



Technology Metals | Advanced Ceramics

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

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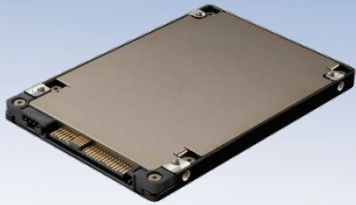
H.C. Starck Tantalum and Niobium GmbH, Germany

Noordwijk, Netherland, 3<sup>rd</sup> SPCD 10.-12. October 2019

# High Voltage Market Trends: Focus High Reliability

Increasing demand for HV applications!

**Data Storage (SSD)**



**Medical Devices**



**Aviation**



**Aerospace**



**Transportation and  
Railroad**



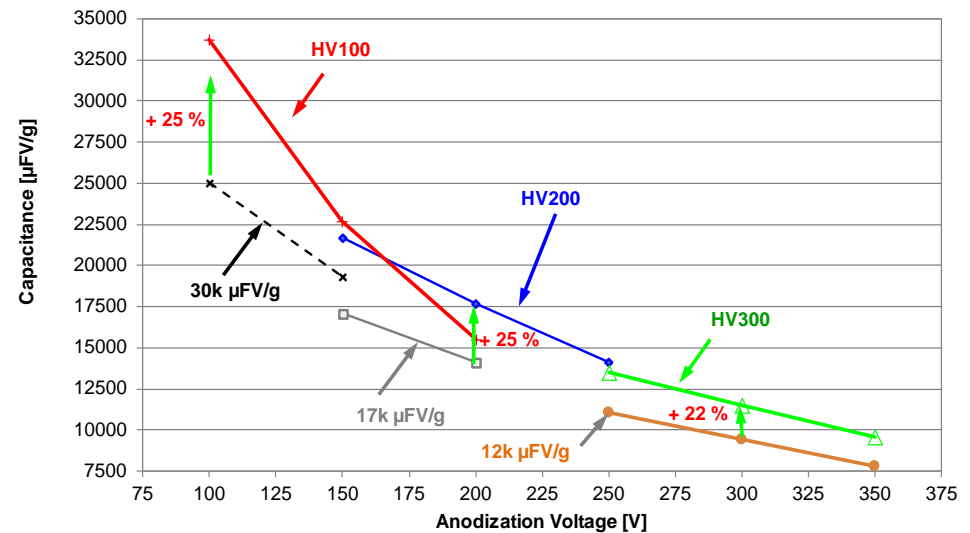
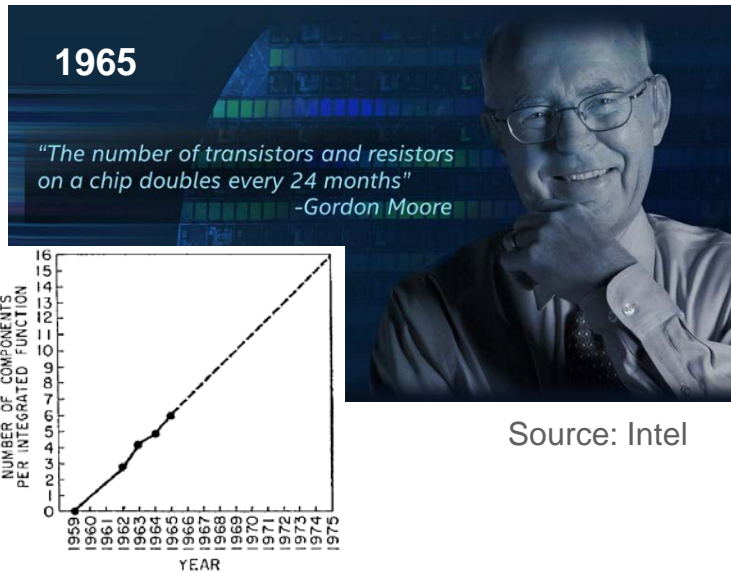
**Automotive**



**Defense**



# Moore's Law – Trends for High Voltage Applications



Also continuous performance improvement for Ta capacitors!

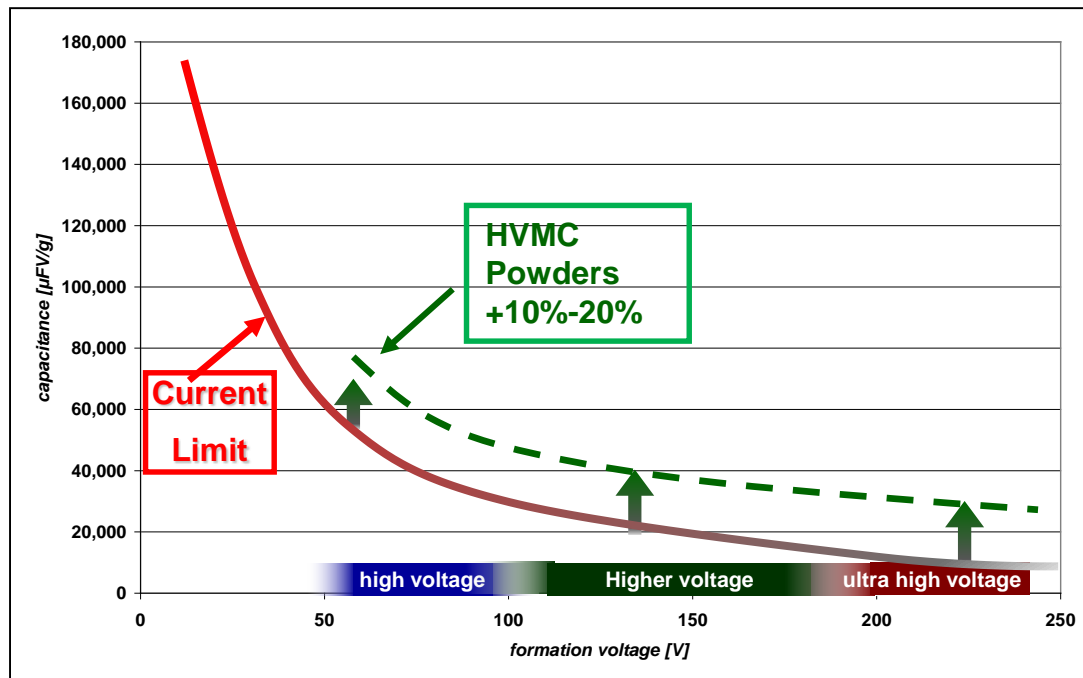
Major trends for the recent years:

1. Increase capacitance at a given voltage e.g. 150 V<sub>f</sub>
2. Increase forming voltage above 300 V<sub>f</sub> → More energy!

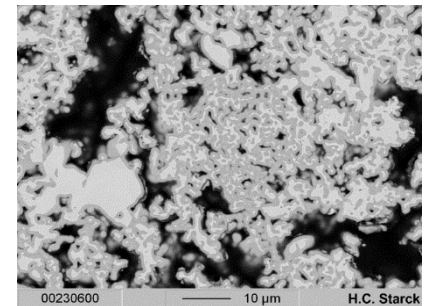
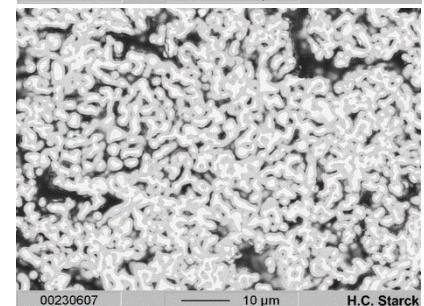
High Voltage Medium  
Capacitance = HVMC

# What Makes HVMC Powder so Unique

1. Superior microstructural homogeneity of pores and particles
2. Pore and primary particle structure can be tailored to application needs
  - ➔ Primary particle size can be varied from 0.3  $\mu\text{m}$  – 3  $\mu\text{m}$
  - ➔ Pore size distribution can be tailored within a specific powder charge category
3. Provides higher purity than Na powder (Fe, Cr, Ni < 10 ppm, and K, Na < 1ppm)



Slide 4

**300 V<sub>f</sub> Anode****Standard  
Powder****HVMC****H.C. Starck**



# 1. Trend: How to Provide More Capacitance?

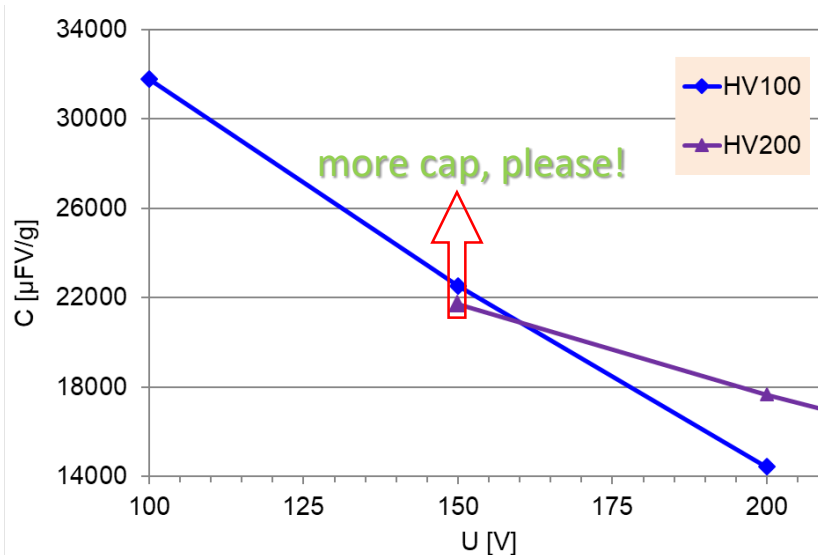
- New capacitors for  $U_f \sim 150 \text{ V}_f$  highly requested
- Task: Provide more cap than existing HVMC powders (HV100/HV200)

## Powder Naming

“High Voltage”

**HV 200**

target formation voltage



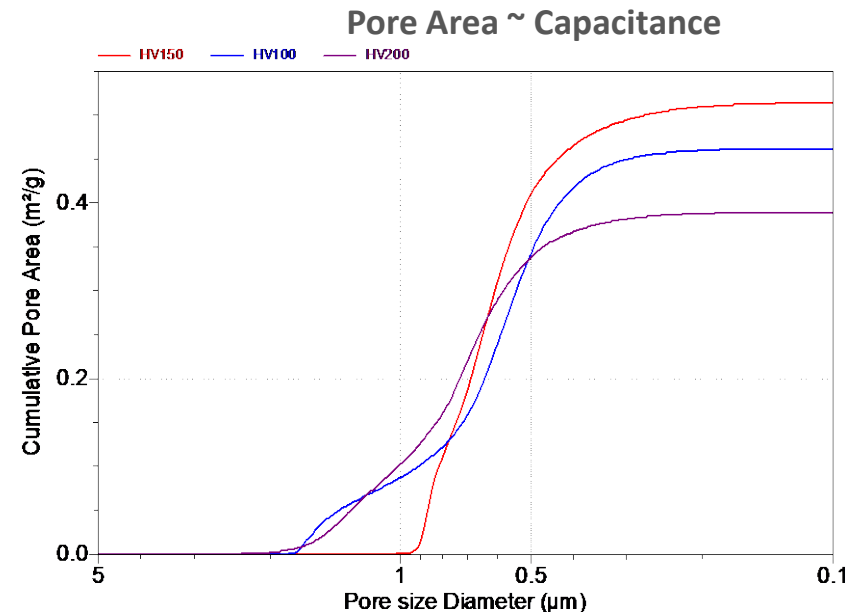
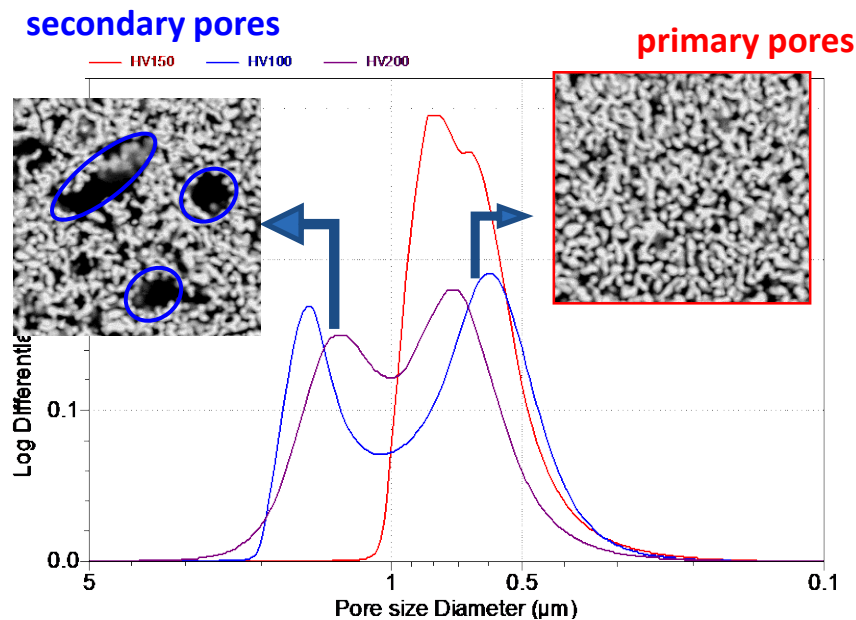
- HV100: pores too small  $\rightarrow$  worse ESR
- HV200: better pores but lower cap

**Develop new powder by improving particle and pores size distribution!**

# 1. Trend: How to Provide More Capacitance?

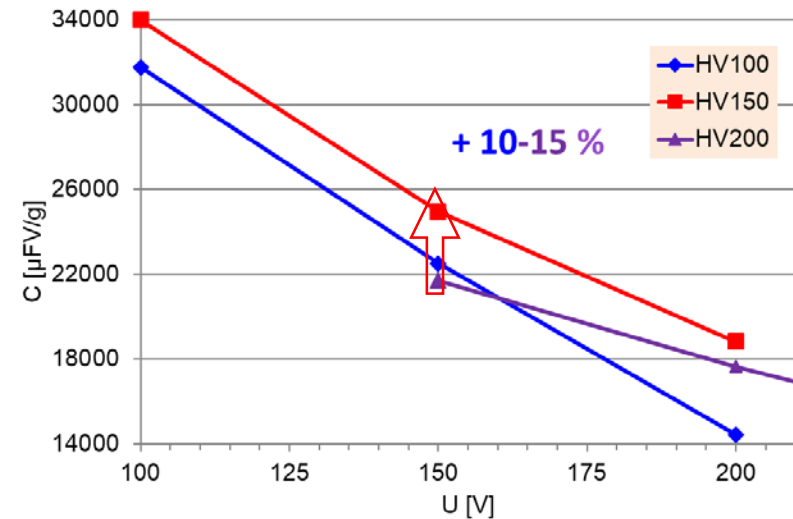
- Production parameters optimized according to microstructure!
- Anode pore size + primary particle distribution was improved → nearly monomodal

Anode Pore Size Distribution (PD 6,0 g/cm<sup>3</sup>, ~10 % shrinkage)



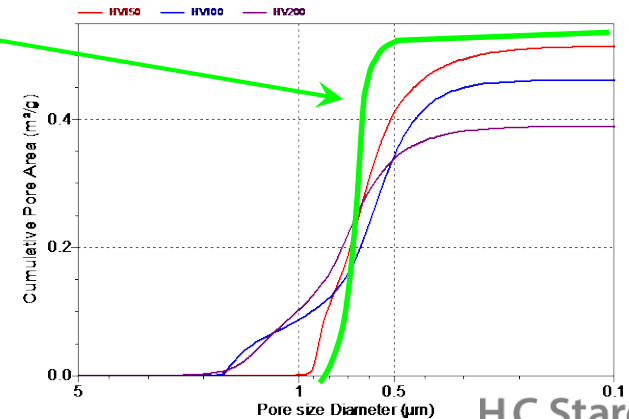
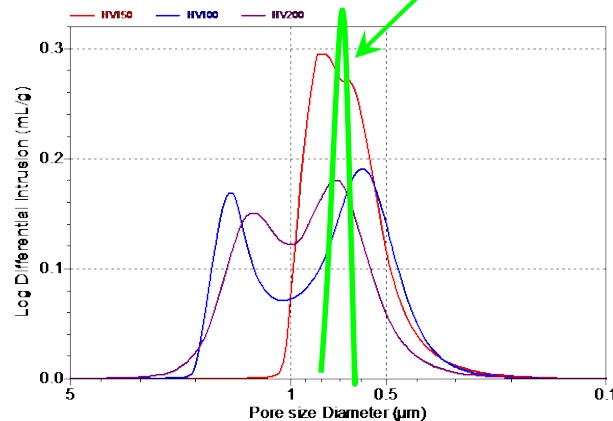
# Structure Impact on Capacitance

- New powder provides 10 -15 % more capacitance than other HVMC powders
- More cap over wide range: 100 – 200 V



Showcase for future developments !

Make anode pore/particle size distribution narrower!



## 2. Trend: Increase Forming Voltage

- Currently, HV300 provides highest energy density @ 250-300 V
- Task: Provide more energy  $W$  by increased forming voltage  $U$

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

➔ Powder microstructure has to be adapted:

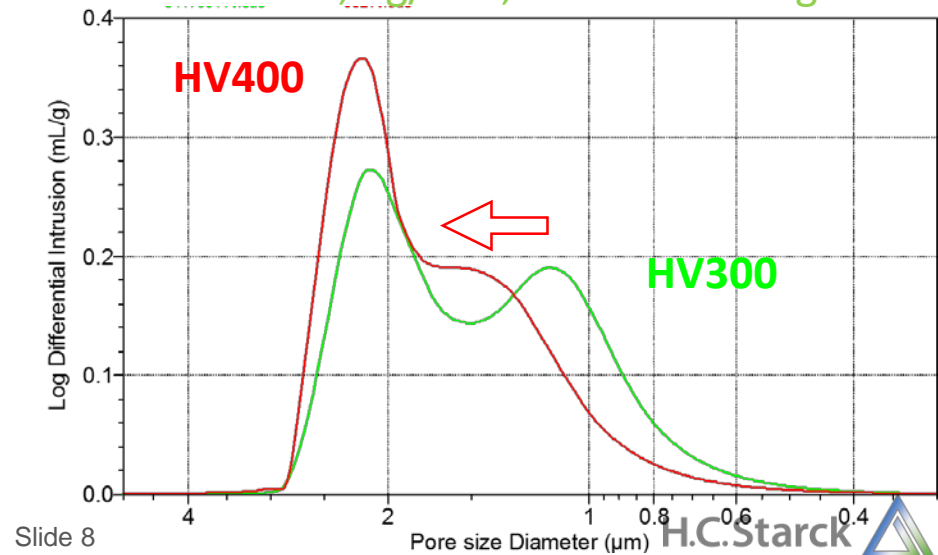
1. Increase primary particle size
2. Increase pore size
3. Improve pore distribution

New HV400 developed



Anode Pore Size Distribution

PD 5,5 g/cm<sup>3</sup>, ~10 % shrinkage

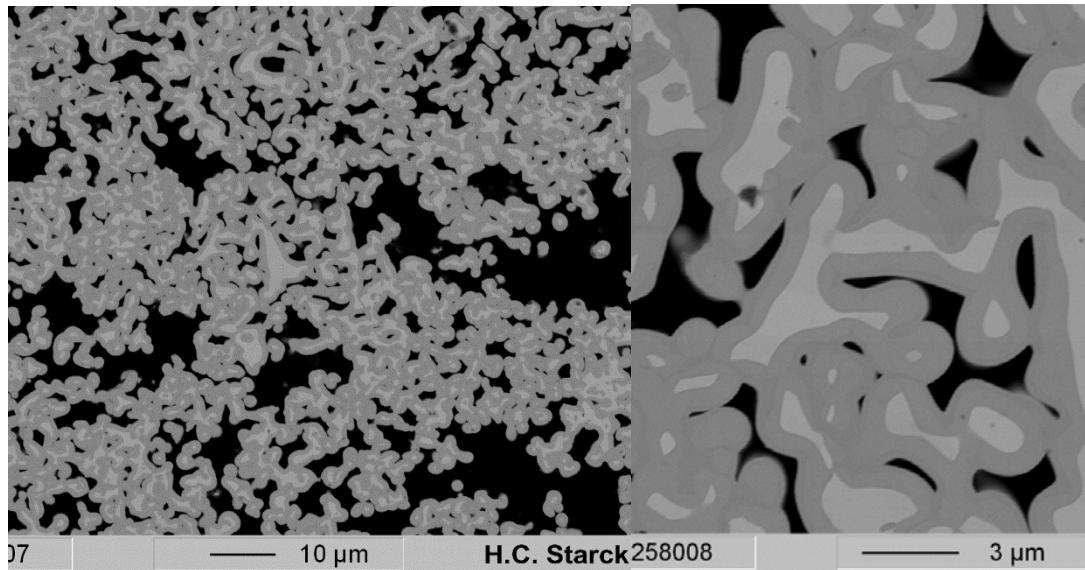




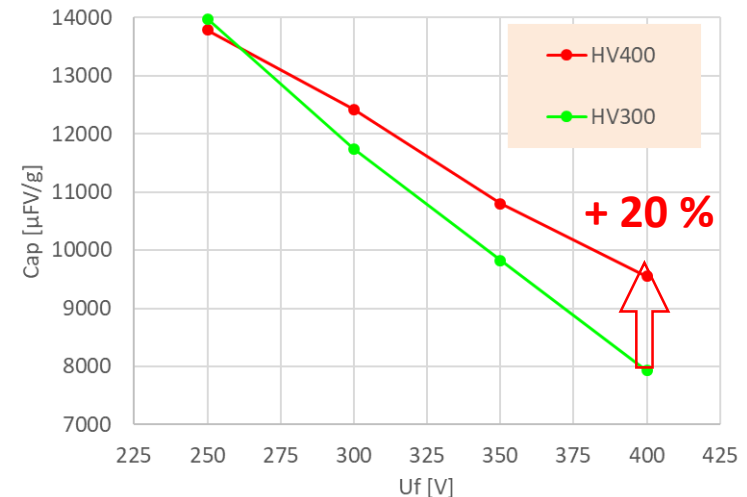
# New HV400 - Properties

- Increased capacitance at 400 V<sub>f</sub>: + 20 %
- Open pore structure, no macroscopic defects observed

Cross section of HV400 @ 400 V<sub>f</sub>



Capacitance

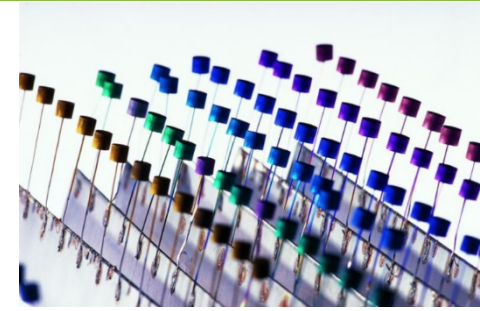


- Could work until 450 V BUT: Increase of Leakage >10 nA/μC for higher voltages

Standard anodization process still sufficient?

### 3. Impact of Anodization

- Anodization has an big impact on capacitance and LC
- Aqueous electrolyte systems not appropriate for  $U_f > 200 \text{ V}_f$
- Additives are used to improve breakdown stability and LC:
  - Ethylene glycol, phosphoric, boric and citric acid

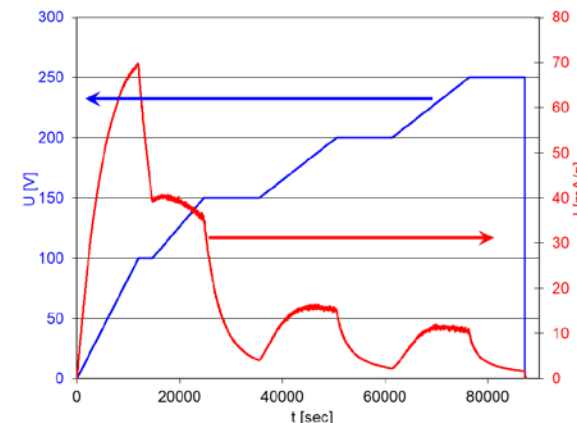
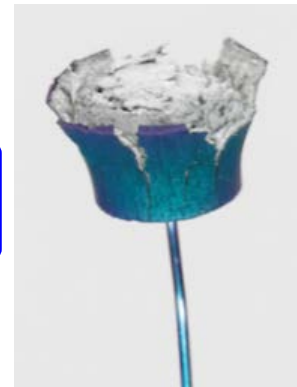


**Task: Separate impact of anodization from powder modification**

#### Experimental part

- HV200 large cylindrical anodes ( $\varnothing 8,0 \text{ mm}$ , 2,2 g, PD 6.0, 10 % shr.)
- Forming  $U_f$ : 150 – 250 V<sub>f</sub> at 60°C, water-glycol bath (2:3), 900  $\mu\text{S/cm}$  by  $\text{H}_3\text{PO}_4$
- Forming with „constant rate“ anodization

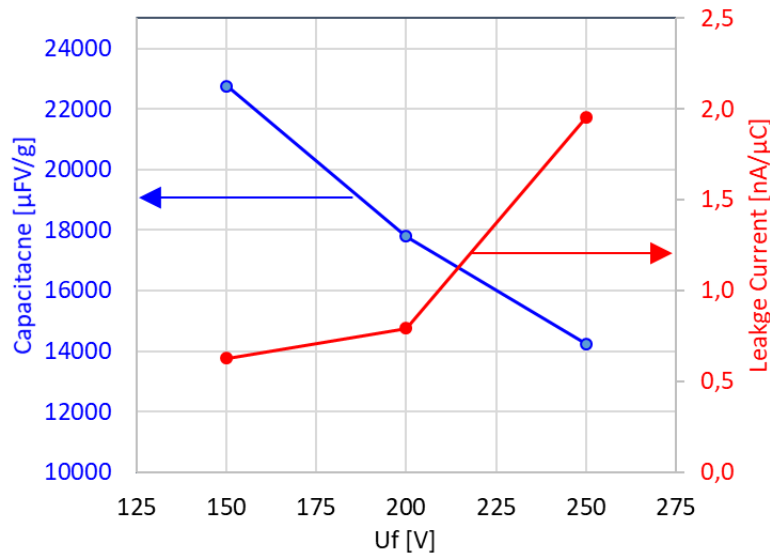
➔ Analyse anodes after forming



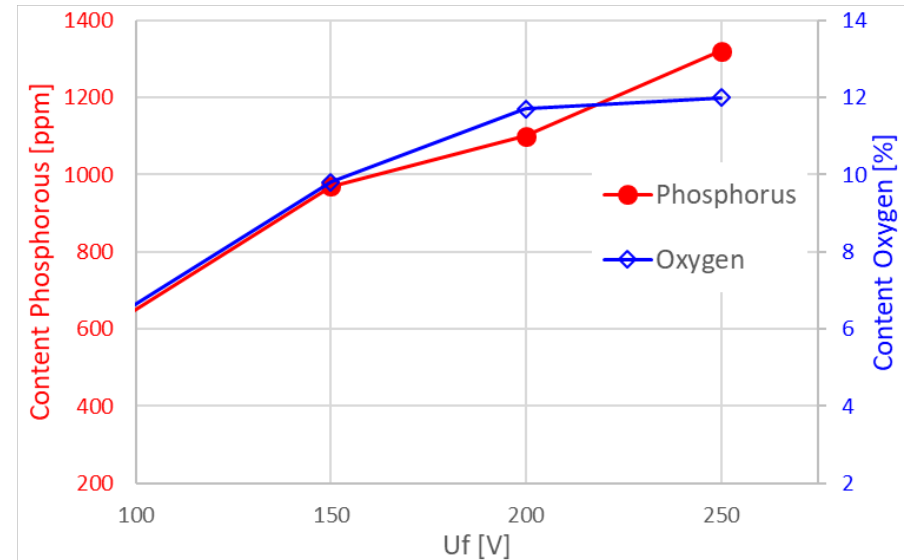
### 3. Impact of Anodization: Results



#### Capacitance



#### Chemical Analysis

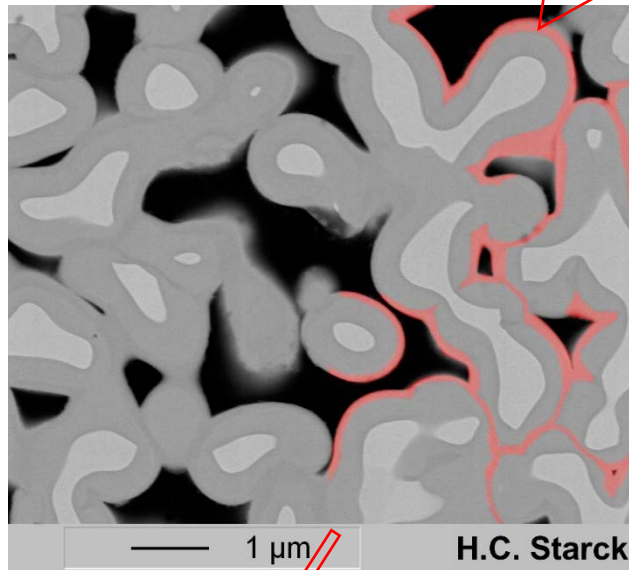


- Increase of oxygen by forming
- Strong incorporation of phosphorus, probably as  $\text{PO}_4^{3-}$
- Strong increase of LC at 250 V

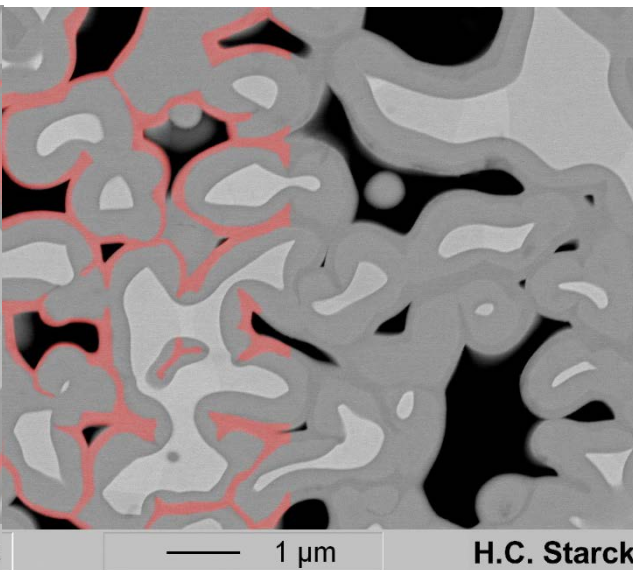
# Incorporation of Phosphorous

- outer oxide layer: incorporation of  $\text{PO}_4^{3-}$

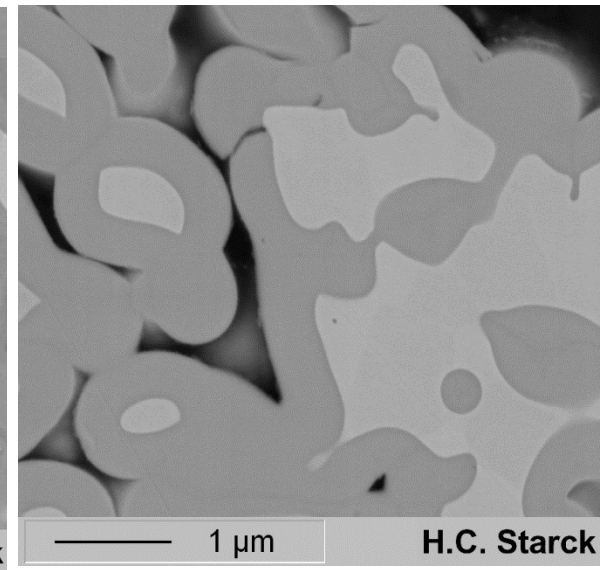
200 V<sub>f</sub>



250 V<sub>f</sub>



200 V<sub>f</sub> formed in  $\text{HNO}_3$



370 nm oxide

1100 ppm P → 3370 ppm  $\text{PO}_4^{3-}$  = 0,53 %

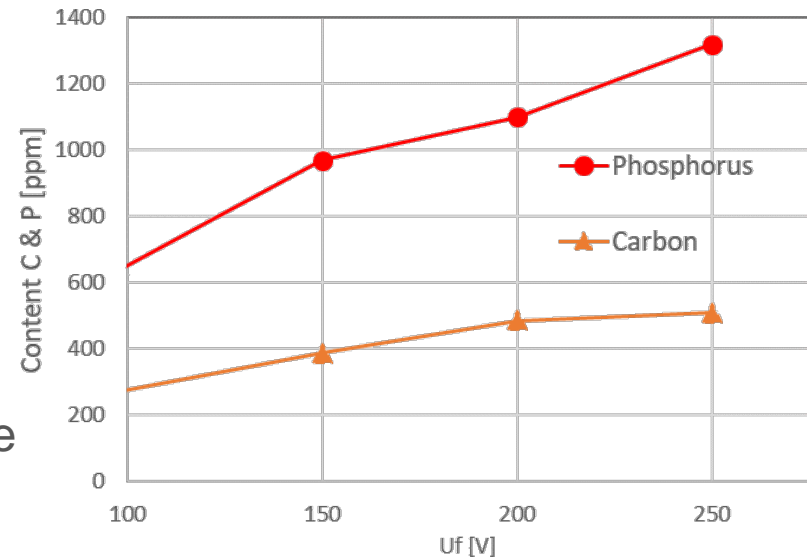
~85 nm outer  $\text{PO}_4^{3-}$  rich layer

117000 ppm O → 637280  $\text{Ta}_2\text{O}_5$

P is only found at the outer layer! Phosphate content is increased to 2,3 wt-% = 9,9 mol%

# Incorporation of Carbon

- High carbon content found: 390 – 510 ppm
- Unclear how it is incorporated
- From decomposition of glycol?
- Powder with >60 ppm C is difficult to anodize for high voltage powder

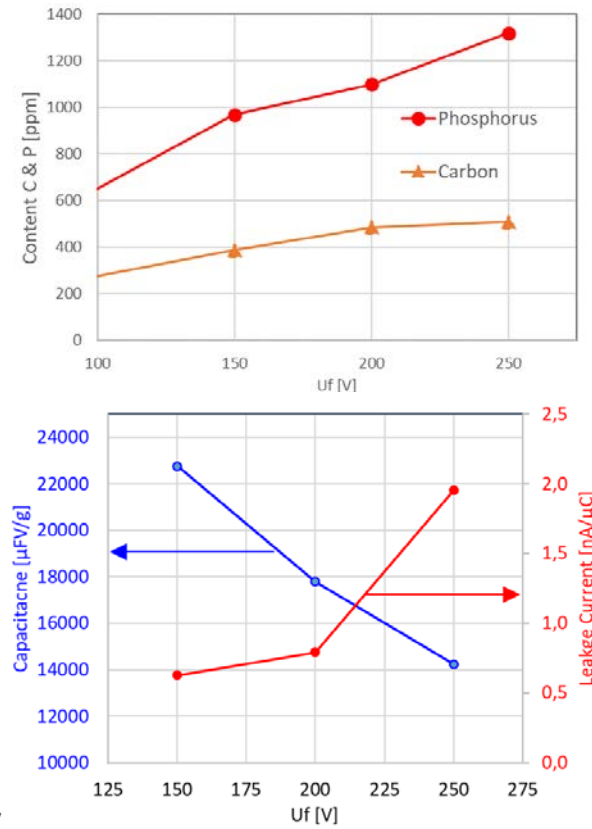
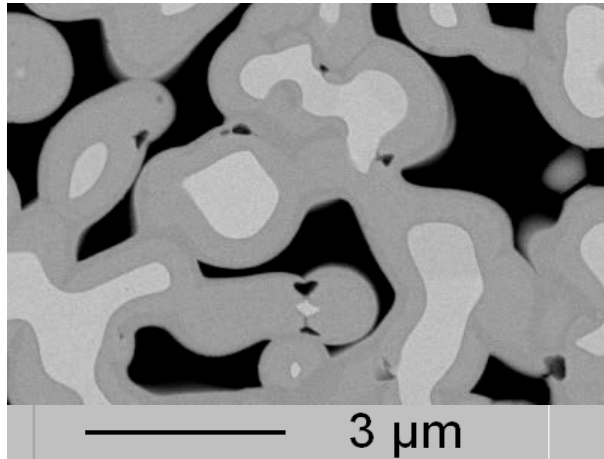


➔ Not only carbon amount also how it is introduced has an big impact!



# Effect of Incorporations

250 V<sub>f</sub>



Defects can be found at the interface outer/inner layer

- caused by PO43-?
- Caused by gas formed during anodization (oxygen?)
- Caused by decomposed electrolyte (carbon)?

HV anodization has to be adapted!

# Summary

## Powders Developments for more capacitance/energy

- New HV150 with increased capacitance by improve microstructure
- New HV400 available than can be formed to 400 V

## Anodization

- Forming to 400 V is challenging
- Strong incorporation of P and C found
- Is Phosphorous really beneficial?



## Search for perfect electrolyte has begun. “Wish list”:

- Stable until 450 – 500 V, no decomposition
- No or limited incorporation of foreign ions
- Good heat conductivity



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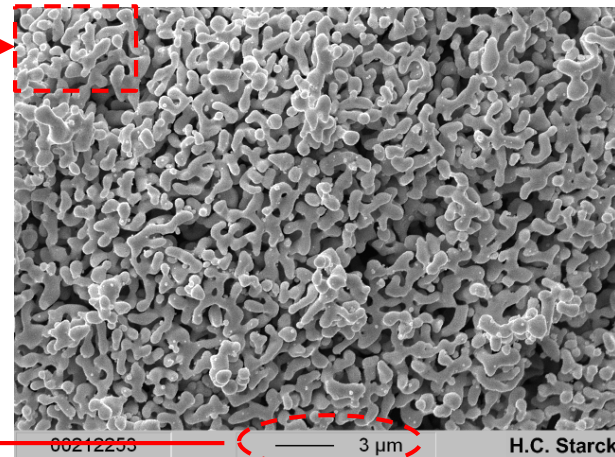
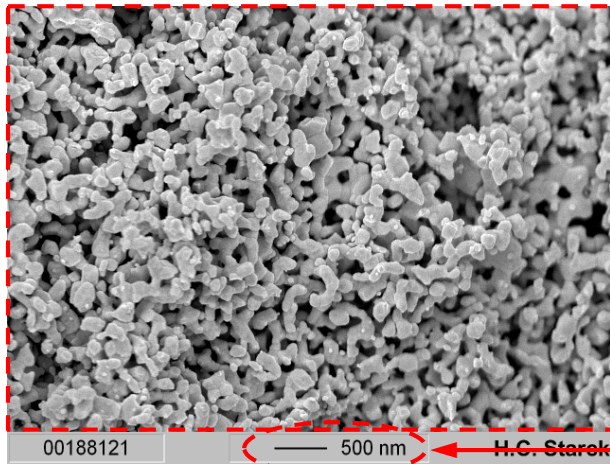
**[marcel.hagymasi@hcstarck.com](mailto:marcel.hagymasi@hcstarck.com)**



# Microstructure of HVMC Anodes

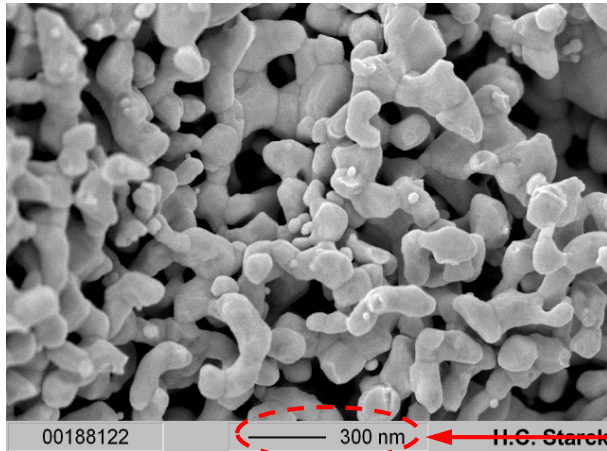
Increasing the dimensions but keep the structure homogeneous!

STA150KA  
6 V-20 V



HVMC 20K  
100 V-200 V

5 x higher magnification



5 x higher

