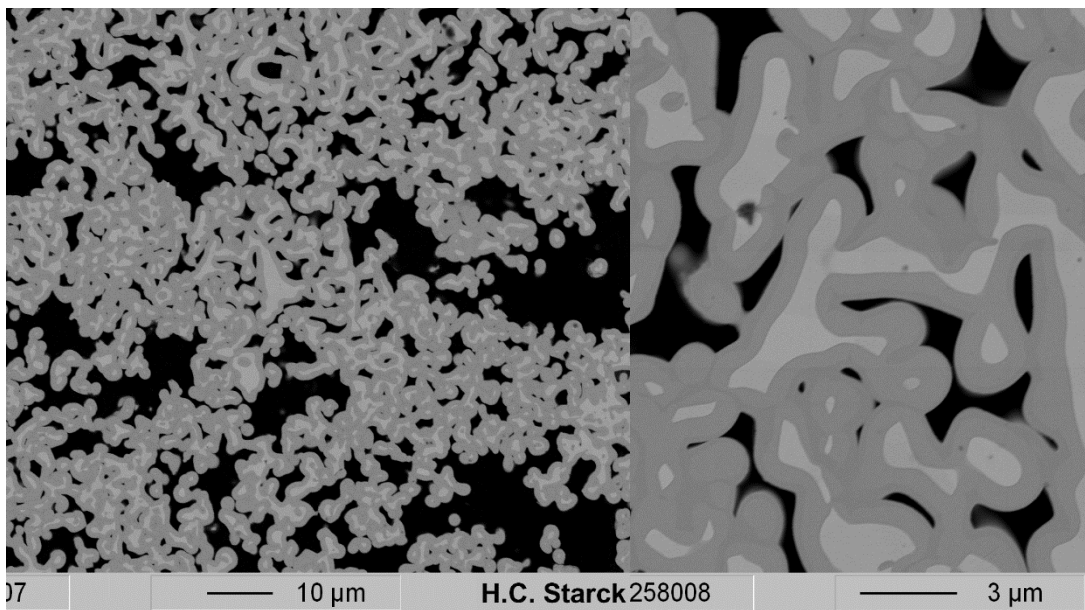


Fig 6. Cross section of HV400 anodes after 400 V formation.

Impact of anodization

The capacitance of an anode body is strongly depending on pressing and sintering conditions. It was shown that for an HV300 powder the capacitance, leakage current as well as breakdown stability can be varied over a wide range by using different pressing and sintering conditions. Each anodization voltage has thereby its own optimum, in case of HV300 powder it was found that a press density of $\sim 6.0 \text{ g/cm}^3$ with a shrinkage $\sim 10 \text{ vol.-%}$ will provide the highest volumetric capacitance and low leakage [3].

But also the conditions of the next processing step – the anodic oxidation of the sintered anodes – have a strong impact on the leakage current as well as the breakdown stability and decide if it is finally possible to reach very high voltages of 400 V and higher. According to our observations, for voltages $> 200 \text{ V}_f$ a pure aqueous electrolyte system is not appropriate since the probability of oxide film breakdown and anode destruction is ever increasing with increasing formation voltage. To improve the breakdown stability, organic additives are used. Commonly used additives found in literature and patents are e.g. ethylene glycol [4] and phosphoric [5,6], boric [7] or citric acid [8, 9]. However, “classical” electrochemistry and anode investigations of the interaction of electrolyte and Ta anodes during formation in a range of 200 – 400 V are scarce [8] or regarded as “company secrets”.

As a leading Ta powder manufacturer H.C. Starck is continuously developing and testing new tantalum powder types under various processing conditions to find the ideal microstructure. The capacitance-voltage curves as shown in fig. 1, 2 and 5, as well as the leakage current behavior are very important parameters to select the most suitable powder. Therefore, the successful development of an HV400 powder is not only depending on physical and chemical powder properties. Without a proper anodization program and electrolyte system, a 400 V anodization without oxide film breakdown and low leakage is hard to realize. It is essential but difficult to separate the impact of anodization from powder modifications.

Thorough investigations have been started to better understand the processes taking place during anodization to high voltages. In our tests we used large cylindrical anodes ($\varnothing 8 \text{ mm}$) with a weight of 2.2 g (press density 6.0 g/cm^3 , shrinkage $\sim 11 \text{ vol.-%}$) made from HV200 powder to come closer to the typical size of large anodes for high reliability applications. These anodes were formed to 150 V-250 V in a glycol-water bath (ratio 3:2) at 60°C with a conductivity of $900 \mu\text{S/cm}$ adjusted by adding H_3PO_4 . The “constant rate” anodization profile as well as the capacitance and leakage current behavior is shown in fig 7.

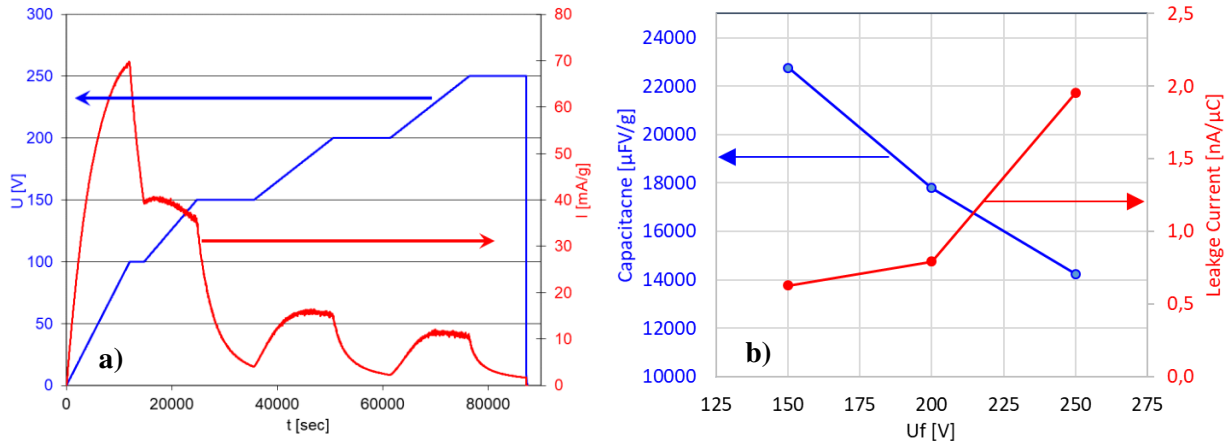


Fig. 7 Anodization of anodes made from HV200 powder a) constant rate program for 250 V b) C-LC-U curve for 150V-250 V

The term “constant rate anodization” refers to the way of anodization. Usually, a fixed current value is used there, such that the formation rate (V/min) is a function of the surface area of the anode. However, since the surface area of a porous anodes is decreasing with increasing voltage by consumption of tantalum during anodic oxidation, the real current density (A/m^2) is continuously increasing and therefore also the speed of anodization (“V/min”) is increased. It is common sense that the higher the speed of anodization, the higher the risk of oxide breakdown. In contrast, the “constant rate anodization” provides a constant forming speed (V/min) by continuous adjustment of the current required to match the desired voltage ramp. Thus, the considerable reduction of the tantalum surface available for further oxide growth during high voltage formation is compensated by a corresponding reduction of the current, resulting in a reduced breakdown probability.

At the beginning of our formation program, i.e. up to 100 V, a fast forming rate of 0.5 V/min is typically used since the probability of breakdown of our anodes turned out to be very low in this range. Then, with increasing voltage, the rate is continuously reduced to 0.3 V/min and later to 0.2 V/min when the anode body is more susceptible to oxide breakdown due to a) smaller and smaller remaining tantalum cores; b) increasing oxide thickness and therefore lower heat conductivity of the overall anode; and c) decrease of the remaining pore volume. The red current curve in fig. 7a is automatically adjusted and correlates with the surface and capacitance loss with increasing voltage. Intermediate dwells at 100, 150 and 200 V reduce the temperature increase during forming and thereby decrease the breakdown probability.

After formation, all anodes were leached for 12 h in de-ionized water to remove all components of the electrolyte bath and were subsequently dried at 90°C. Several elements were then analyzed, the contents of oxygen (carrier gas reduced fusion), carbon (non-dispersive infrared adsorption following combustion in oxygen) and phosphorus (ICP-OES) as a function of forming voltage are presented in fig. 8. Please note, that all concentration data refer to weight. The sintered unformed anodes had a phosphorous content <20 ppm, 0,33 % oxygen and 33 ppm carbon.

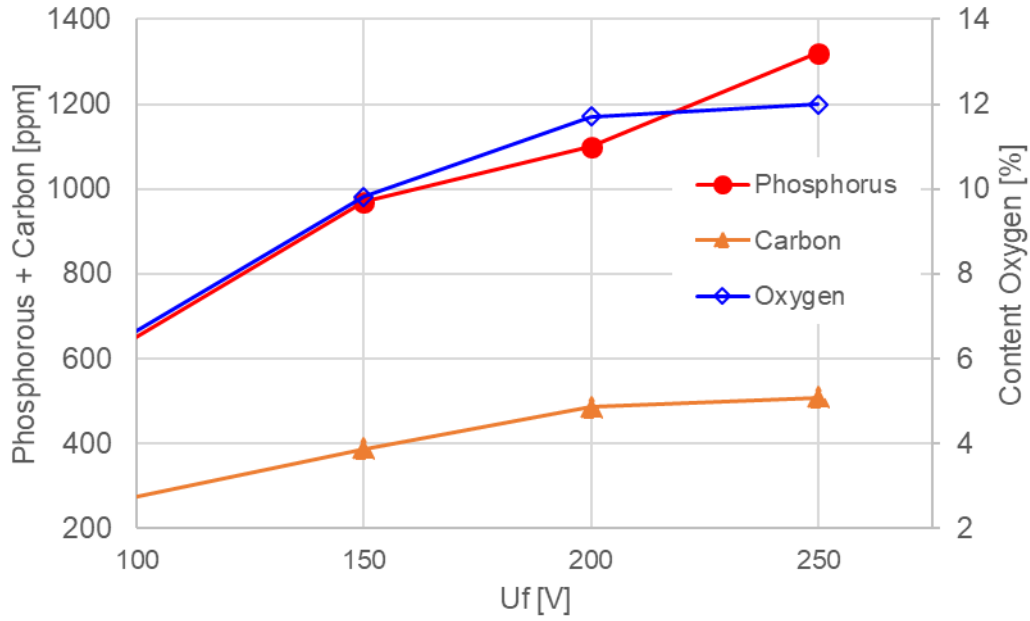


Fig. 8 Contents of P, C and O after anodization in a range of 100-250 V @ 60°C of anodes made from HV200 powders.

As a consequence of anodization, the oxygen content is increasing with increasing oxide thickness and therefore decreasing capacitance. It is known by several former publications that phosphorus is incorporated in the outer regions of the oxide film during anodization, probably as PO_4^{3-} ions while the inner regions of the anodic Ta_2O_5 layer do not contain any phosphorus [6, 10-14]. However, a lot of these investigations have been only done on sputtered films under forming conditions not typically used today, i.e. mostly in water and not glycol-water solvent systems and mostly at lower voltages. To our knowledge, this is the first time that such investigations on phosphorus contents of high voltage anodes with nodular structure anodized under typical high voltage conditions are reported.

The increased incorporation of phosphorus with increasing anodization voltage is in accordance to former findings. However, the phosphorus content of 970 ppm for anodes anodized to 150 V increases significantly to 1320 ppm for those anodized to 250 V. The incorporation of phosphorus is assumed to occur as phosphate. In accordance with literature [6, 10-14], we found a double layer oxide structure, i.e. a PO_4^{3-} containing outer oxide layer and a presumably phosphate-free inner layer. This was detected in anodized HV200 anodes after polishing by using a special orientation contrast (in backscattering mode) with a FE-SEM (fig. 9). The darker scale of grey color corresponds to a lower relative atomic weight caused by the incorporated phosphate ions and the uniform appearance of this layer implies that this layer has a uniform PO_4^{3-} distribution.

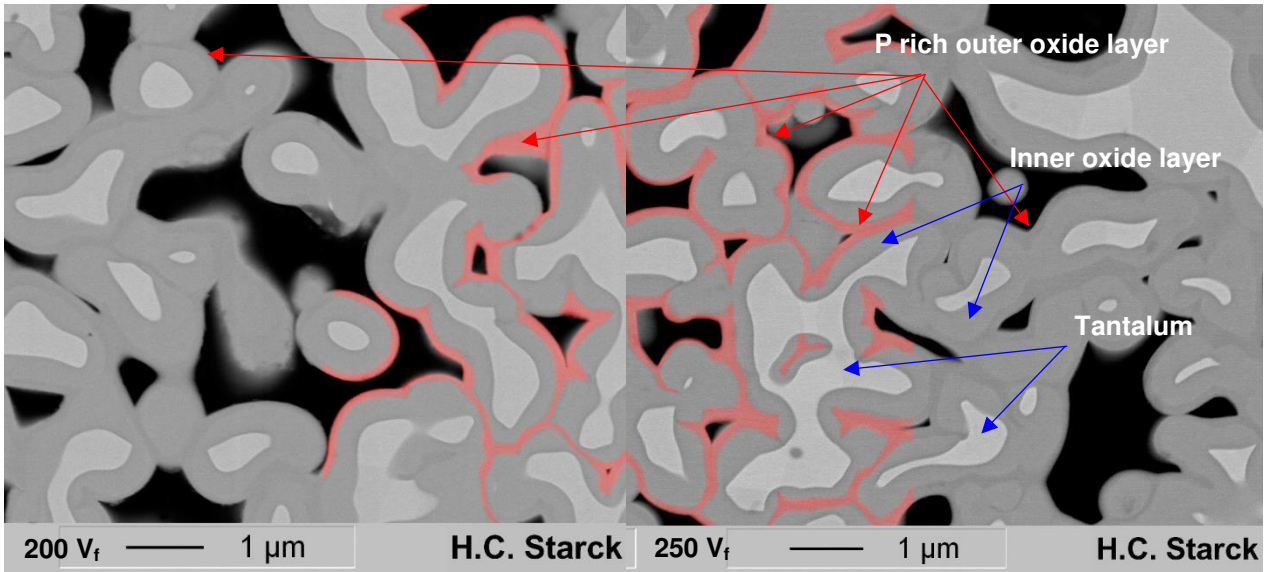


Fig. 9 Impact of electrolyte on oxide structure: Anodes made from HV200 powder anodized in H_3PO_4 /glycol/water solution to 200 V and 250 V (backscattering mode) show an outer layer with lower density. The P rich outer oxide layer was partial red colored.

By anodization of similar anodes in glycol-water based solution using HNO_3 to adjust to same conductivity of $900 \mu\text{S}/\text{cm}$ it could be shown that this is not an artifact of sample preparation. These anodes, shown in fig. 10, do not show any two-layer structure as observed for those anodized in H_3PO_4 before but the oxide film consists of only one layer as indicated by one scale of gray color using the same microscope adjustments.

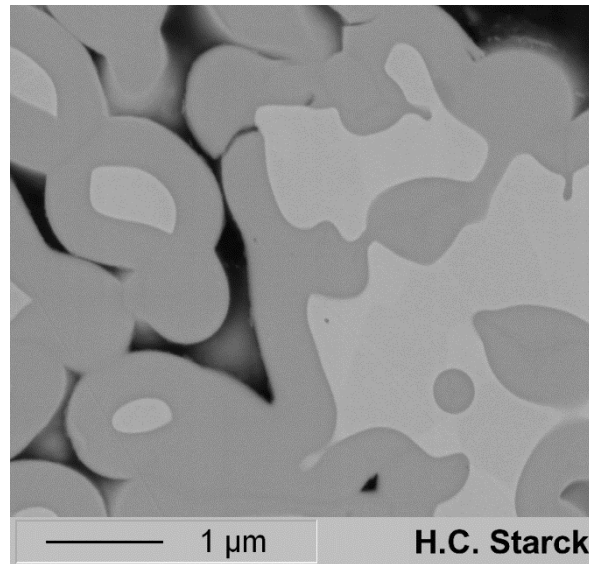


Fig. 10 Impact of electrolyte on oxide structure: Anodes made from HV200 powder anodized to 200 V_f in HNO_3 /glycol/water solution do not show a double but a single layer oxide structure.

The total oxide thickness of anodes made from HV200 powders anodized to 200V_f was determined to 370 nm, the outer phosphate rich layer being 85 nm. *Shimizu et al.* [10] investigated the incorporation of phosphorous into tantalum foils

via SIMS depth profiling. They formed the foil at 25°C with a constant current up to 100 V_f. The total oxide layer thickness was about ~ 162 nm, while the P rich outer layer had a thickness of ~80 nm while in the following region between 80 to 110 nm the phosphorus content decreases constantly until zero level. Our anodes made from HV200 powders show a thinner outer layer which might be a result of totally different formation conditions: higher anodization temperature (60°C vs. 25°C), different anodization program (constant rate vs. constant current) and different size and shape of specimen (anode with nodular structure vs. foil).

The phosphorus content of 1100 ppm observed for anodes anodized to 200 Vs is corresponding to 3370 ppm Phosphate while the oxide content of 117000 ppm is corresponding to 637280 ppm Ta₂O₅ (oxide content of phosphate was already excluded in this calculation). This means that the total phosphate content of the oxide layer is 0.53 % what might be enough to have a negative impact on the breakdown stability under the assumption the phosphate weakens the amorphous oxide structure.

But it must be further considered that only the outer area comprises the phosphate. This means, that the phosphorus content in the outer layer is according to the ratio of the layer thicknesses (85 nm of 370 nm) as high as 2,3 wt.-%. Taking the large difference of the molar weights into account (441,9 g/mol for Ta₂O₅ to 95,0 g/mol for PO₄³⁻) this is equal to 9,9 mol% phosphate. On the other hand, it is still an open question if this double layer structure created during anodization in phosphoric acid is beneficial or detrimental at very high formation voltages. Anodes anodized to 250 V and higher (fig. 11) show at some places non-destructive defects (these anodes had good leakage current!), which means that these anodes suffered no breakdown during anodization: cavities and holes have formed exactly at the interface between the outer phosphorus-rich and the pure Ta₂O₅ inner layer. These pores could contain gas (e.g. oxygen formed during anodization) or electrolyte or other unknown products of decomposition formed at high voltages. It will need further investigation to understand this observation. It should be mentioned, that these defects were also found in anodes formed to these voltages made from standard Na reduced powders so that it can be excluded that the Mg reduction process used for the HVMC powder production is responsible for these cavities. The coincidence of the location of the cavities with the interface between the outer, phosphorus-rich oxide layer and the phosphorus-free inner oxide layer suggests that phosphorous may play a role for the formation of the cavities.

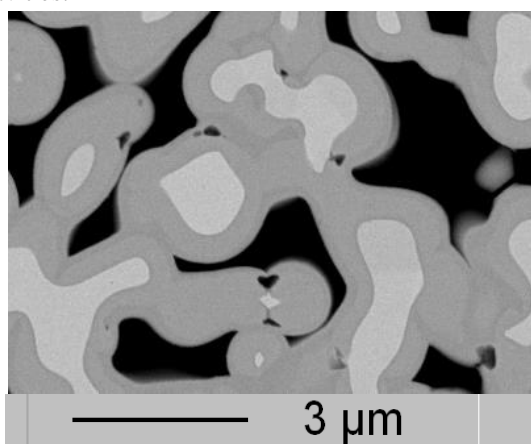


Fig. 11 Defects observed after 250 V anodization in glycol-water based H₃PO₄ electrolyte: cavities and holes formed at the interface from PO₄³⁻ rich outer oxide layer and inner oxide layer.

Surprisingly, not only phosphorus but also a remarkably increased carbon amount above the 33 ppm before anodization was analyzed. At 150 V, the anode has already picked up 390 ppm of carbon and towards 250V this is continuously increasing to 510 ppm. It is not known how carbon is incorporated into the anodic oxide film and how it is distributed but it is assumed that the main source might be the glycol that may decompose during anodization to these high voltages. In [15], it is mentioned that ethylene glycol-based electrolytes used for anodizing aluminum, must be almost totally esterified to be suitable for anodization voltages $>400\text{ V}_f$. Otherwise oxidation products from free ethylene glycol like oxalic or formic acid will be generated and will attack the oxide film of the Al capacitor.

According to our own anodization experience, it is very hard or nearly impossible to form a Ta anode to 150 V or even 250 V without breakdown or bad leakage current when the powder used would already have a carbon level of $> 60\text{ ppm}$. However, the much higher carbon content after anodization did not result in an immediate breakdown during anodization or a bad leakage current in the case of anodes made from our HV200 powder. This implies that it is of great importance for the manufacturing of tantalum capacitors in which production step/and how carbon is “introduced”. Carbon rich areas in the powder (e.g. caused by insufficient debinding) could result in the local formation of tantalum carbide during sintering. Later, during anodization the carbide will cause oxide breakdown or crystallization. In contrast to that, the carbon that is, howsoever and as whatsoever compound incorporated during anodization seems to be less dangerous. However, the acceptable limit of C pick-up during anodization is unclear since surpassing a critical carbon level might be a reason for the increased leakage current observed at 250 V. The decomposition of forming electrolyte that contains organic components is a limiting factor for the realization of a new kind of Ta capacitor that is anodized to 400 V or higher. Oxide defects, as illustrated in fig. 10 could also be a consequence of the carbon pick-up (and interaction with PO_4^{3-} ?) during anodization. Further investigations are necessary to clarify the impact of bath temperature, electrolyte type and concentration but also of the anodization program and total forming time.

How should a perfect anodization concerning bath composition and forming program look like? Additives are needed that are stable during the whole formation process. The entrapment or incorporation of additives in which form whatsoever should be prevented so that a perfect oxide film can be generated otherwise the breakdown strength might be reduced. Also, the thermal conduction of such electrolyte should be sufficient to dissipate the heat that is generated during anodization of large size anodes to high voltages.

Conclusion

We have presented the latest development of our HVMC high voltage tantalum powders that provide highest capacitance due to their improved microstructural homogeneity when compared to current standard powders. The newly developed HV150 powder provides a further capacitance increase up to 15 % at 150 V_f anodization by optimization of the primary particle and anode pore size structure. The primary pore peak is much narrower and higher compared to that of our HV100 and HV200 products. Moreover, the secondary pore peak is very close to the primary pore peak. Improved homogeneity is the key for future powder developments enabling even higher capacitance at high formation voltages.

We were also successful to further increase homogeneously the primary pore and particle size distribution by adjusting our process resulting in our new HV400 powder that extends the anodization range for tantalum powders from currently 300 V to 400 V allowing to store even more energy in a given size. We found that besides adjustment of the powder structure the anodization process must be adapted as well. We have shown that not only phosphorous, which was already known, but also carbon is incorporated significantly into the formed anodic oxide film. Both components are introduced by the used electrolyte system. In contrast to former investigations reported in literature, this was to our knowledge the first time that such investigations on phosphorus contents of high voltage anodes with nodular structure anodized under typical high voltage up to 250 V_f conditions are reported. Nevertheless, finding a “perfect” anodization program in combination with a “perfect” anodization bath preventing the incorporation of critical amounts of foreign ions remains a task to be followed up in the future.

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