Tailoring the microstructure: Optimization of Tantalum powders for highest voltage applications up to 350 V

Marcel Hagymási
Tel.: +49 5321 751 3160, e-mail: marcel.hagymasi@hcstarck.com
Kamil Paul Rataj,
Tel.: +49 5321 751 53817, e-mail: kamil-paul.rataj@hcstarck.com
Helmut Haas
Tel.: +49 5321 751 3937, e-mail: helmut.haas@hcstarck.com
Christoph Schnitter
Tel.: +49 5321 751 3939, e-mail: christoph.schnitter@hcstarck.com
Holger Brumm
Tel.: +49 5321 751 3294, e-mail: holger.brumm@hcstarck.com

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

The pursuit of powerful electronic applications in medicine, automotive and telecommunication demands Tantalum capacitors with continuously increasing energy densities and working voltages. To support this H.C. Starck is currently developing new tantalum powders for anodization voltages >250 V. The key for improvement is to optimize the microstructure of the powder by adjustment of the primary-particle and pore-sizes. The superior homogeneity and tailor-made size of both – pores and particles - allows achieving higher capacitance densities than with other available tantalum powder today. In addition, these powders exhibit excellent impregnation properties due to their optimized pore structure allowing achievement of low ESR.

Especially for formation voltages above 200 V, a change from aqueous media to organic solvent containing electrolytes is necessary to achieve high quality dielectric layers. The understanding of the resulting change in formation mechanisms is challenging but essential for powder optimization. The electrochemical effects and limits that occur at such high voltages and resulting capacitance densities will be discussed.

Introduction

Pushing the limits of tantalum capacitors by development of new powder grades is one main task of H.C. Starck as a leading technology company. The increasing request for high voltage tantalum capacitors in recent years is an ongoing trend that will continue to demand new capacitor designs and will extend to other application fields. These include high reliability applications such as automotive and medical devices as well as telecommunications and new data storage devices like SSDs, all potentially requiring new tantalum powder grades that can meet the new requirements.

In contrast to high CV applications, a proper high voltage powder has to fulfill different needs. There is an optimum primary particle size for each anodization voltage which will result in the highest capacitance. If the primary particles are too large valuable tantalum powder will be wasted, if the pores are too large volume will be jeopardized. On the other hand, if primary particles are too small they will be totally anodized to Ta_2O_5, if pores are too small they will be closed during anodization preventing penetration with the cathode material resulting in lower capacitance densities. To push the high voltage performance of tantalum capacitors H.C. Starck has recently developed a new class of powders called HVMC grades. This new powder class is produced using our patented Mg vapor reduction technology which provides superior microstructural homogeneity when compared to Na

reduced tantalum powders. In detail this means the primary particle size distribution as well as the pore size distribution of these powders are much narrower than those of conventional Na reduced powders allowing production of capacitors with higher capacitance densities. Therefore the utilization of tantalum material in these capacitors is significantly increased[1,2,3]. The latter property is, aside from strong sinter necks and higher chemical purity, the main reason why the HVMC powders have drawn such high interest from capacitor makers.

Novel HVMC powder developments

It was previously published that these HVMC powders could be used for anodization ranges of 60-200 V[3,4]. Through extensive research and development during the last year it was possible to extend this range to even higher voltages of up to 350 V. Moreover, proper production parameter adjustments allows designing the pore structure of these powders in a broader range as well. According to different demands H.C. Starck has three formation voltage classifications for these powders:

1. High Voltage: 40 – 100 V
2. Highest voltage: 100 – 200 V
3. Ultra-high voltage: >250 V

The naming system for this powder class is correlated to customer needs and will be explained for two different powders

Powder 1: HV64-4500
Powder 2: HV200-570

"HV" refers to "High Voltage" applications, the first number after that corresponds to the recommended anodization voltage while the second number gives the capacitance at this voltage in µF/cm³ since capacitor makers are more familiar with this unit. For example Powder 1 was developed for 64 Vf and provides 4500 µF/cm³ while powder 2 is recommended to be used at 200 Vf and will provide 570 µF/cm³. For the high voltage range anodes (40 – 100 V) a press density of 5.5 g/cm³ was used and the sinter temperature adjusted to achieve a final shrinkage of 5-7 vol.%. Anodes for the highest and ultra-high voltage range were produced with higher press density of 6.0 g/cm^3 and sinter temperature adjusted to achieve a final shrinkage of 10-12 vol. The higher press density and final shrinkage conditions of the latter are recommended in order to create a stronger anode body that can withstand the significant strain at these high voltages without breakdown. However, these are recommendations valid for our anode conditions and do not necessarily mean that an HV200 powder can only be used at 200 V. Depending on the pressing and sintering conditions of anodes it might be possible to use this powder efficiently even at 250 V and higher.

Tailoring the pore structure

As described above the pore structure of the powder has a significant impact on the impregnation behavior of the anode with the cathode material and therefore on the electrical characteristics such as capacitance, ESR and leakage of the finished capacitor. Anodes made from two HVMC powders – one with tailored pores - will be compared in fig. 1 to those made from the best in class 50k µFV/g standard powder from Na reduction process (same pressing and shrinkage conditions). Both HVMC powders were developed for a 64 V formation but have slightly different cap behavior which is correlated to different pore structures. Both powders have a bimodal anode pore size distribution

that supports the anode infiltration. The larger "secondary" pores act as a highway for the cathode material to the interior regions of the anode, from there the material is distributed to the smaller primary pores. Since the smaller primary pores, which are generated by the primary particles, are responsible for the majority of the surface area (in other words the majority of capacitance), this bimodal pore distribution is crucial for optimum utilization of the entire tantalum surface area. The SEM pictures in fig. 1 (right top and bottom) show case the two different types of pores and the corresponding microstructure within the anode body. The anode made from the standard 50k powder (from Na reduction) has a less pronounced bimodal pore size distribution and a broader peak for the primary pores than those made from the HV64 powders.
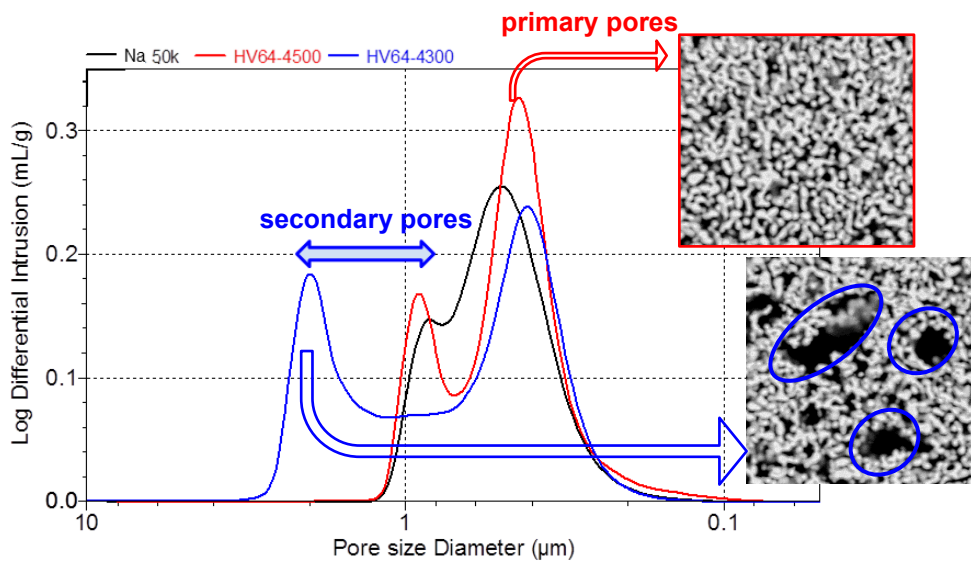

fig. 1: Pore size distributions of two anodes made from two HVMC powders in comparison to anodes made from a Na reduced 50k µFV/g powder. The secondary pores in the SEM picture on the right side are marked with blue circles.

The anodes made from the HV64-4500 powder show a slightly smaller primary pore diameter than those from the standard 50k powder but the pore peak is narrower and the peak height is higher. This means that the anodes made from the HV64-4500 powder have a higher surface area than those made from the standard 50k material (compare the pore area diagram). This is confirmed by the capacitance measurement shown in fig. 2 – the HV64-4500 with the highest primary pore peak also has the highest capacitance over the entire range.

In contrast, the HV64-4300 powder was designed to allow better pore impregnation to achieve lower ESR values. To achieve this, the powder production process was modified in a way such that the secondary powder pores are larger. The pore size distribution for anodes made from the HV64-4300 show clearly that the peak for the secondary pores was shifted from 950 nm to 2 µm. It results in a much broader bimodal pore distribution compared to those made from the HV64-4500 and the standard 50k powder. In spite of a smaller primary pore peak height, anodes made from HV64-4300 powder have higher capacitances than those made from the standard 50k powder for the formation range from 40 to 100 V. This can be explained by the more homogeneous microstructure. This means, compared to the standard 50k powder, it was possible to improve the pore structure and increase the capacitance at the same time. This clearly shows that the production process for these HVMC powders can result in tailor-made pore structures: adjusting the bimodality keeping the capacitance at the same high level!
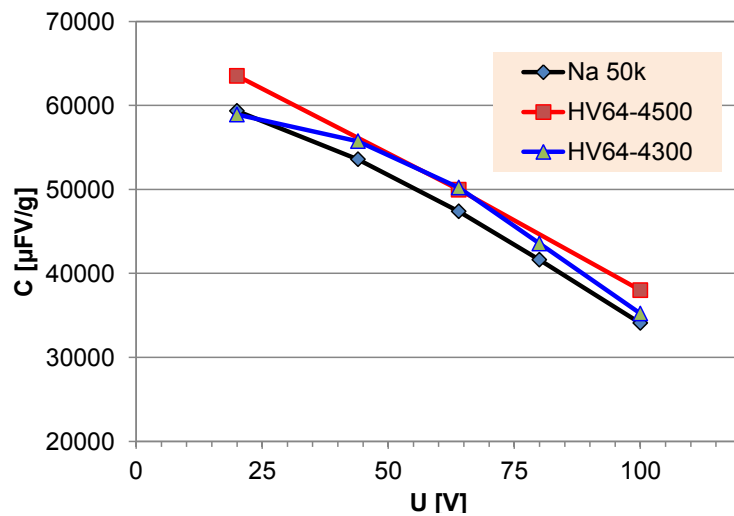
fig. 2: Capacitance behavior of anodes made from two different HV64 powders and from a standard 50k powder for a formation voltage range from 20 – 100 V.

Increasing the capacitance and application range

Also new HVMC powders were developed for the formation range of 100 to 200V which will be compared to standard Na reduced powders (fig 3). The first powder developed in this formation range, the HV100-1900 powder, has shown at a formation voltage of 100 V a significant increase in capacitance of +14 % in comparison to the best in class 30k powder. By additional process adjustments it was possible to further improve the performance of this powder resulting in the new HV100-2100 which is recommended for the formation range of 100 V - 150 V providing an additional increase in capacitance at 100 V formation voltage to + 29 % in total. It has to be noted that the slope of the capacitance over voltage is a critical factor for the high voltage capability: the lower the slope the better the high voltage stability! The capacitance over voltage curve for the anodes made from the HV100-2100 is nearly parallel to those made from the HV100-1900 powder, and anodes of both powders provide significantly higher cap compared to those made from the standard 30k powder over the entire investigated range.
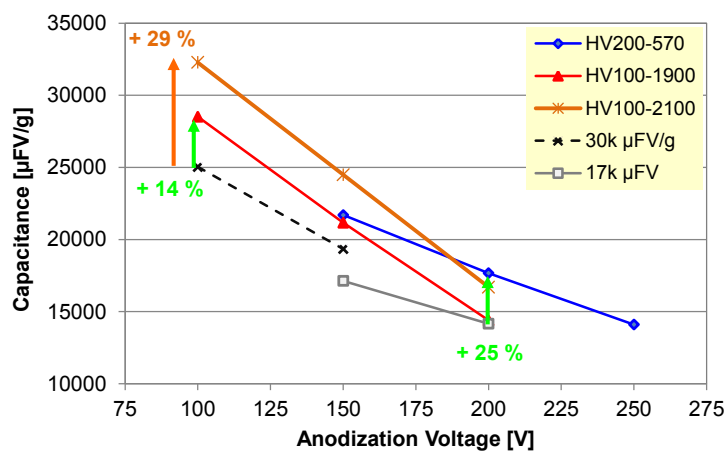

fig. 3: Capacitance behavior of HV100 and HV200 powders in comparison to standard 30k and 17k Na reduced powder.

Capacitance wise HV200-570 is the best in class powder for 200 – 250 V formation range. In comparison to anodes made from a 17k µFV/g powder (which has been approved for high reliability

application in this range) anodes made from the HV200-570 powder provide a 25% increase in capacitance at 200 V formation. It is also notable that the slope of the capacitance over voltage curve, as degree of the high voltage capability, is on the same level as for the anodes made from the 17k standard powder. This means anodes made from this powder show both, higher capacitance and excellent high voltage capability and can even be used for formation voltages up to 250 V!

Highest Voltage: 250 – 350 V

As a result of extensive microstructural investigations and resulting process modifications, it was recently possible to extend the application range for the HVMC powder class to formation voltages up to 350 V. Anodes made from the newly developed HV300 powder show the highest capacitance at formation voltages of 300 V and above. According to our investigations no Na reduced powder can deliver anodes showing such high capacitance values (fig. 4a). In comparison to anodes made from an often used 12k µFV/g powder those from HV300 show 20 – 28 % higher capacitance over the whole range from 250-350 V formation voltage. The advantage to anodes made from other ultra-high voltage powders is even more significant (fig. 4a). To explain this significant increase in capacitance it is again essential to investigate the powder and anodes pores as well as their micro structure. The anodes made from HV300 powder show a very narrow pore size distribution: they have less large pores (→ waste of space) and also less small pores (→ which will be closed during anodization) than anodes made from the standard 12k µFV/g powder (fig. 4b). As a result of this, the pore size distribution for HV300 anodes has a significantly higher peak height. The anodes made from 10k and 9k µFV/g powder, have both too large pores and a too broad pore size distribution which corresponds to a low volumetric tantalum usage resulting in much lower capacitance values.
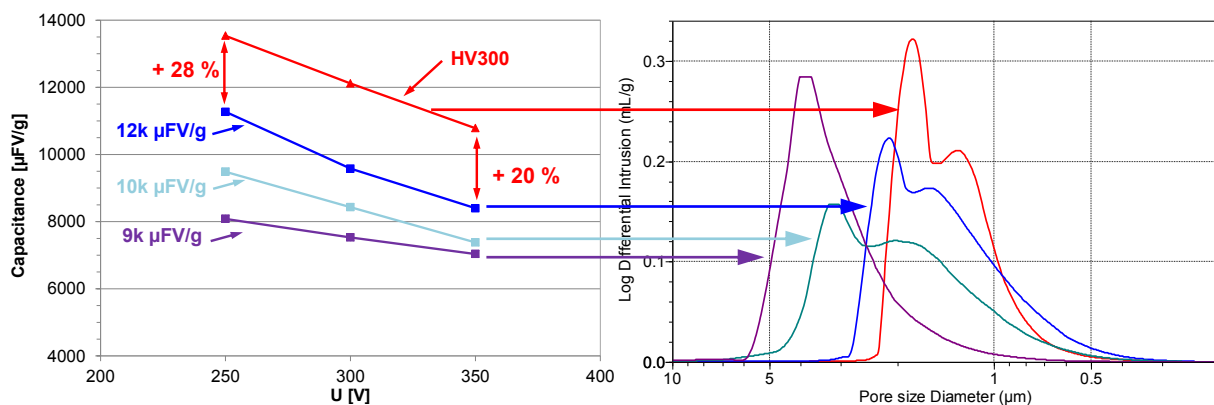

fig. 4: Comparison of anodes made from the newly developed HV300 powder with such made from standard Na reduced ultra-high voltage powders a) Capacitance behavior for the range from 250 – 350 V. b) Anode pore size distribution (same sinter density!)

The effect of the pore size distribution becomes apparent when the anode pore area, which is correlated to anode surface area and therefore to a higher capacitance is compared (fig. 5). The unformed HV300 and 12k µFV/g anode have the same total pore area of 0.254 m²/g but after 300 V anodization the narrower pore size distribution of HV300 leads, as explained above, to a pore area that is 18 % higher than 12µFV/g - this is a good correlation to the measured capacitance in fig. 4.
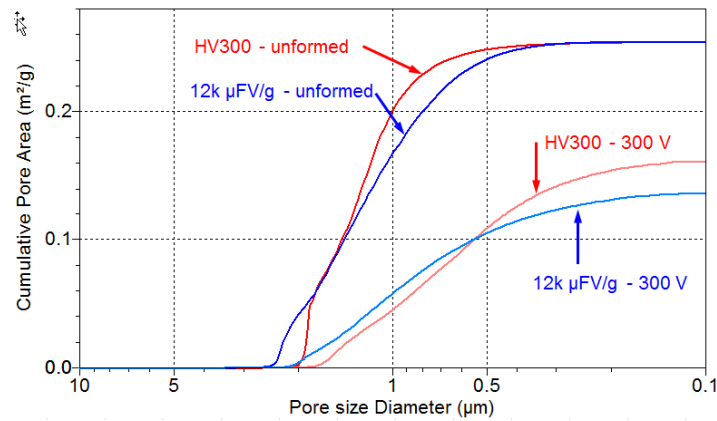
fig. 5 Anode pore area of HV300 and 12µFV/g: unformed and after 300 V anodization.

This is confirmed by investigation of the microstructure of anodes made from standard 12k µFV/g powder compared to HV300 powder and formed to 300 V.– (fig. **6** is a graph displaying the main differences). First the anodes made from the Na reduced 12k µFV/g powder show a less homogenous anode structure. Large particles (1) with a size of 5-9 µm can be observed having very low surface area and therefore contribute minimal capacitance while occupying valuable space. This is also true for pores that are too large (3). Last but not least areas with too small primary particles which are mostly connected with too small pores (2) having a negative impact on capacitance – most of the tantalum core is already formed to oxide and the small pores are nearly blocked with the formed oxide film. These areas are hard to impregnate and give only a low contribution to capacitance as well. Looking at fig. 5b it is very obvious that the formed HV300 anodes having an improved, much more homogeneous microstructure – it is superior concerning homogeneity of the primary particle size distribution (neither too big nor too small particles) and also has a more homogeneous pore structure without closed areas.
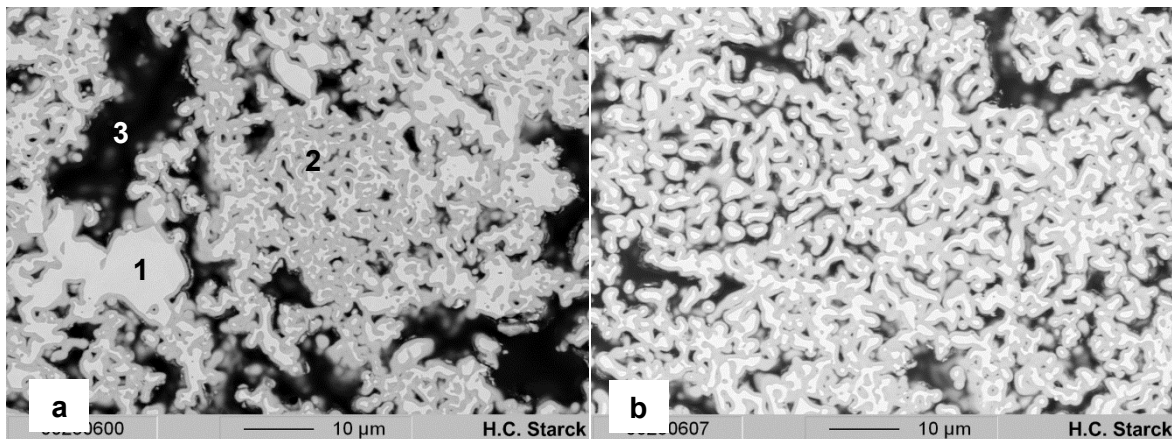

fig. 6: Microstructure of anodes formed to 300 V a) made from 12k µFV/g standard powder: (1) too big primary particles, (2) areas with closed pores and too small primary particles (3) big pore area b) made from new HV300 powder with superior homogeneity

Conclusion

It was shown that using the new HVMC powders significant improvements for tantalum capacitors are possible. The anode pore size structure can be tailored over a broader range than before and the bimodal pore distribution has a positive impact on electrical properties due to the improved cathode

infiltration. An additional capacitance increase was realized for the anodization range of 100 – 250 V. HV300 is a new HVMC powder that extends the capacitance range for ultra-high formation voltages up to 350 V. The HVMC process based on Mg reduction is the key competence of H.C. Starck and provides unique homogenous powders for anodization range from 50 to 350 V! These new HVMC powders with increased capacitance were mainly developed for customers with the following focus:

1. Enable the production of new capacitor types where a standard Na reduced powder does not deliver enough capacitance.
2. Provide an increase in volumetric efficiency which allows a reduction in the powder volume, thus supporting the trend toward miniaturization.
3. Improve the pore structure which in turn ensures an increase in impregnation efficiency for lower ESR.

Again, the HVMC powder development is not at its limits! H.C. Starck is continuously working on new high voltage powder in order to find the maximum capacitance for each anodization voltage.

Formation and Evaluation of high voltage powders

There is not much public knowledge available on anodization of tantalum anodes to very high voltages above 250 V. However, powder producers, like H.C. Starck need to evaluate the performance of their new developments like the HVMC powders discussed above at these highest and ultra-high formation voltages. This performance cannot be simulated by only using simple powder data like specific surface area or pore size distribution. It is necessary to produce and form anodes at the required voltage and then measure properties like the real capacitances, leakage currents and pore size distributions. This poses not only a challenge to the design of the particles, but also to the formation process and the electrochemical characterization of anodes made from these new powders.

Electrolytes for high voltages

As a result of the continuously decreasing pore sizes during anodization it is challenging to form thick, dense oxide layers with a uniform thickness. With thinner necks, the resistance increases dramatically during formation of the dielectric layer in liquid electrolytes. Thus, the conductivity of water-based electrolytes must be increased via higher acid concentrations or additives[5]. However, using additives can generate additional side reactions like decomposition/oxidation of the electrolyte and may reduce the yield of oxide growth during formation. Alternatively the formation program (ramps, constant rate, current limit) can be modified but this will result in disproportionately longer formation times. Therefore tailored, smart programs with optimized conditions for every powder are required.

1. **Formation in aqueous solutions**

In literature it is described that in aqueous solution the main side reaction is oxygen evolution[6] according to equation 1, this reaction consumes 4% of the total applied charge.

$$2\,H_2O\ \rightarrow\ O_2 + 4\,H^+ + 4\,e^-$$ (1)

For low current densities and anodes having low surface areas the reaction is not critical or observable (e.g. on tantalum foil or wire) due to a fast diffusion of oxygen from the anode surface

into the electrolyte and low charge volume. But during anodization of pressed pellets with high surface areas (> 200 cm² per pellet) a strong gas evolution can be observed. Upon first observation this side reaction seems to have no influence on the oxide growth (equation 2),

$$2\,Ta + \,5\,H_2O\,\rightarrow\,Ta_2O_5 + 10\,H^+ + 10\,e^-\qquad\qquad(2)$$
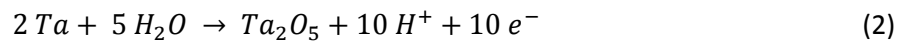
but pores within the anode will fill with bubbles from the product of the side reaction and become electrically disconnected during formation. As a result of this the oxide thickness does not grow in these pores and the total current decreases in such potentiodynamic experiments. When a critical size of the bubble is exceeded it leaves the pore and the blocked area is reconnected again. This leads to a post-anodization of the surface and thus a higher total current. In cyclo-voltammograms this is observed as an oscillation (fig. **7**).
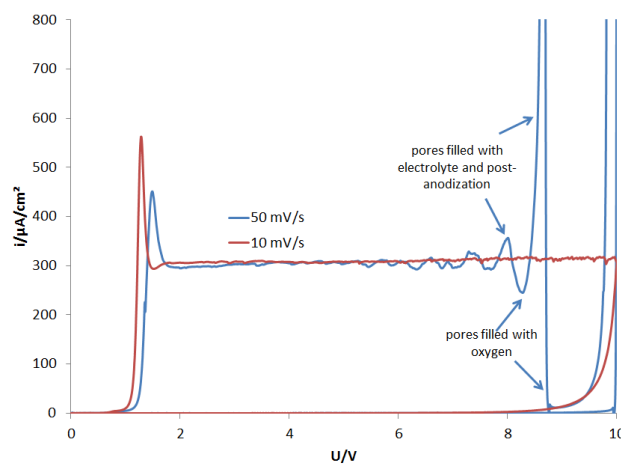

fig. 7: Cyclovoltammogram of an anode with constant rates of 10 mV/s respectively 50 mV/s in 1.8 mol/L sulfuric acid. The oscillation at higher potential rates is caused by blocking of the pores with oxygen bubbles and releasing of them by a post-anodization.

If the current density is too high, the dielectric layer can spall off or crack due to the formed oxygen. One possible solution for this is to decrease the total current in galvanostatic formation or of the constant rate in potentiodynamic formation to reduce the charge volume for the described side reaction. By doing this, oxygen can diffuse out of the pores before gas bubbles form and blockage of active surface area takes place. Most importantly, anodes made from high capacitance powders have to be anodized slower otherwise breakdown of the oxide layer is observed at low potentials which, in the end, result is uncontrolled oxidation of the anodes.

2. Formation using organic and inorganic additives

For very high formation voltages of tantalum anodes, additives are used to increase the conductivity of the electrolyte and the resistance of the dielectric layer. In fact it can be observed that higher potentials (e.g. 200 V) cannot be reached in common aqueous electrolytes like pure phosphoric acid without breakdown of the formed oxide. In literature the prevalent compounds are additives like ethylene glycol[16], phosphate[17,18], borate[19] or citric acid[15,20]. The addition of such anions result in modifications of the oxide layers in structure[7,12] or incorporation of those anions into the oxide layer which can affect the breakdown. The influence of glycol during oxide growth was described on silicon[8-11] and also on tantalum[14]. *M. Corset et. al.* have studied the source of oxygen for oxide formation by [18]O marking for different additives[13]. They described that oxygen is mainly (80 %) provided by water whereas the rest was coming from the additives (dissolved salts). A further

description of the improvement using citric acid is that it can form chelating complexes with metallic surface impurities. This was also observed with other organic acids like tartaric acid[15]. Jackson has shown that additives inhibit the oxide's electric field induced crystallization[14]. However a clear model about the mechanism at higher potentials is still under discussion.

Experimental part

In this work the anodization of high voltage anodes at high potentials (200 V and above) is described. Effects and limits caused by additives were defined. Aqueous (phosphoric acid in water) and mixed media (glycol and phosphoric acid in water) were compared concerning their potentiodynamic formation behavior independent of the concentration of the additive, the conductivity and the constant rate. The breakdown areas of the anodes have been investigated by SEM pictures and three different stages of cracking have been identified.

Influence of additives

Anodes made from 17k µFV/g tantalum powder that was used as reference for HV200 have been anodized in common phosphoric acid electrolyte with a conductivity of 350 µS/cm and compared to anodization behavior in the same electrolyte containing ethylene glycol. The constant rate was kept constant for both experiments (fig. 8). It was observed that in the aqueous electrolyte a complete breakdown of the samples occurs at about 186 V. In contrast, by adding ethylene glycol all anodes could be formed up to 250 V without any issues and breakdown of the formed oxide layer. Therefore further experiments have been performed in electrolytes containing ethylene glycol and phosphoric acid.
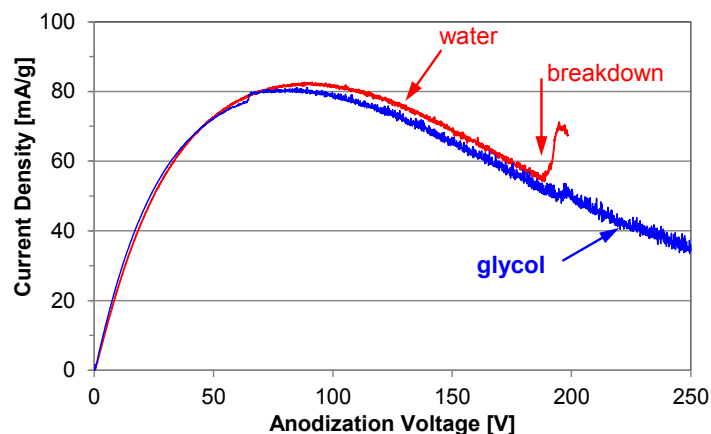

fig. 8: Anodization of 17k µFV/g anodes in water based (red) and glycol based (blue) systems with a constant rate of 0.75 V/min (350 µS/cm). The growth is delayed and smeared out over the whole potential range.

Influence of constant rates during formation

To further improve the oxide quality two different constant rates have been compared. fig. 9 shows cyclo-voltammograms of 17k µVF/g anodes with two different constant rates. The first plot (upper curve) shows the anodization using a constant rate of 2 V/min. At about 150 V the current starts to struggle and oscillates until first breakdown occurs at 300 V followed by an increasing current. The lower plot shows the same experiment but with a constant rate of only 0.75 V/min. At 0.75 V/min the current is steady and we only start seeing noise at 200 V, however non –destructive breakdowns are also observed at 260 V. This means that a repassivation of the cracked area takes place (see also chapter breakdown stages). Although the first breakdown occurs at the lower constant rate, in repeating experiments it was observed that the non-destructive breakdown potential is not totally dependent on the constant rate but also the oscillating current.
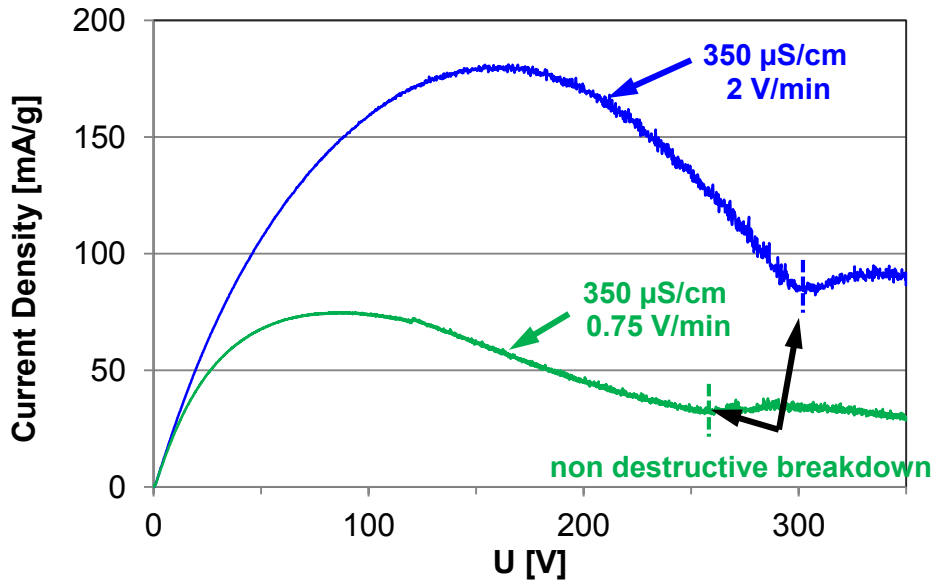
fig. 9: Cyclo-voltammograms of 17k μFV/g anodes using two different constant rates in ethylene glycol electrolyte.

With increasing voltage it seems that the constant rates have to be adjusted and lowered to reduce oscillation of the current. Therefore a new ramp program was developed where high constant rates were used at the beginning with stepwise decreasing of the rates. Therefore, for further experiments dynamic constant rates have been chosen to slow down the oxide growth at high potentials. Independent of the powder used the constant ramps were divided into 2 or 3 segments with lower rates (see next chapter).

Influence of conductivity of the electrolyte

HV200 Anodes were anodized up to 200 V in either 3.5 mS/cm or 0.35 mS/cm conductive electrolyte (both phosphoric acid with ethylene glycol in water). The formation was done with a dynamic constant rate in three steps shown in fig. 10. The first step was a ramp with a high constant rate of 0.6 V/min. At potentials higher than 100 V the constant rate was decreased to 0.4 V/min and finally in the potentiostatic phase the potential was kept for about two hours at 200 V. In electrolytes with 3.5 mS/cm conductivity, the peak current is reached after a short time with a fast ramp and decreases slowly caused by further formation of the oxide layer in pores and necks. During the second ramp the current decreases continuously but shows after 20000 s first current peaks which have been identified as local breakdowns of the samples with a fast re-passivation.

The red plot shows the same experiment processed in the electrolyte that has one tenth the conductivity of the previous trial. In the first stage the current rises much slower and the peak current is shifted. This means that the formation is decelerated and therefore the oxide has more time to form. In the second ramp the current decreases slower compared to the previous experiment and no breakdowns are observed. At the end the current reaches the same value in both experiments. We can assume that by increasing conductivity of the electrolyte the inner parts of an anode, which are connected via pores, reach their formation potential faster than in low conductive media. This means that a reduction of the electrolyte conductivity can be compared to a reduction of the formation rate and therefore a slower oxide growth, which is positive for the formation at high potentials. The lower current density results in a reduction of thermal stress and crystallization. However the same oxide thickness can be reached in both electrolytes if the time is adapted and the consumed charge is the same according to:

$$Q = \int I \cdot \Delta t \qquad (3)$$

Comparison of the leakage currents after anodization show that the high conductive electrolyte results in 4 times higher DCL values than the lower conductivity electrolyte.
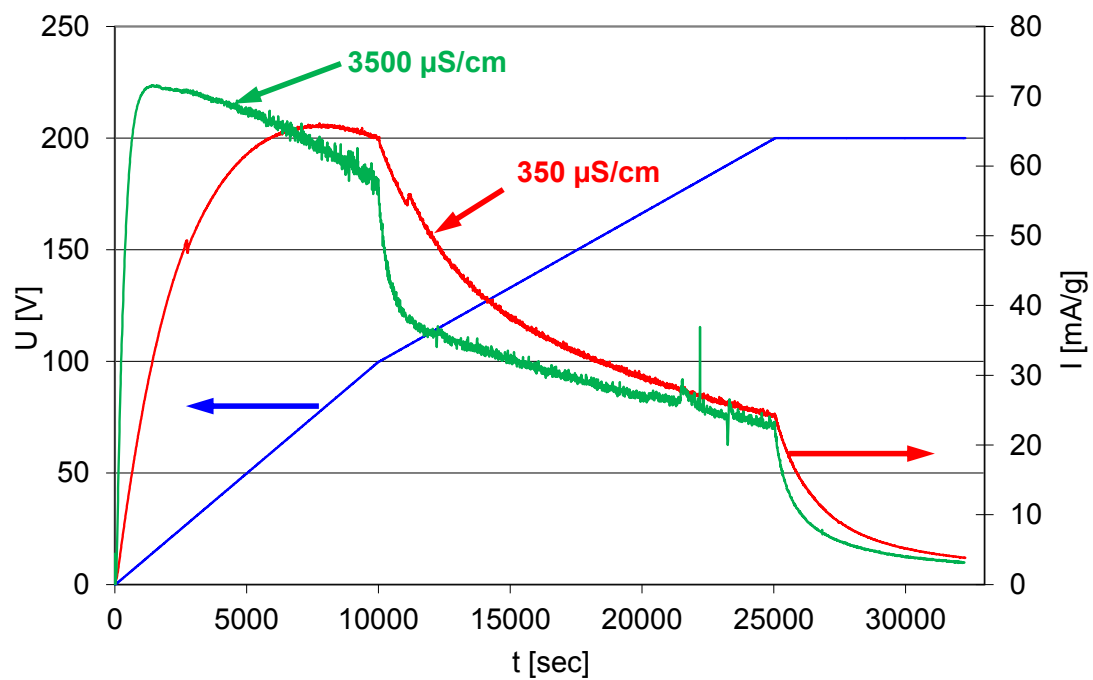

fig. 10: Formation program of HV200-570 anodes formed in 0.35 mS/cm (red) respectively 3.5 mS/cm (green) conductive electrolyte containing glycol. The anode formed in the higher conductive electrolyte shows breakdowns with repassivation during anodization seen as spikes (21.000-24.000 sec).

To exclude aging effects of the electrolyte, two identical solutions were prepared. Several formation cycles were processed in one of the solutions to mimic a "used" solution. The experiment was then repeated in both the fresh and used solution. No increase in leakage current was observed with increasing anodizing cycles.

Comparison of formation using ethylene glycol vs diethylene glycol

Two different glycols, ethylene glycol and diethylene glycol, with different steric sizes but similar chemical behavior have been tested (fig. 11). No differences were observed during the formation up to 320 V. Nevertheless during reformation (> 38000 s) an increasing current was detected in diethylene glycol. This effect was reproduced several times. It can be assumed that ethylene glycol inhibits the formation of crystalline tantalum oxide stronger than diethylene glycol and results therefore in lower leakage currents.
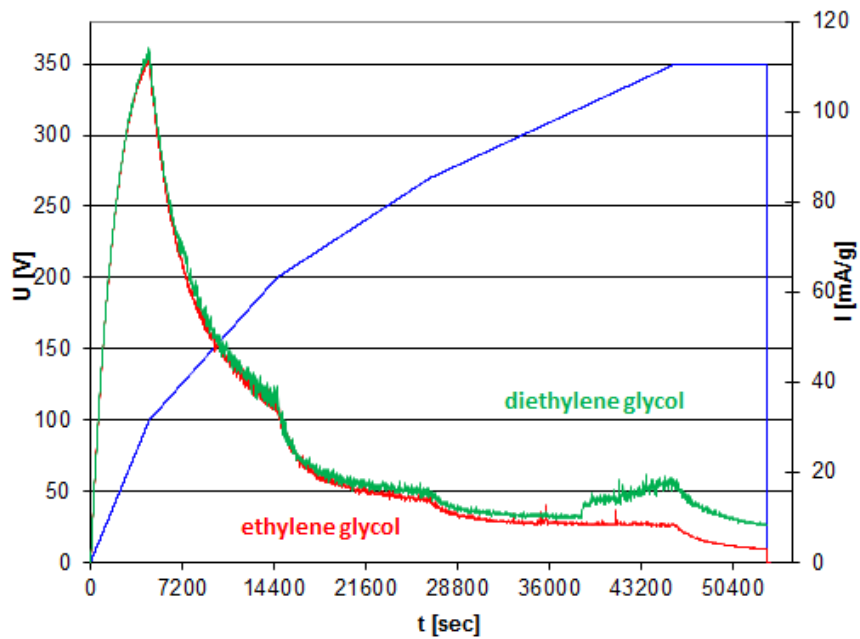
fig. 11: Formation current of 12k µFV/g anode in dependence of time. At potentials higher than 300 V the current increases in diethylene glycol containing electrolyte.

Investigation of breakdown stages

To characterize the local breakdown of the oxide layer, SEM pictures have been taken from 9k µFV/g anodes and different states of the breakdown were observed. Results of anodization in water were compared with those of anodization in ethylene glycol.

The breakdown in water can be separated into three different stages. The first stage is the appearance of dark spots (fig. 12) that cannot be directly chemically identified. These may be impurities or the effect of the beginning of a morphology change from amorphous to crystalline oxide state. However they will be interpreted as a source of breakdowns and in fact more breakdowns occur there than on spot free areas. In contrast to current statements that especially the sinter necks are "weak spots" for breakdowns it was observed that mostly plain areas are affected (fig. 13). Additionally first oxide peel-off is visible with an exposure of the underlying metal.
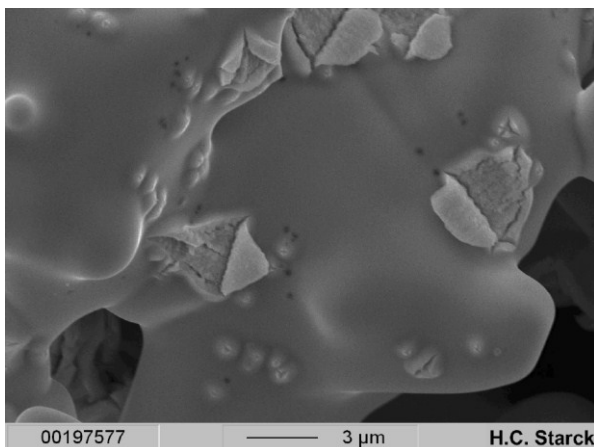

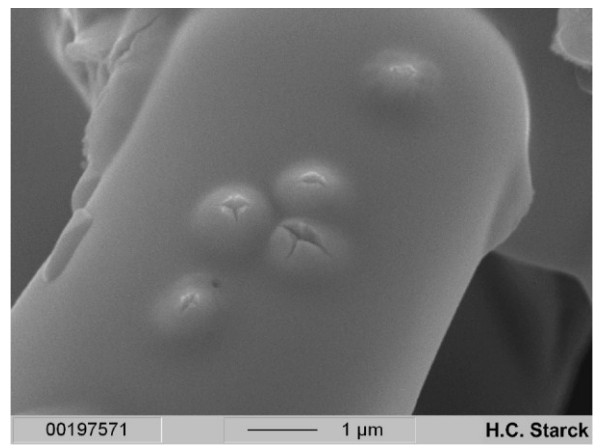fig. 12 : First stage with the appearance of dark spots on the oxide (water system).

fig. 13: First stage dark sports that break through on a plain area (water system).

In the second stage (fig. 14) the oxide forms cracks and reveals the underlying metal until the last stage (fig. 15) is reached where the breakdown proceeds uncontrolled over the whole area and even over the whole sample. The formed oxide grows in an irregular structure; oxide and metal core cannot be distinguished anymore.
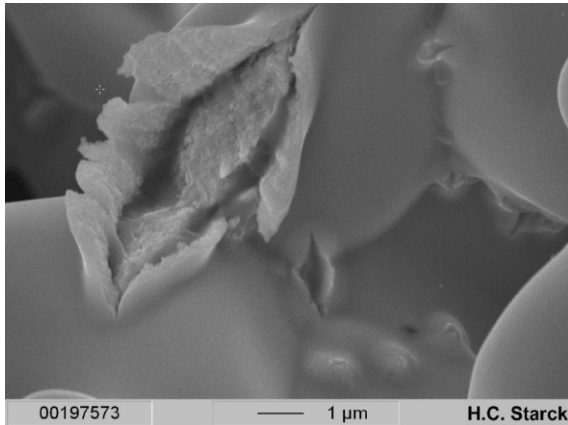

fig. 14: Second stage with oxide forming cracks revealing the metal underneath with further uncontrolled oxidation (water system).
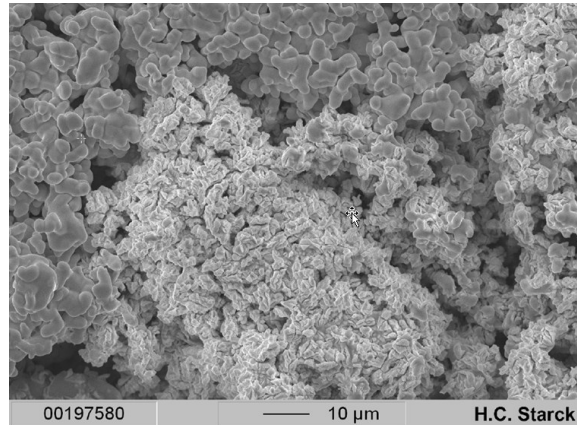

fig. 15: Last stage of breakdowns with a complete oxidation of metal in an irregular structure (water system).

Comparison of these stages for anodization in pure water to those for anodization in ethylene glycol similar behavior was observed (compare fig. 12 and fig. 14). However in the last stage in glycol the uncontrolled breakdowns look a bit different with huge cracked holes and less continuous oxidation (fig. 17).
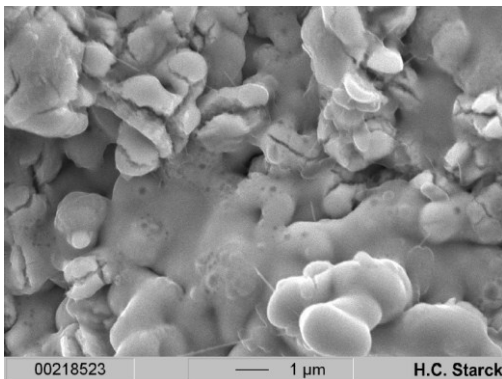

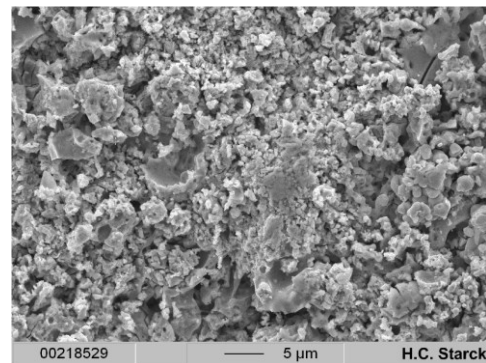fig. 16: First stage with the presence of dark spots on the oxide (glycol system).

fig. 17: Oxide structure in last stadium in glycol electrolyte.

Conclusion

The formation of tantalum based anodes to higher potentials above 200 V requires a modification of the common electrolytes and anodization programs. In galvanostatic anodization mode the current density increases with decreasing surface area and therefore at potentials >90 V a higher formation rate occurs. A decrease of the electrolyte conductivity seems to increase the accessible formation voltage but can be explained as a delayed oxide growth with reduced formation rates. Therefore lower constant rates lead to similar positive results as well. Additives, especially ethylene glycol, inhibit the crystallization of tantalum oxide at higher potentials and decrease the leakage current. From our experiments on these parameters our recommendations for the formation of anodes to highest voltage are usage of:

- ethylene glycol containing electrolytes instead of water based

- lower constant rates and a stepwise reduction of the rates or lower conductivity electrolytes

- ethylene glycol is favored compared to diethylene glycol

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 H. Haas, M. Hagymási, "Tantalum capacitor anodes providing highest capacitances: Where are the limits?" CARTS Europe, Nice, France 2011

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. Hagymási, H. Haas, H. Brumm, O.Thomas, C. Schnitter, "Recent advances in the development and processing of Tantalum and Niobium capacitor powders" CARTS International 2014, Santa Clara CA, US 2014

5 H. Haas, C. Hammer, M. M. Lohrengel, K. P. Rataj, C. Schnitter, M. Stenzel,"Dielectric oxide films on sintered tantalum", CARTS International 2012, 2012 Las Vegas, NV, p. 274-285

6 K. P. Rataj, C. Hammer, B. Walther, M. M. Lohrengel "Quantified oxygen evolution at microelectrodes", Electrochim. Acta, 90 (2012), p. 12-16

7 Yu H, Zhu S, Yang X, Wang X, Sun H, et al. "Synthesis of Coral-Like Tantalum Oxide Films via Anodization in Mixed Organic-Inorganic Electrolytes" PLoS ONE 8(6): e66447. doi:10.1371/journal.pone.0066447, 2013

8 Xiaoge Gregory Zhang, "Electrochemistry of Silicon and Its Oxide", Springer, 2001

9 J ean-Noël Chazalviel, François Ozanam, "Electrochemically Formed Porous Silica", Materials 2011, 4, 825-844;

10 M. J. Madou, W. P. Gomes, F. Fransen, F. Cardon, "Anodic Oxidation of p-Type Silicon in Methanol as Compared to Glycol" J. Electrochem. Soc. 1982 Vol. 129, issue 12, 2749-2752

11 J. A. Bardwell, K. B. Clark, D. F. Mitchell, D. A. Bisaillion, G. I. Sproule, B. MacDougall and M. J. Graham, "Growth and Characterization of Room Temperature Anodic SiO_2 Films", J. Electrochem. Soc. 1993 Vol. 140, issue 8, 2135-2138

12 Nageh K. Allam, Xinjian J. Feng and Craig A. Grimes, "Self-Assembled Fabrication of Vertically Oriented Ta_2O_5 Nanotube Arrays, and Membranes Thereof, by One-Step Tantalum Anodization", Chemistry of Materials 2008 20 (20), 6477-6481

13 M. Croset, E. Petreanu, D. Samuel, G. Amsel, J.P. Nadai, "An O[18] 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

14 N. F. Jackson, "Field crystallization of anodic films on tantalum", J. Appl. Electrochem. 3 (1973), 91-98

15 M. Fernandez, J. Baonza, J. M. Albella and J. M. Martinez-Duart, "Influence of electrolytes in the electrical characteristics of anodic films on tantalum", Electrocomponent Science and Technology, 1981, Vol. 7, pp. 205-210

16 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

17 D. M. Smyth, T. B. Tripp, G. A. Shirn, "The Heat-Treatment of Anodic Oxide Films on Tantalum IV. Anodization in Phosphoric Acid Solutions", J. Electrochem. Soc. 1966 Vol. 113, issue 2, 100-104

18 Q. Lua, S. Matoa, P. Skeldona, G.E. Thompsona, D. Mashederb, H. Habazakic, K. Shimizud, "Anodic film growth on tantalum in dilute phosphoric acid solution at 20 and 85 °C", Electrochimica Acta, Vol. 47, Issue 17, 2002, p. 2761–2767

19 Herman A. Johansena, George B. Adams Jr., Pierre Van Rysselbergheb, "Anodic Oxidation of Aluminum, Chromium, Hafnium, Niobium, Tantalum, Titanium, Vanadium, and Zirconium at Very Low Current Densities", J. Electrochem. Soc. 1957 Vol. 104, issue 6, 339-346

20 D. Gerstemberg, "Handbook of Thin Film Technology", chapter 19, Ed. L. I. Maissel and R. Glang, McGraw-Hill, N.Y. (1970).