# BCP and EP for Nb Cavities

Charles Reece

USPAS Course:

SRF Technology: Practices and Hands-On Measurements

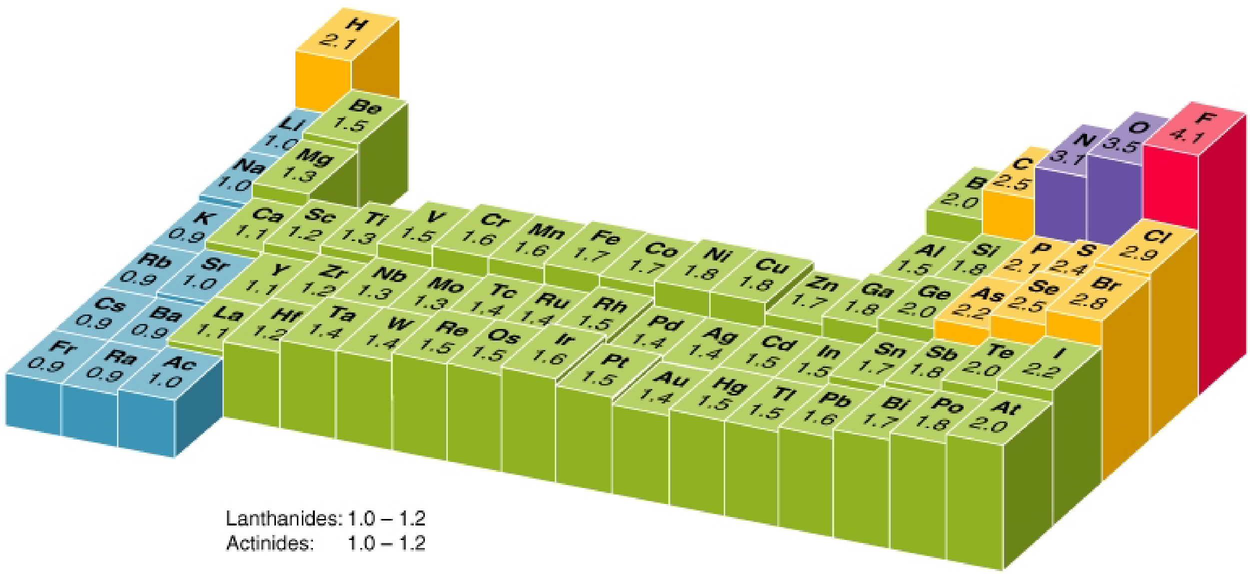
January 2015

# Nb Cavity Surface Removal

**SRF cavity surfaces must be "pure", "clean", and "smooth"**

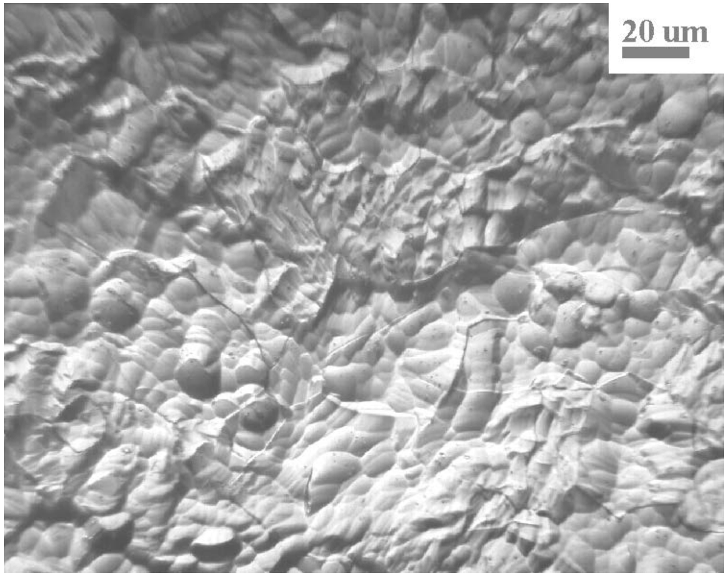
- "Ideal" surface is defect-free Nb crystals with only $Nb_2O_5$ ~4 nm capping layer and planar surface topography.
- After practical cavity fabrication, the real surface is "disturbed" and "polluted."
- Empirically found that >100 µm removal is typically required to reliably expose "good" bulk Nb material, i.e. predictable SRF performance.
- The naturally-forming $Nb_2O_5$ is a very stable oxide – weak acids don't touch it
- $F^-$ ions are electronegative enough to consume $Nb_2O_5$
- Thus the role of hydrofluoric acid (HF) in processing Nb cavities

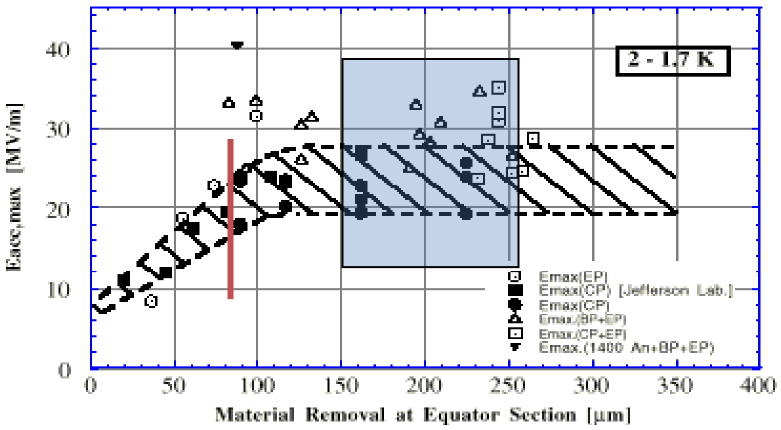
# Electronegativity of the elements




Lanthanides: 1.0 – 1.2
Actinides: 1.0 – 1.2

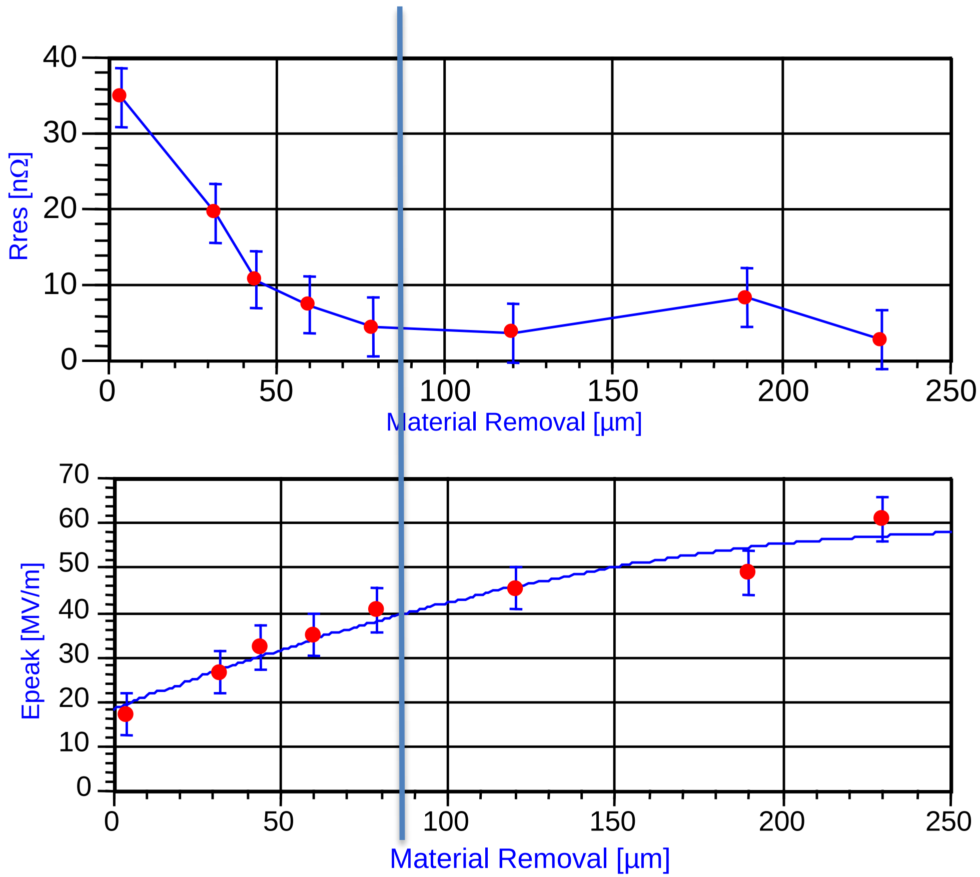
# The Need For Material Removal



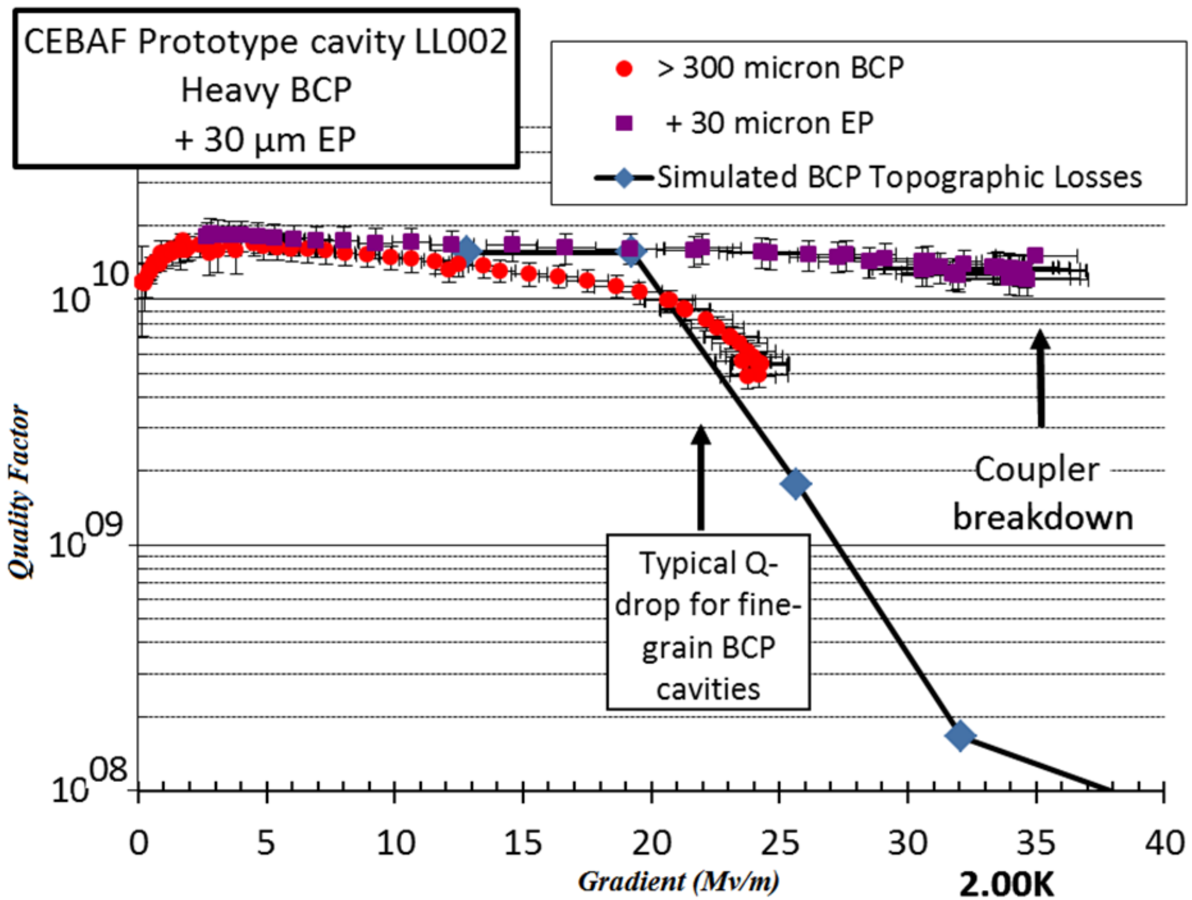

K. Saito

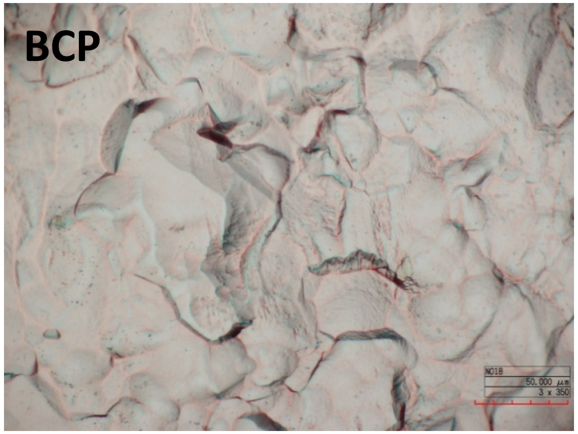
Study of performance with integrated removal by BCP circa 1995

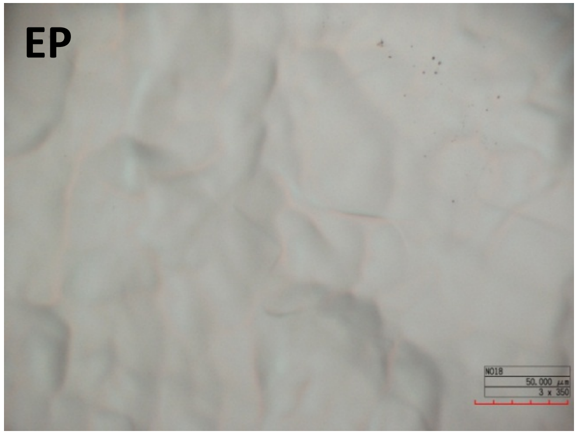



P. Kneisel

# Importance of topography




C. Xu, C. E. Reece and M. J. Kelley, "Simulation of non-linear SRF losses derived from characteristic Nb topography: comparison of etched and electropolished surfaces," *http://arxiv.org/abs/1406.7276,* 2014.

**EP cavities often have higher field gradients**

**Difference between BCP and EP: topography**

# Nb Cavity Surface Removal

**SRF cavity surfaces must be "pure", "clean", and "smooth"**

- **Etching** with "buffered chemical polish" (BCP) - $\boldsymbol{HF:HNO_3:H_3PO_4\ (1:1:2)}$
  - Nitric acid aggressively oxidizes Nb
  - HF ($F^-$ ions) dissolves the oxide
  - Phosphoric acid only slows down, "buffers," the exothermic process
  - Vulnerable to variations in local reaction rates → inherent roughness
- **Electropolishing** (EP) - $\boldsymbol{HF:H_2SO_4\ (1:10)}$
  - With applied potential, sulfuric acid anodizes Nb, growing $Nb_2O_5$ layer
  - $F^-$ ions diffuse to the surface and dissolve the oxide
  - Find a balance for polishing (surface leveling), not etching
  - Diffusion-limited conditions yield better smoothing

# Surface polishing of niobium for superconducting radio frequency (SRF) cavity applications

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Thomas Jefferson National Accelerator Facility

Committee Members:

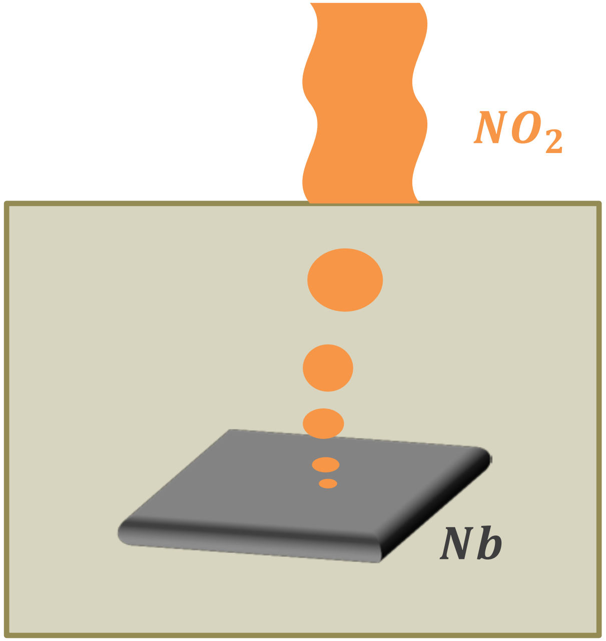
Dr. Michael J Kelley
Dr. Gunter Lüepke
Dr. Charles E Reece
Dr. Rong-Li Geng

# Current techniques for surface polishing

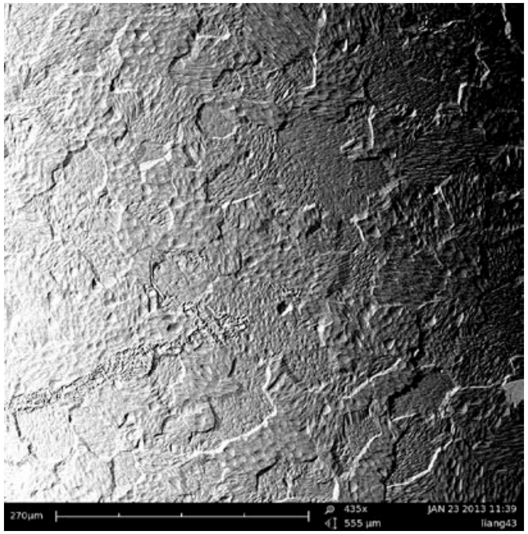
| | Chemicals involved? | Complicate shape? | Removal rate? | Surface roughness | Routinely used? |
|---|---|---|---|---|---|
| Mechanical grinding | N | Hard | Fast | Y | N |
| BCP | Y | Easy | Fast | Y | Y |
| EP | Y | Hard | Slow | N | Y |
| CBP | N | Hard | Very slow | N | N |

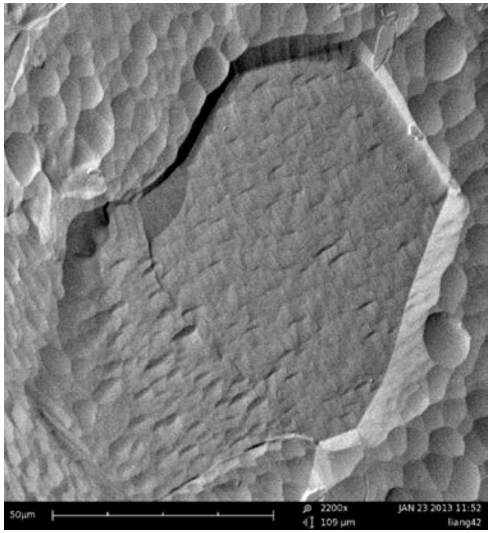
- Mechanical grinding: remove local defects; but rough and needs following chemistry
- BCP: fast and simple (not limited by cavity shape); but rough
- EP: smooth; but complicated (limited by cavity shape) and slow
- CBP: smooth and uniform; but slow and needs final chemistry

# Buffered Chemical Polishing (BCP)




$HF:HNO_3:H_3PO_4\ (1:1:2)$




**Fine grain, 20°C, 6 minutes**

**Cavity processing conditions:**

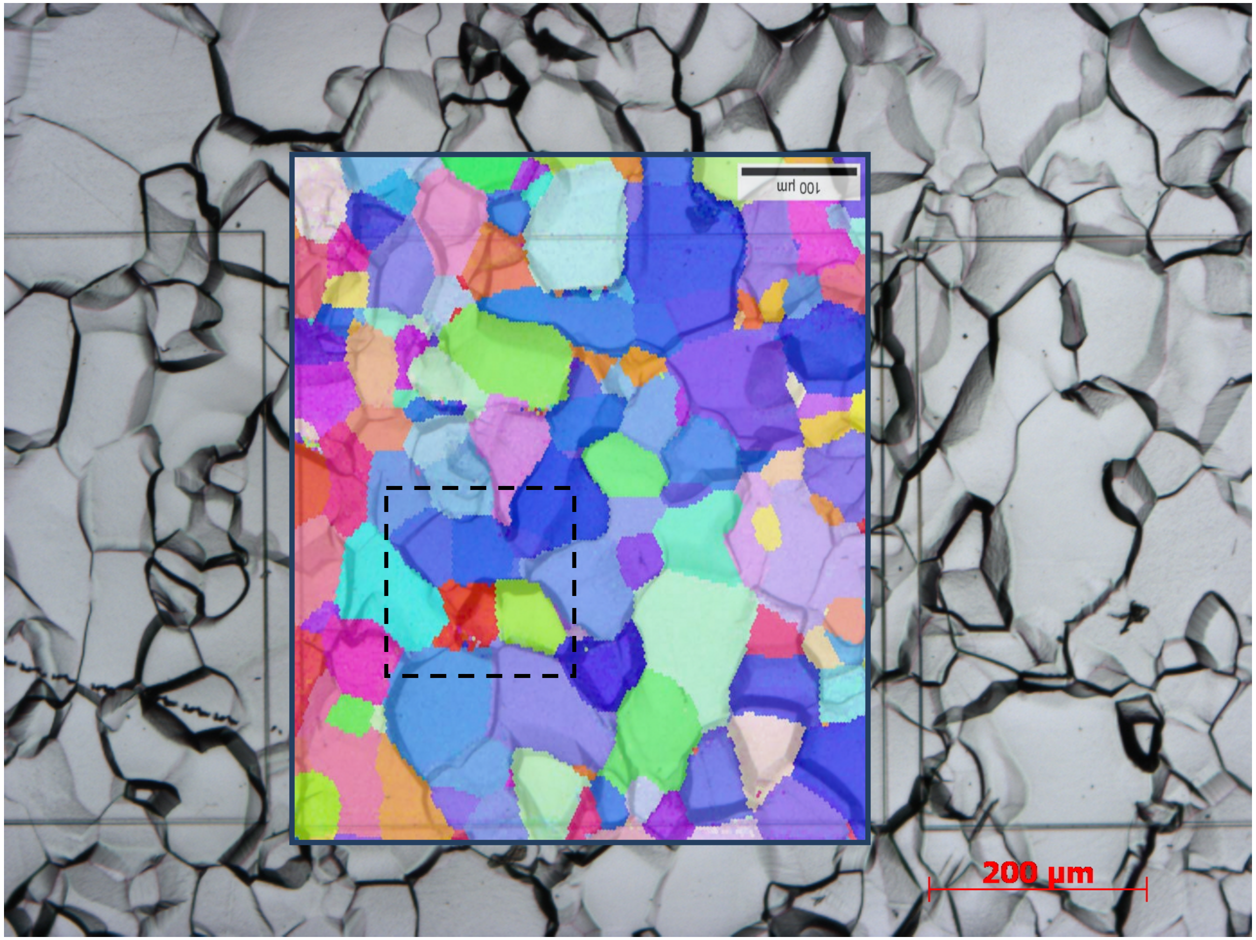
- **Acid temperature below 15 °C**
- **“dunking” or acid circulation**

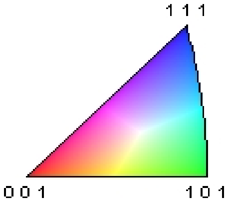
# BCP experiment conditions

- **Temperature:** 0, 10, 20, 30 °C
- **Duration:** 1, 2, 4, 6, 8, 10, 12, 90 minutes
- **Material type:** fine grain, single crystal, bi-crystal
- **Sample orientation:** facing up, facing down, facing horizontally
- **Flow condition:** sample static, sample rotating

# EBSD – BCP on fine grain, nano-polished niobium

## 6 minutes BCP at room temperature



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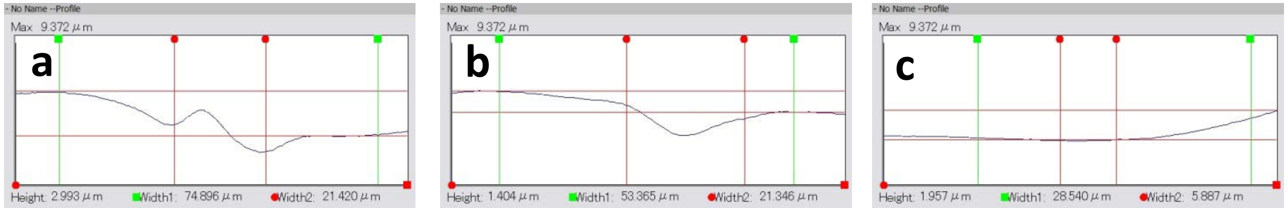
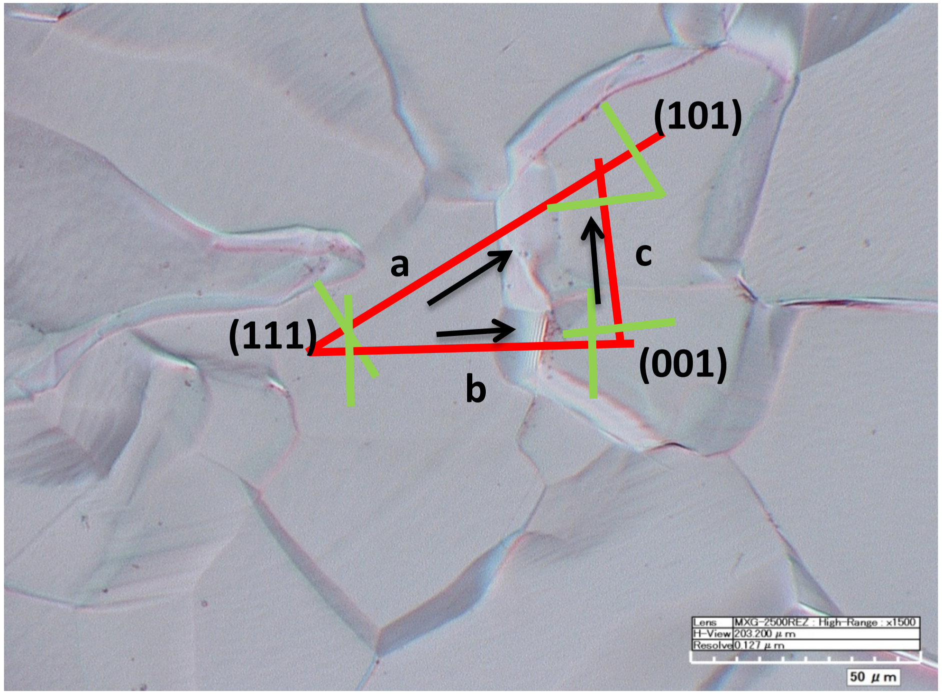
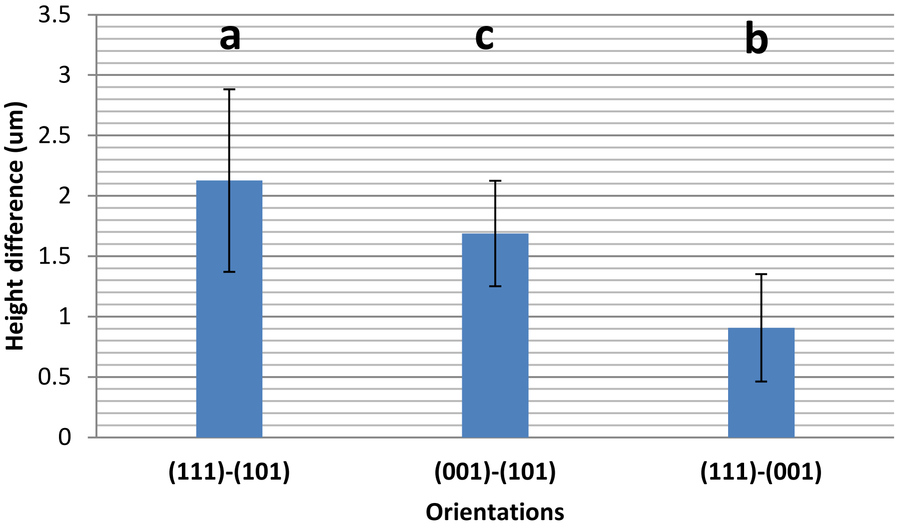
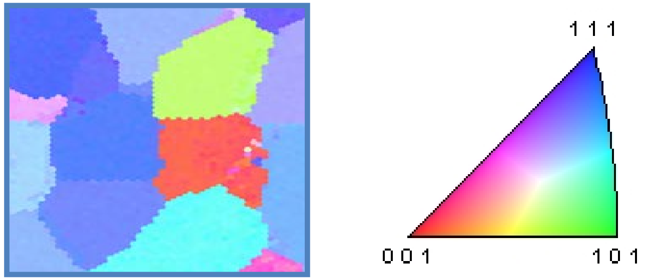



**Polishing rate:**
**(110)>(100)>(111)**

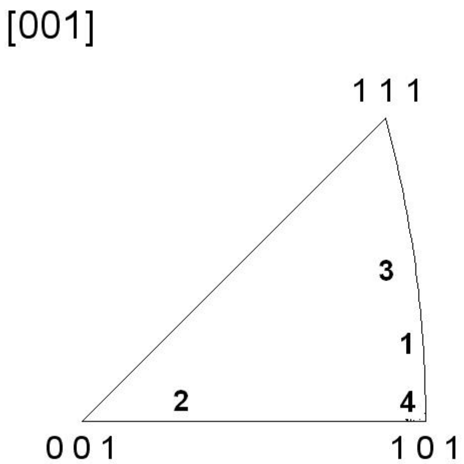


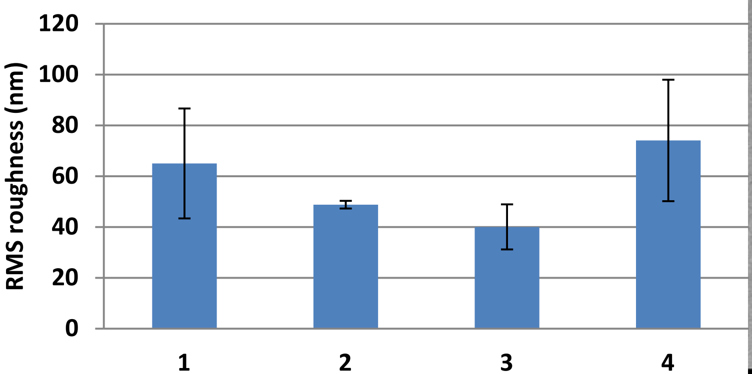



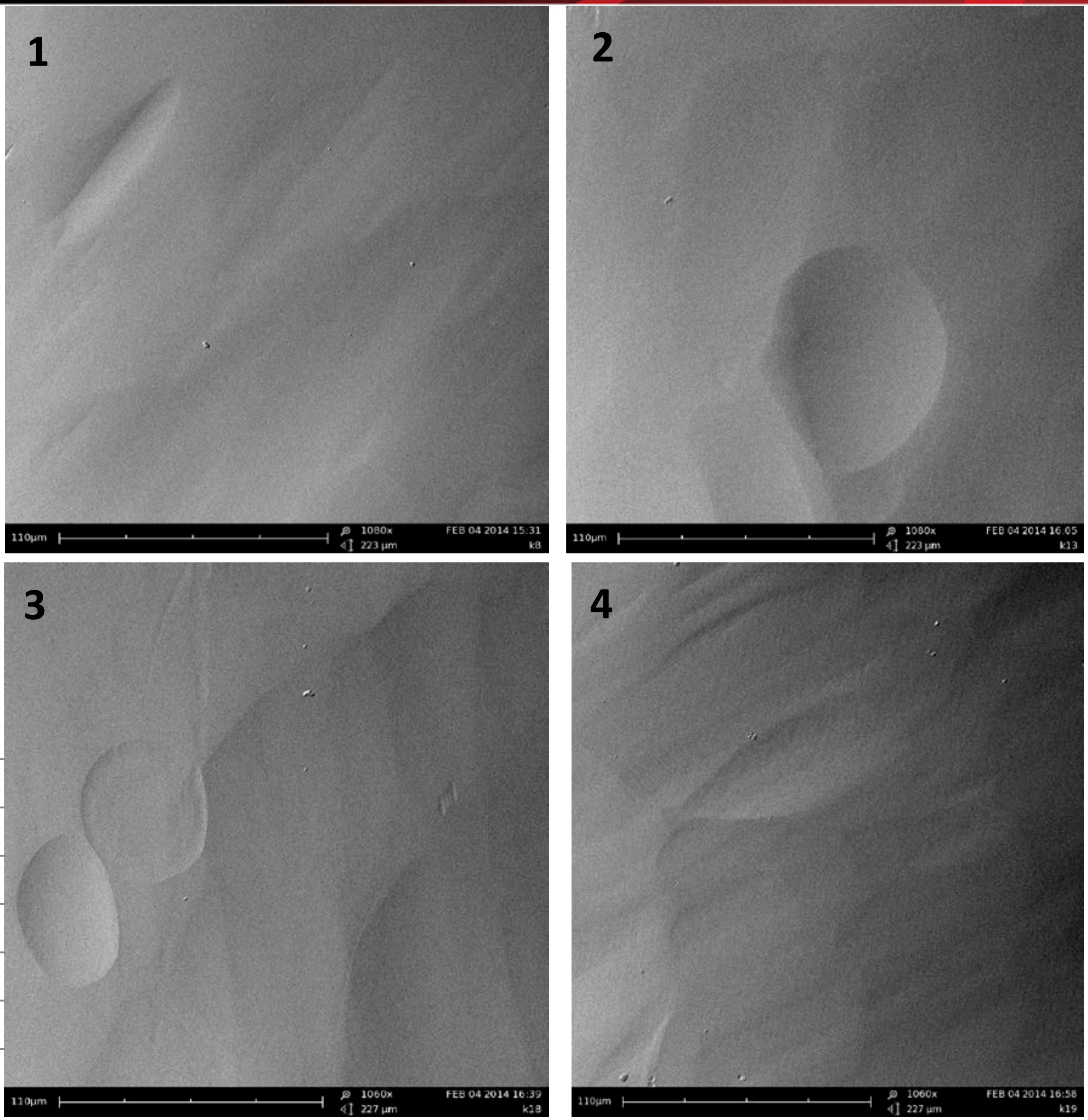



# SEM – BCP on single crystal niobium – very smooth

## 22°C, 90 min, x1000

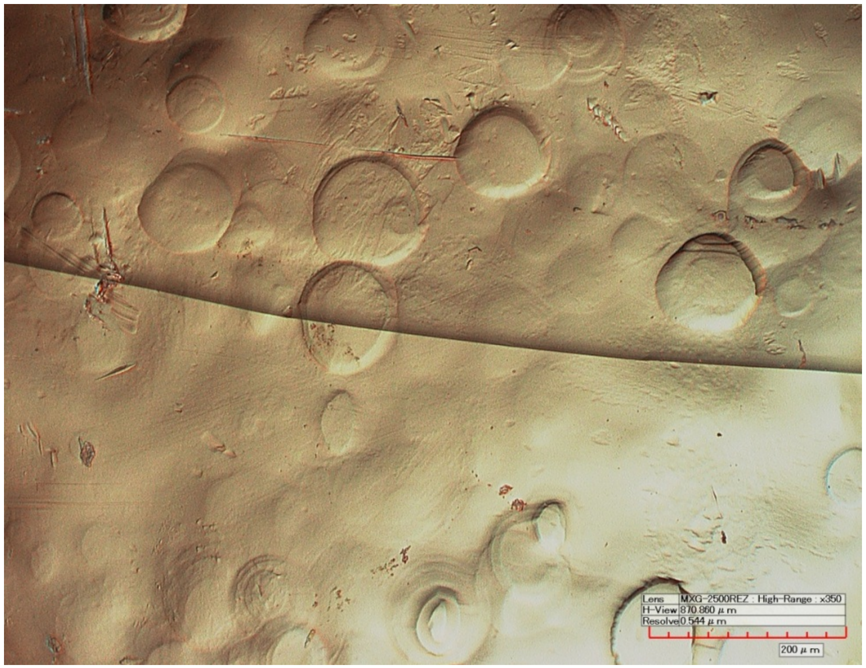


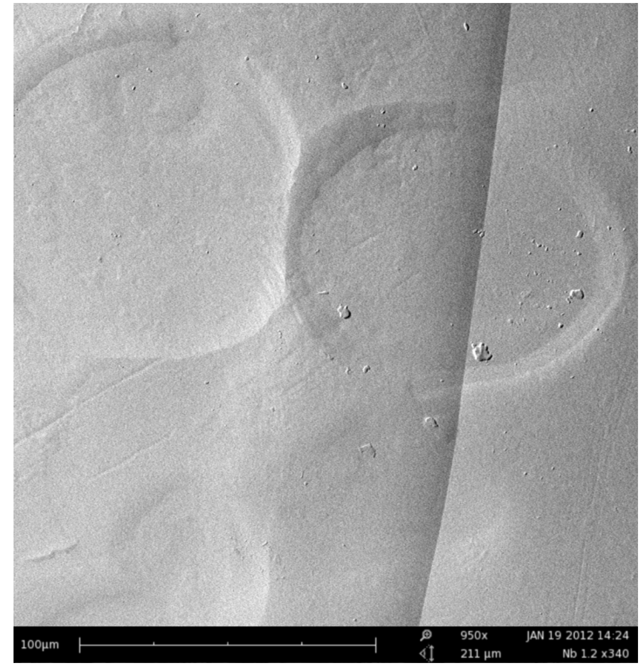



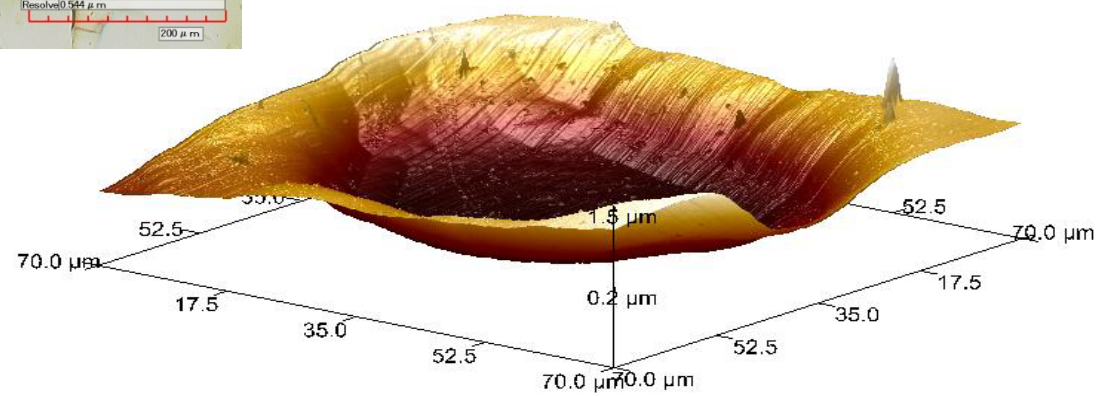



# Optical, SEM, AFM - Bubble prints, BCP on bi-crystal niobium

Used large grain material to distinguish bubble effects from grain effects





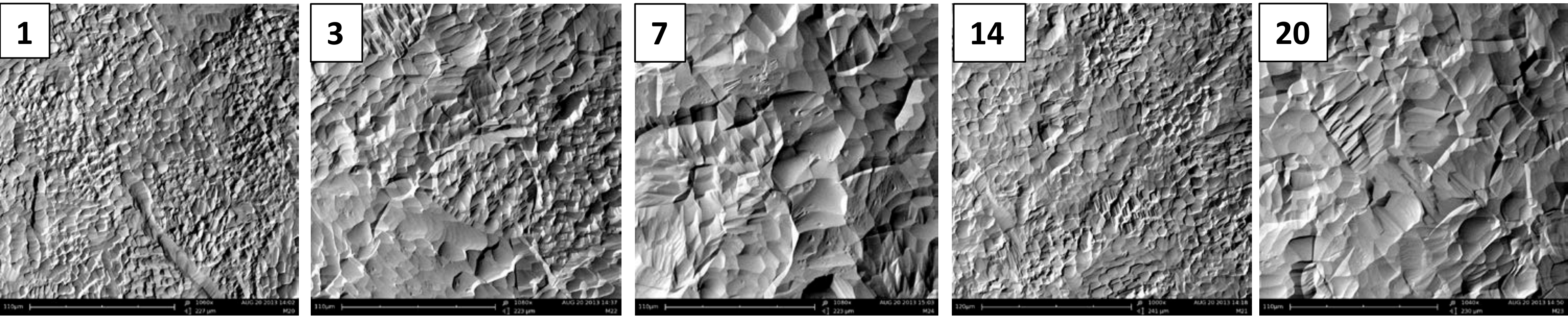

**BCP 20°C, 12 minutes**

**Print radius ~ 50 µm**

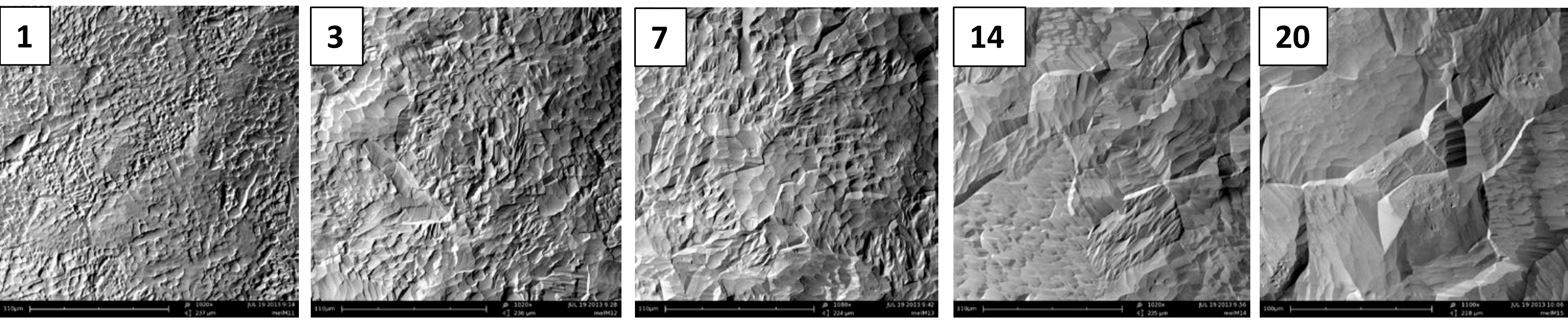
**Print depth ~ 1 µm**

# SEM – BCP on fine grain niobium, 10°C vs. 22°C

**10°C**

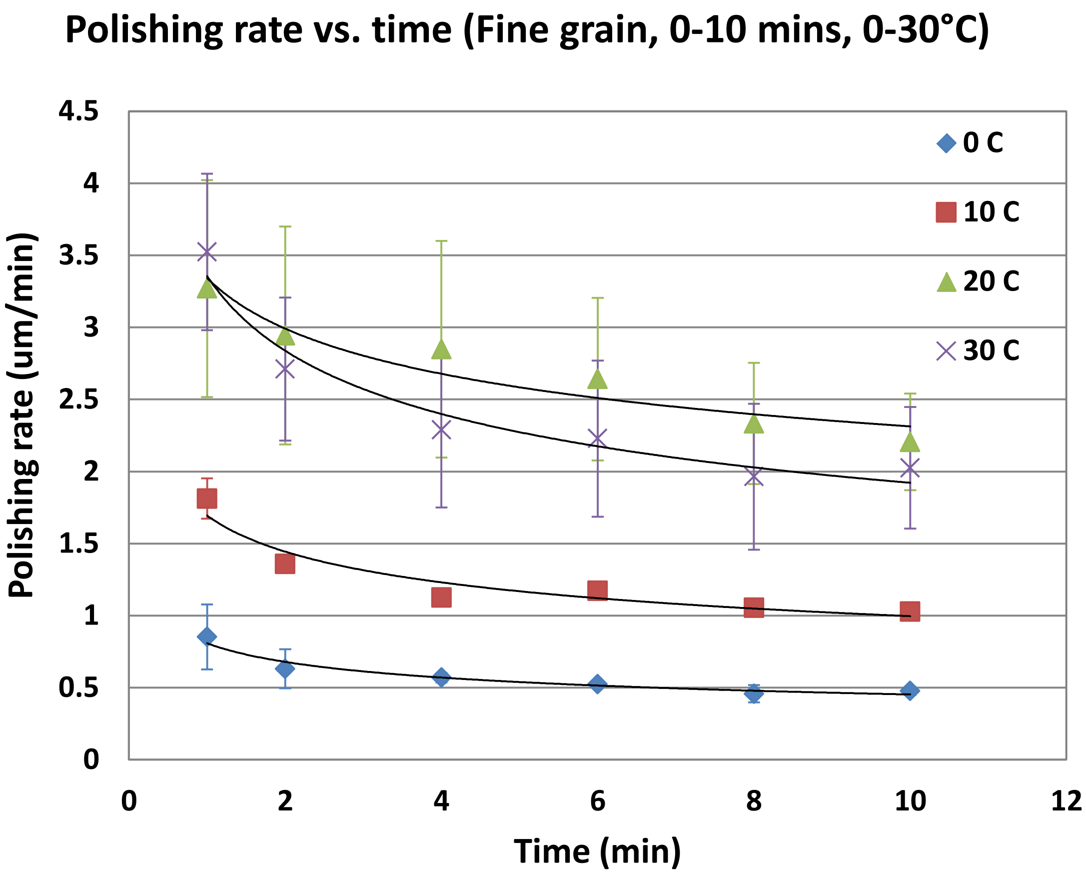



**22°C**




- **Shallow etching reveals fine features within individual grains. Deep etching smooth surface within individual grains, but causes facets, steps and edges.**
- **From 10 °C to 22 °C, higher temperature results in faster etching. Temperature does not change topography significantly.**

# BCP - polishing rate vs. time, different temperatures




High defect density in top mechanically disturbed surface produces higher initial reaction/removal rate.

Beware of using sample materials for short periods to predict extended removal rates.

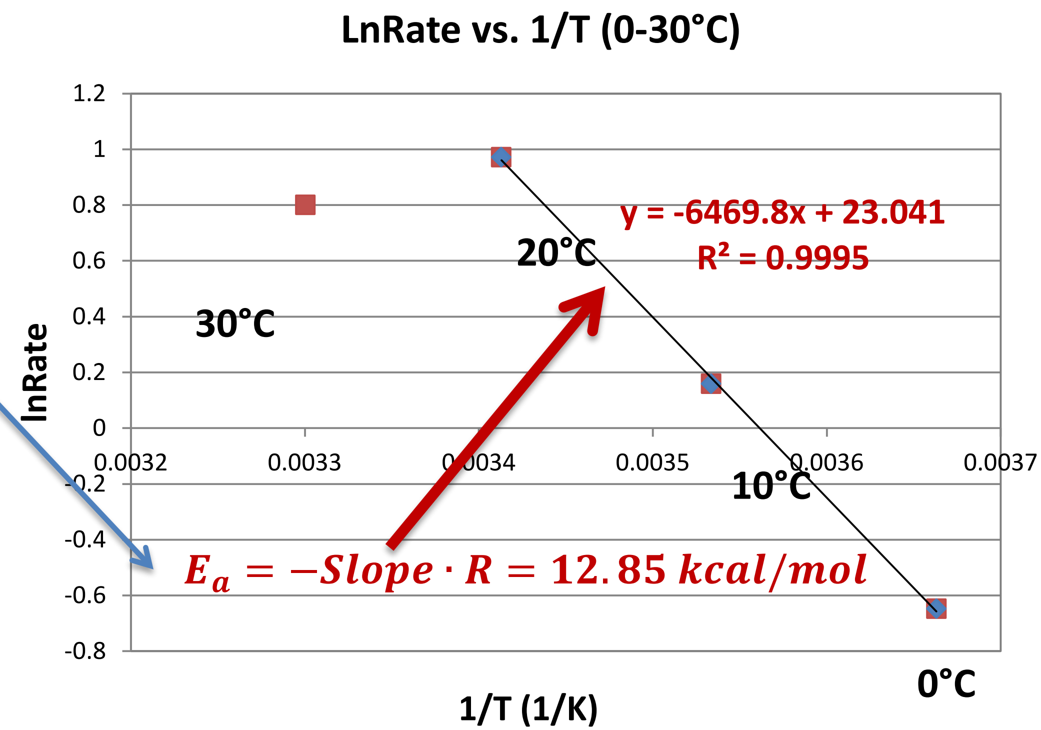
# Analysis of BCP Reaction Rate

**reaction rate constant $k$, activation energy $E_a$, temperature $T$**

$$Nb + 5HNO_3 + 5HF = H_2NbOF_5 + 5NO_2 \uparrow + 4H_2O$$

$$k = A\,exp(-E_a/RT)$$

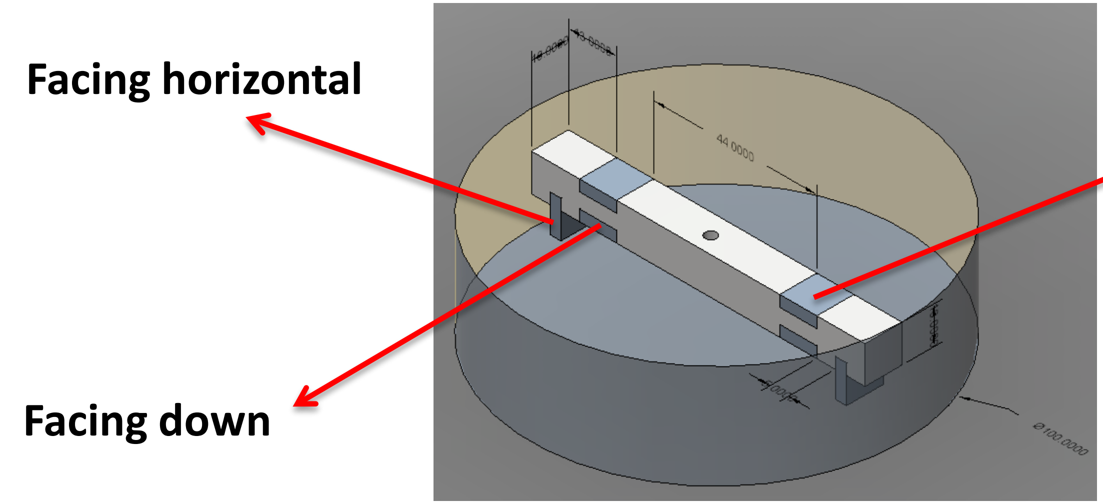
$$Rate = k \cdot [HNO_3]^a \cdot [HF]^b$$



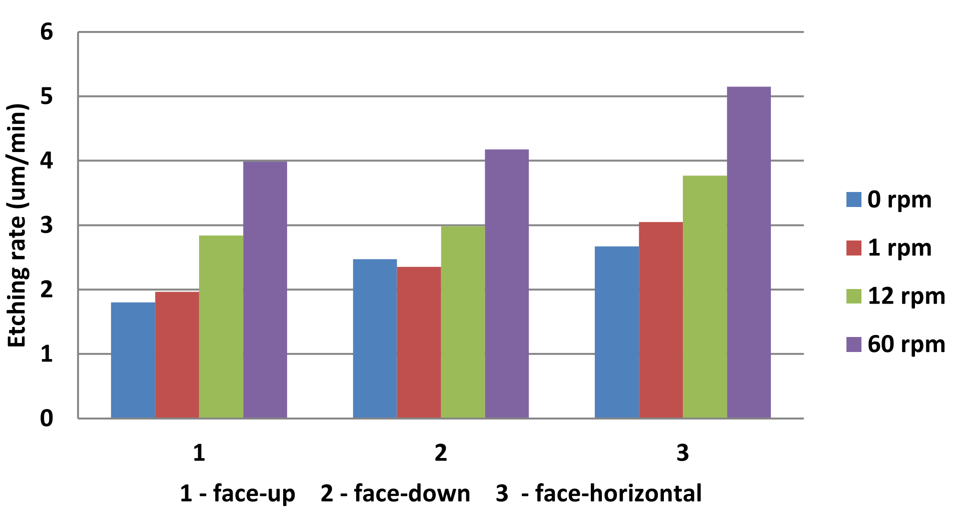

- **Chemical reaction control dominates at 0-20 °C, diffusion control takes over at higher temperature**

- **Activation energy relates to reaction mechanism:**
- **> 7 kcal/mol, chemical reaction controlled**
- **< 7 kcal/mol, diffusion controlled**

# BCP polishing rate vs. sample orientation and flow rate



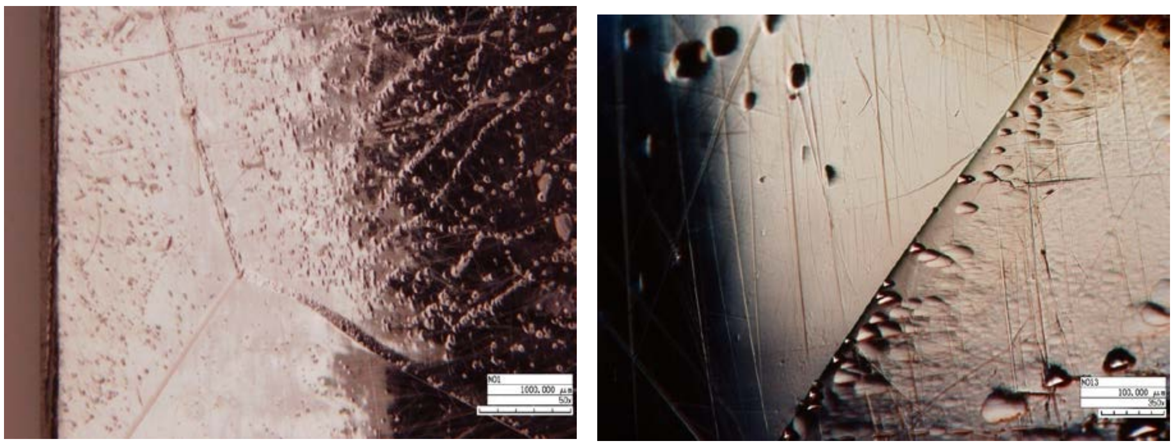

**Room temperature**
**6 minutes**
**Fine grain**




| | 1 rpm | 12 rpm | 60 rpm |
|---|---|---|---|
| Facing up | 2.3 ~ 3.4 mm/s | 27.6 ~ 40.2 mm/s | 138.2 ~ 201.1 mm/s |
| Facing down | 2.3 ~ 3.4 mm/s | 27.6 ~ 40.2 mm/s | 138.2 ~ 201.1 mm/s |
| Facing horizontal | 3.9 mm/s | 46.5 mm/s | 232.5 mm/s |

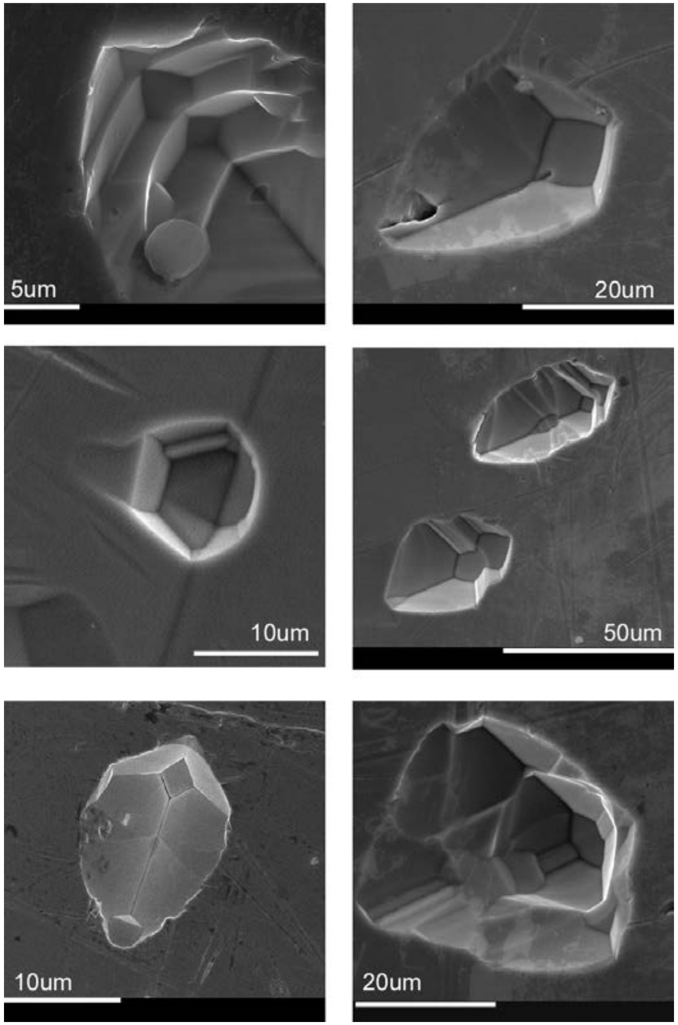
# Etch pits at crystallographic defect sites

BCP of large grain Nb samples reveals vulnerability highly faceted local etching induced by crystallographic defects – inadequate annealing



Optical imaging of cavity cut-out sample, showing pit density varies on distinct crystal grains.

[Study of Etching Pits in a Large-Grain Single Cell Bulk Niobium Cavity]



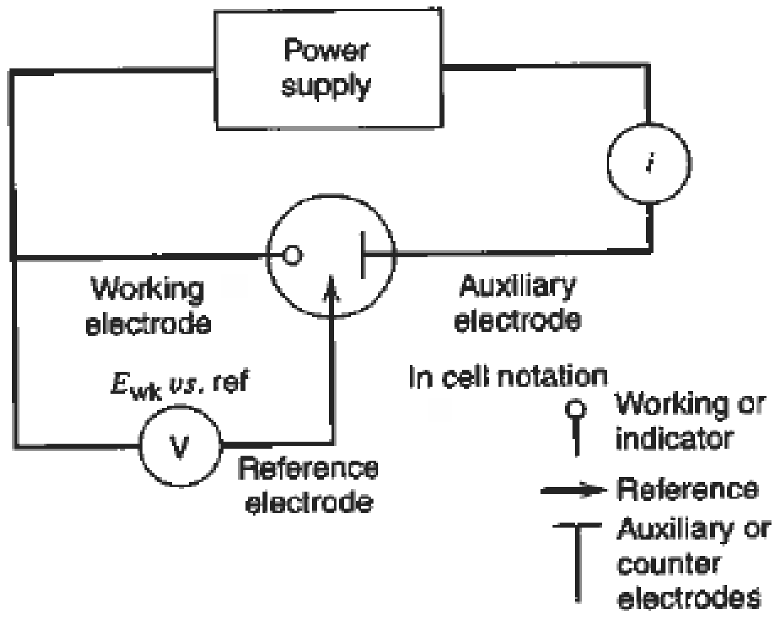

Etching pits with complex and symmetric geometry are observed in contrast to typical tetrahedral pits.

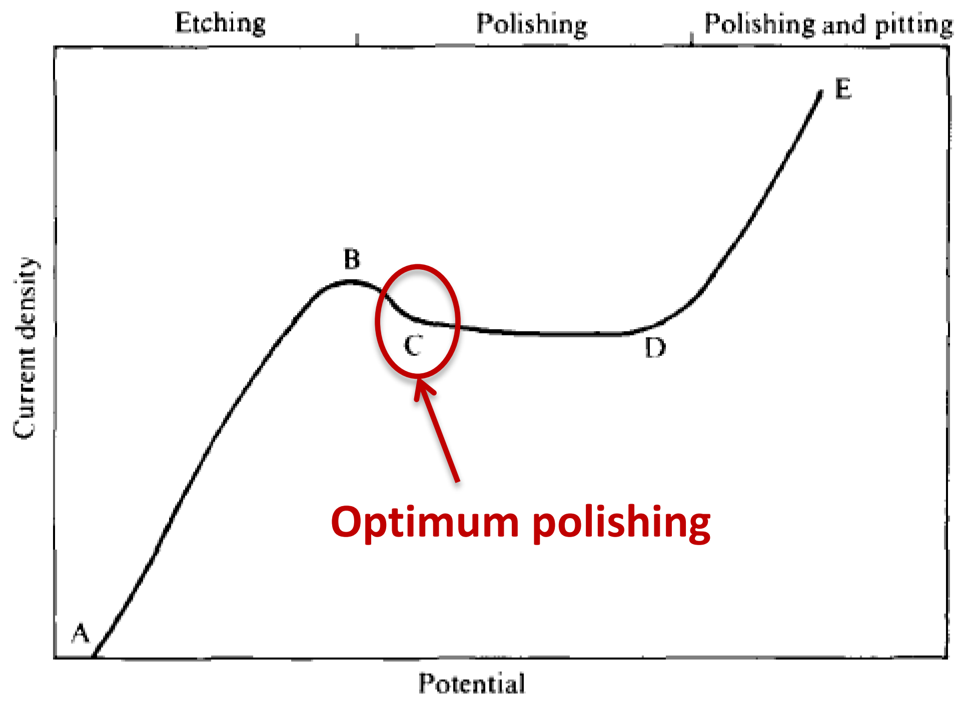
# BCP summary

- Preferential etching plays an important role in the genesis of BCP topography; gas evolution plays a secondary role by leaving dents.
- For polycrystalline niobium, the BCP topography depends on the total removal. Single crystal niobium showed smooth surface even after heavy BCP. Bi-crystal with little orientation difference did not show strong differential etching and grain boundary attack.
- Within 0-20 °C, the average removal rate increases with temperature and mass transfer through surface flow or sample orientation. Agitation also helps prevent gas accumulation on niobium surface.
- The roughness from BCP on FG Nb is inherent and fundamental.
- For cavity production, low temperature and surface flow are recommended to better control removal rate and avoid gas accumulation on niobium surface.

- "Genesis of topography by buffered chemical polishing of niobium", Liang Zhao, Charles E. Reece, Michael J. Kelley, Oral presentation at 7th SRF Materials Workshop, July, 2012, Jefferson Lab

# Electropolishing (EP)

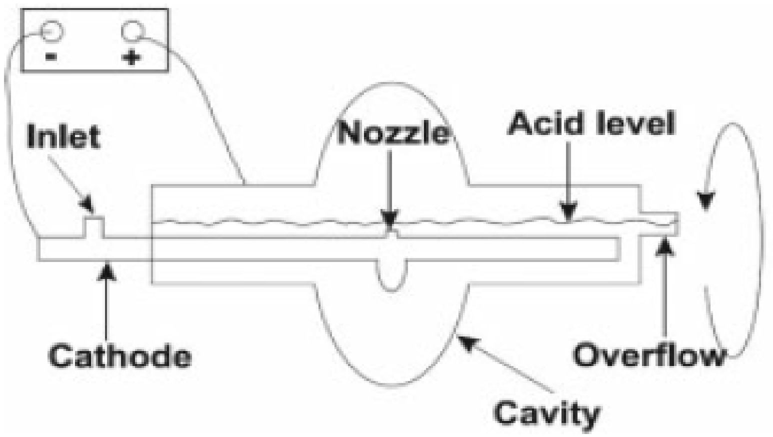



**Concentrated acid (sulfuric acid + hydrofluoric acid)**

- **Macro smoothing: geometrical leveling: removal rate proportional to solid angle of exposure**
- **Micro smoothing: exploit local near-surface concentration gradient of reactant to encourage fine leveling**

# EP in practice




**Typical cavity EP conditions:**

- **Current density** 10-50 mA/cm$^2$
- **Voltage** 8-16 V
- **Electrolyte temperature** 20-25 °C
- **Rotation speed** 1-2 rpm (1-4 cm/s)
- **Acid flow rate** ~1-3 L/min

- **Removal rate** 0.3-0.4 µm/min
- **Polishing time** 1-10 hours
- **RMS roughness** <0.5 µm

**Anode (Nb) reaction** $2Nb + 5SO_4^{2-} + 5H_2O \rightarrow Nb_2O_5 + 10H^+ + 5SO_4^{2-} + 10e^-$

**Cathode (Al) reaction** $2H^+ + 2e^- \rightarrow H_2 \uparrow$

# Basic Mechanisms of “Standard” Niobium “EP”

**Hui Tian**

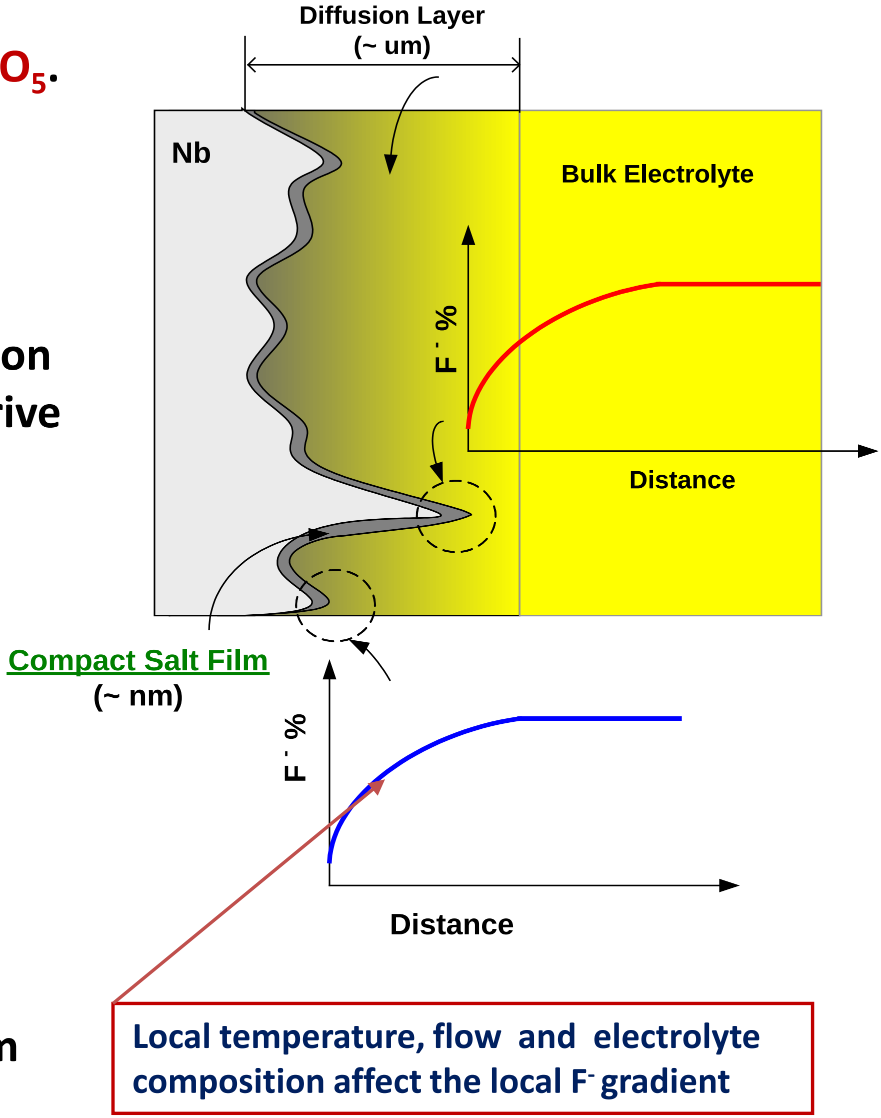
**Charles Reece**

# Past studies show that the diffusion-limited access of $F^-$ to the surface oxide produces "best" polishing

- **Anodization of Nb in $H_2SO_4$ forces growth of $Nb_2O_5$.**
- **$F^-$ dissolves $Nb_2O_5$.**
- **These competing processes result in sustained current flow and material removal.**

- **Above a certain anodization potential, the reaction rate plateaus, limited by how fast fresh $F^-$ can arrive at the surface. (*diffusion-limited*)**
- **In this steady-state case, this $Nb_2O_5$ layer is a "compact salt film" with specific resistivity.**
- **The thickness of the salt film increases with applied potential, although the steady-state current does not change (*plateau*).**

- **In the diffusion-limited circumstance, material removal is blind to crystallography (avoids crystallographic *etching*).**
- **The diffusion coefficient *sets a scale* for optimum leveling effects**



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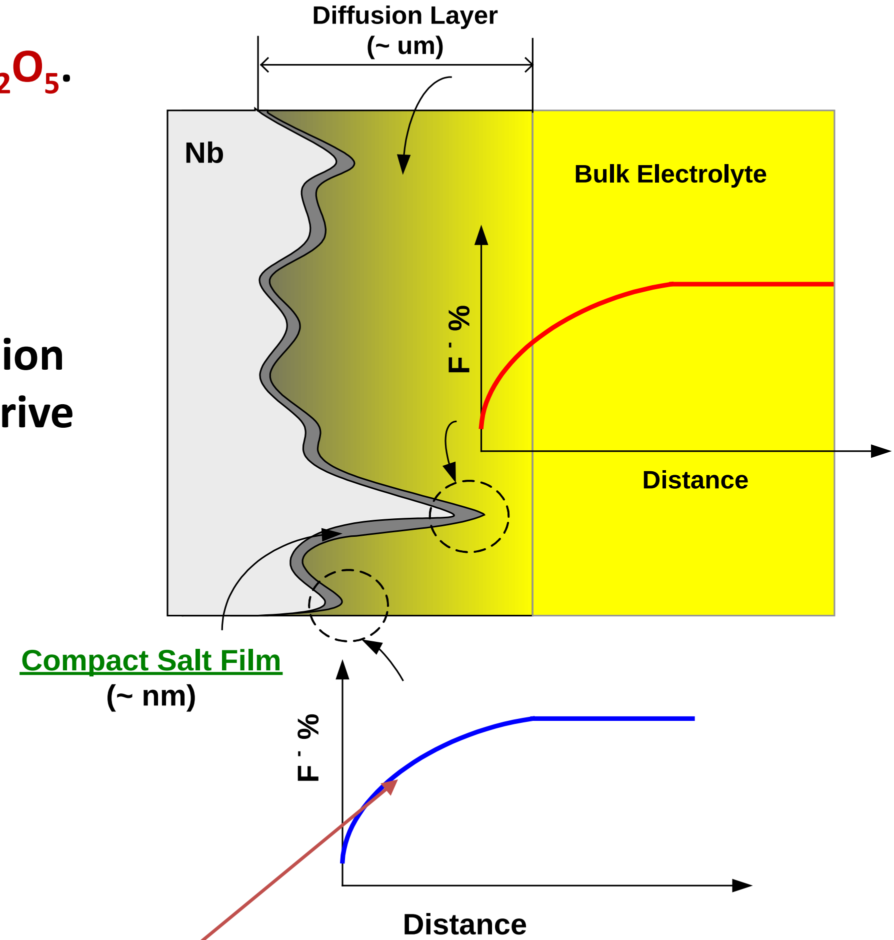


Local temperature, flow and electrolyte composition affect the local $F^-$ gradient

So we want to understand this diffusion coefficient

# Current-limited plateau is the result of a "mass-transport" limitation

Mass transport may occur by three mechanisms in an electrochemical cell. It is described by the Nernst-Planck equation, written for one–dimensional mass transfer along the x-axis as:

$$J_i(x) = -D_i \frac{\partial C_i(x)}{\partial x} - \frac{z_i F}{RT} D_i C_i \frac{\partial \phi(x)}{\partial x} + C_i \upsilon(x)$$

**Diffusion** - movement of species ( $F^-$ ) driven by a concentration gradient

**Migration** - movement of ions driven by a gradient of electrical potential

**Convection** - *natural* convection driven by density gradient and *forced* convection (stirring, vibration, circulation)

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$$J_i(x) = -D_i \frac{\partial C_i(x)}{\partial x} - \frac{z_i F}{RT} D_i C_i \frac{\partial \phi(x)}{\partial x} + C_i v(x)$$

In ideally static case, only diffusion matters.

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One may learn about $D_i$ by deliberately controlling convection.

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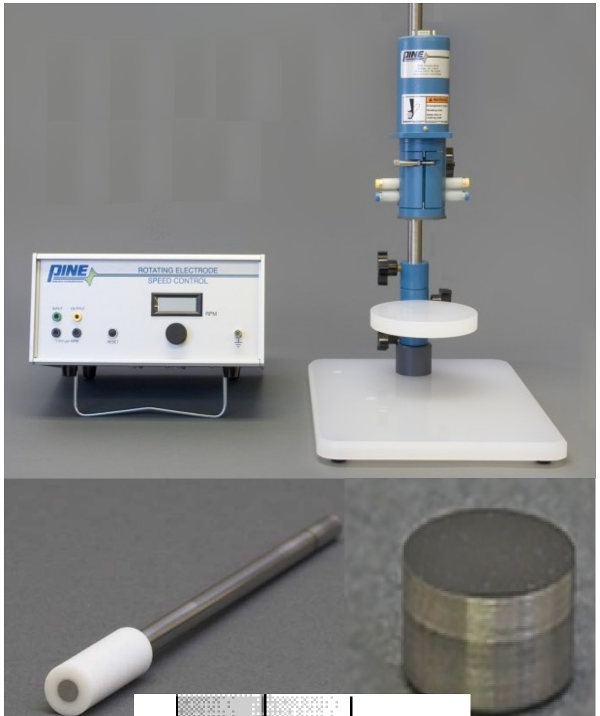
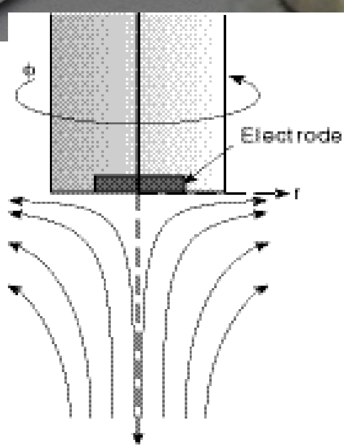
# Determination of the limited species diffusion coefficient by rotating disk electrode (RDE)




**RDE : creates a defined solution flow pattern in which the mass transport of species is almost completely due to convection. By solving the convection equation with the boundary condition, the Levich equation can be used to describe the relationship of limiting current to the physical properties of electrolyte bath - diffusion coefficient (*D*) and kinematic viscosity (ν).**

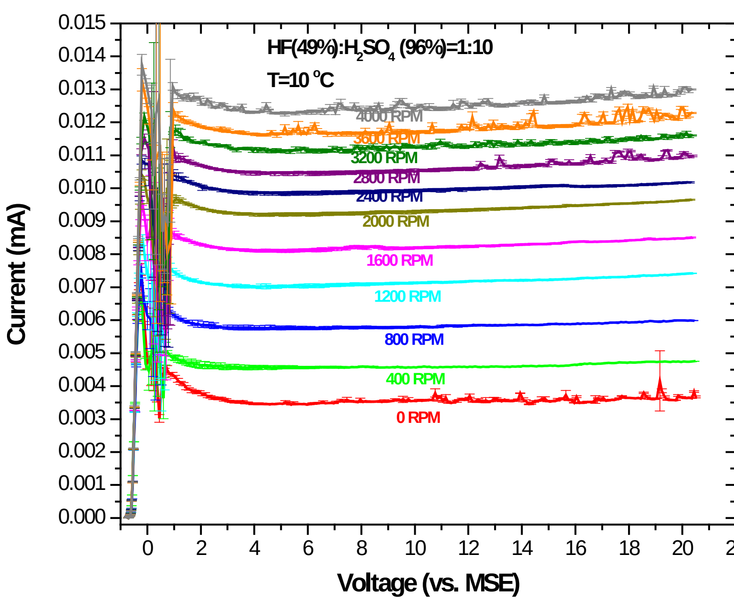
## Levich equation

$$J = 0.62nFD^{0.67}\upsilon^{-0.166}c\omega^{0.5}$$

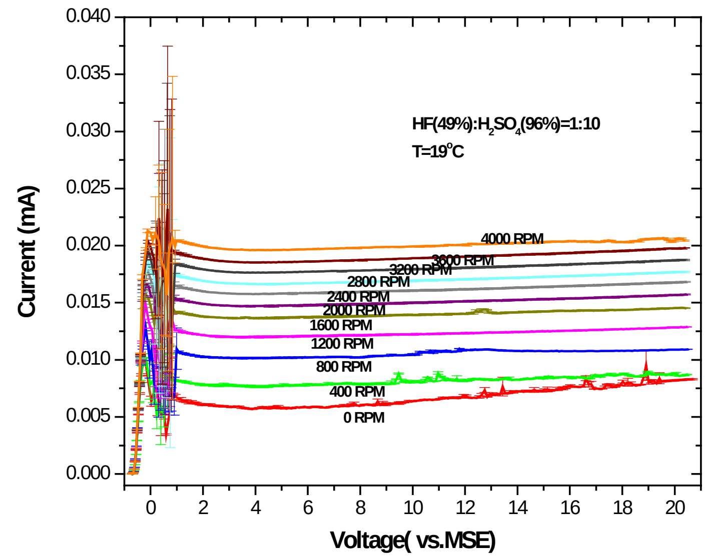
$$slope(J\ vs.\ \omega^{0.5}) = 0.62nFD^{0.67}\upsilon^{-0.166}c$$

$\upsilon$ : *kinematic vis cos ity*
$\omega$ : *rotation speed of the electrode*
*c: concentration of active species*

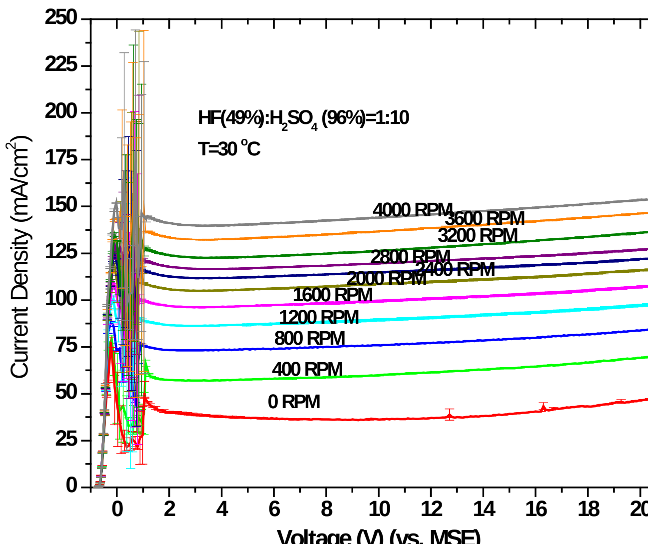
# I-V curves of Nb electropolishing at different temperatures with RDE



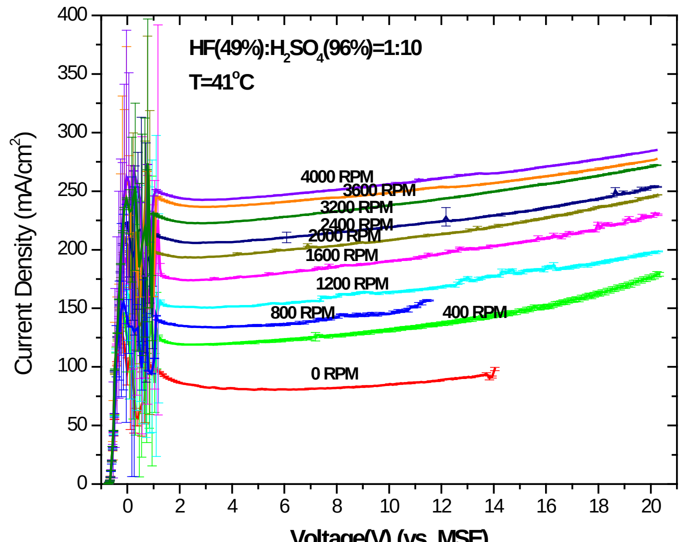

10 °C




19 °C



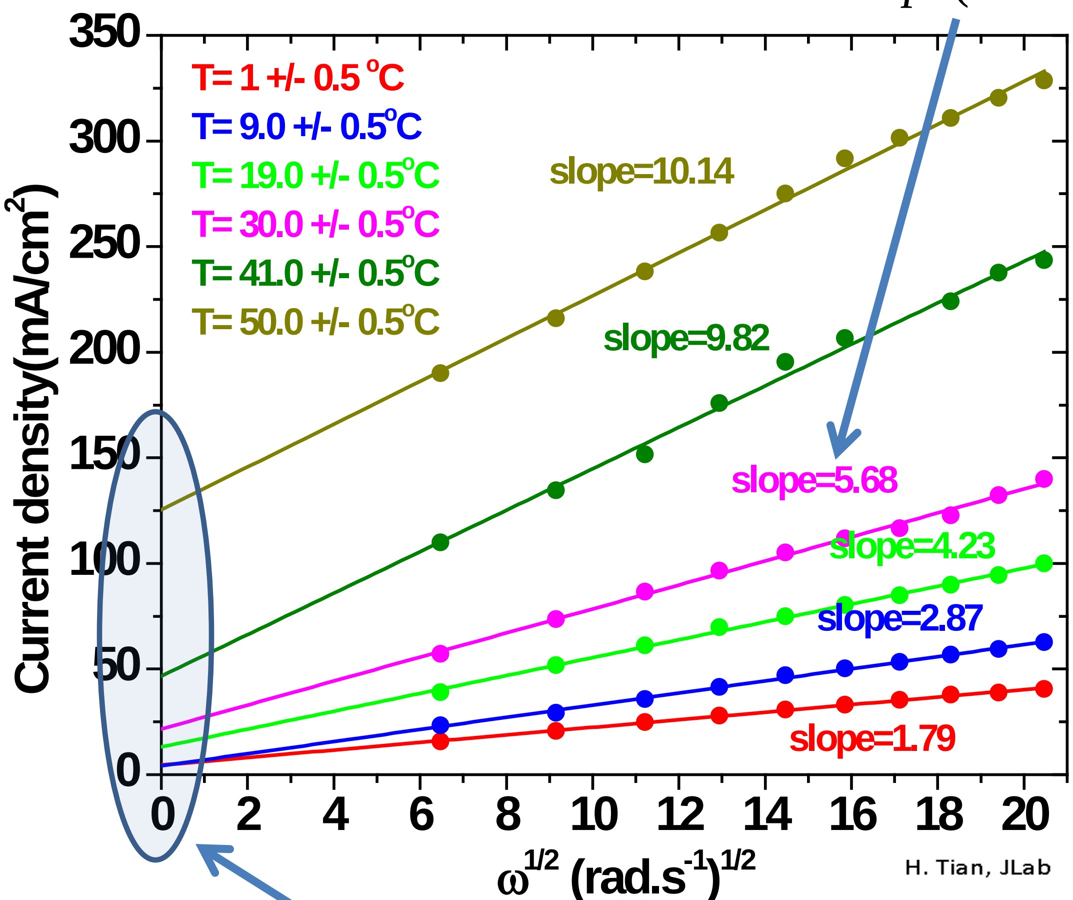

30 °C




41 °C

# RDE measurements

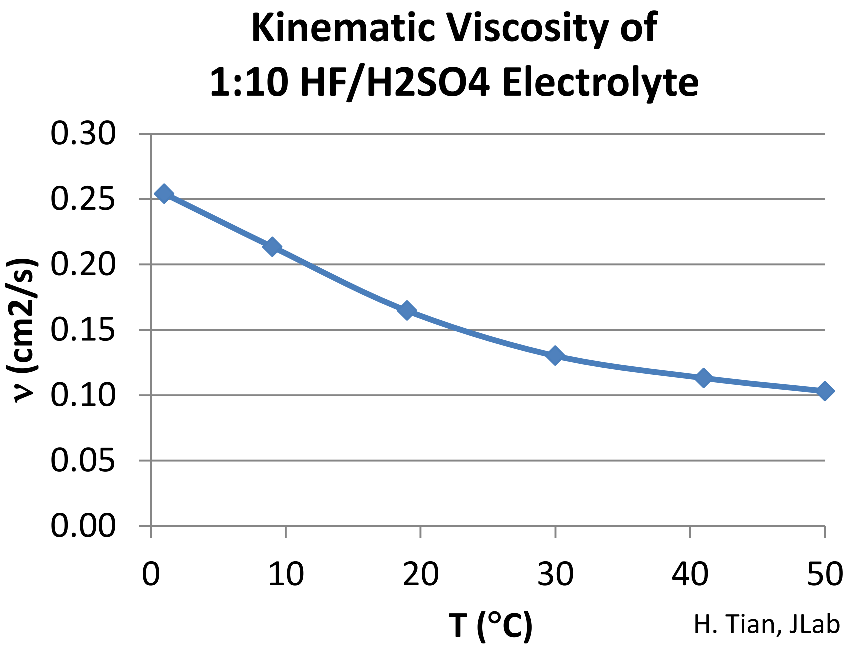
$$slope(J\ vs.\ \omega^{0.5}) = 0.62nFD^{0.67}\upsilon^{-0.166}c$$



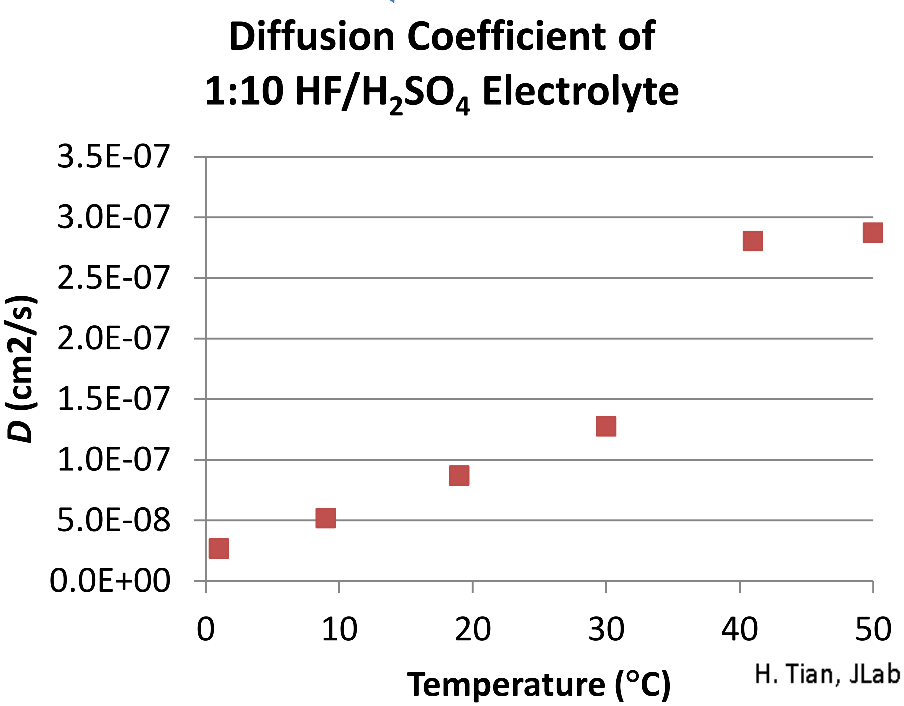

Excellent linear fit provides definitive evidence of a diffusion-limited process. Knowing ν and *c* yields *D*.

$c_F = 2.67\times10^{-3}$ M/cm$^3$

Strong evidence for temperature-dependent electrochemical **etching** in parallel with the diffusion-limited process. For analysis, we must separate these current contributions.




RDE measurements
+ viscosity measurements
+ concentration
determine the Diffusion coefficient

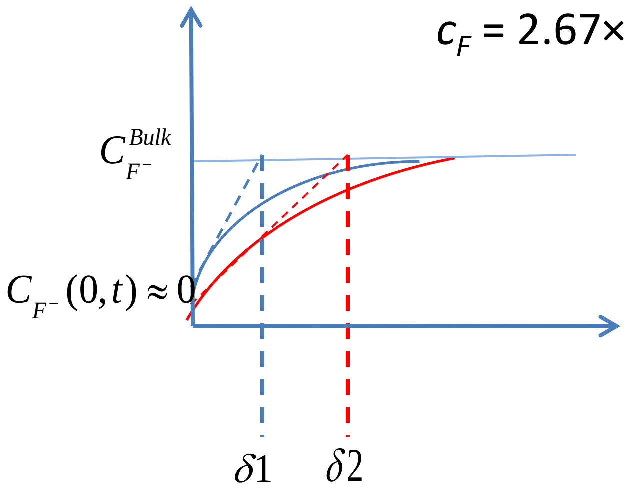



Measured using a
*Brookfield DV-II pro viscometer*

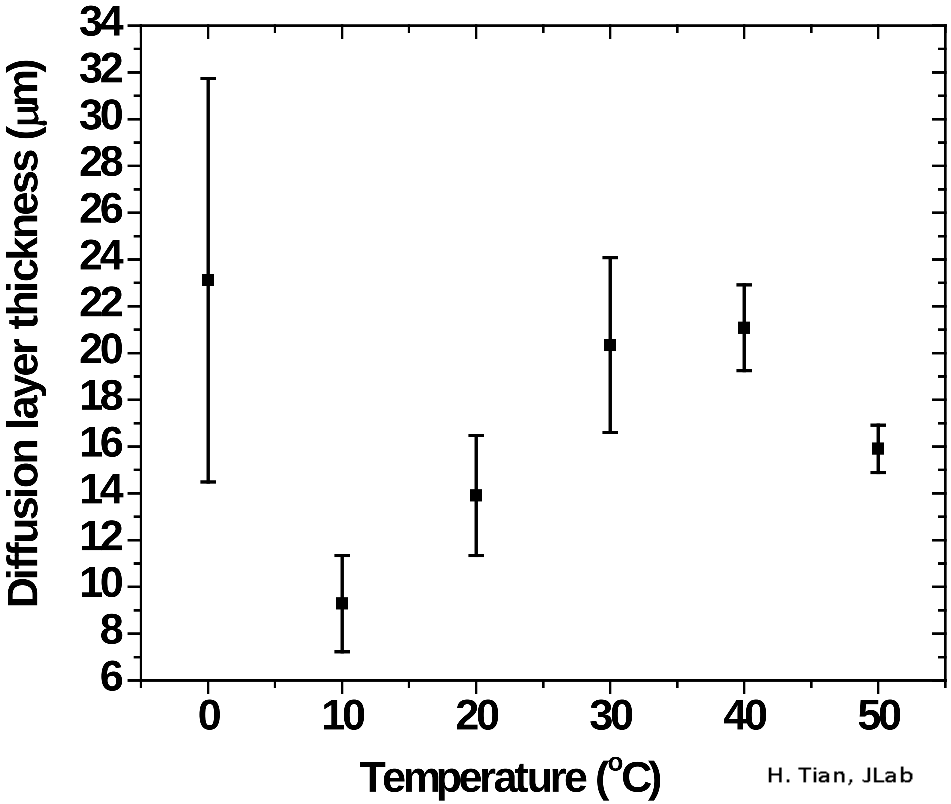
$c_F = 2.67\times10^{-3}$ M/cm$^3$

# Estimation of diffusion layer thickness in 1:10 $HF/H_2SO_4$ Electrolyte at different temperatures

$c_F = 2.67\times10^{-3}$ M/cm³



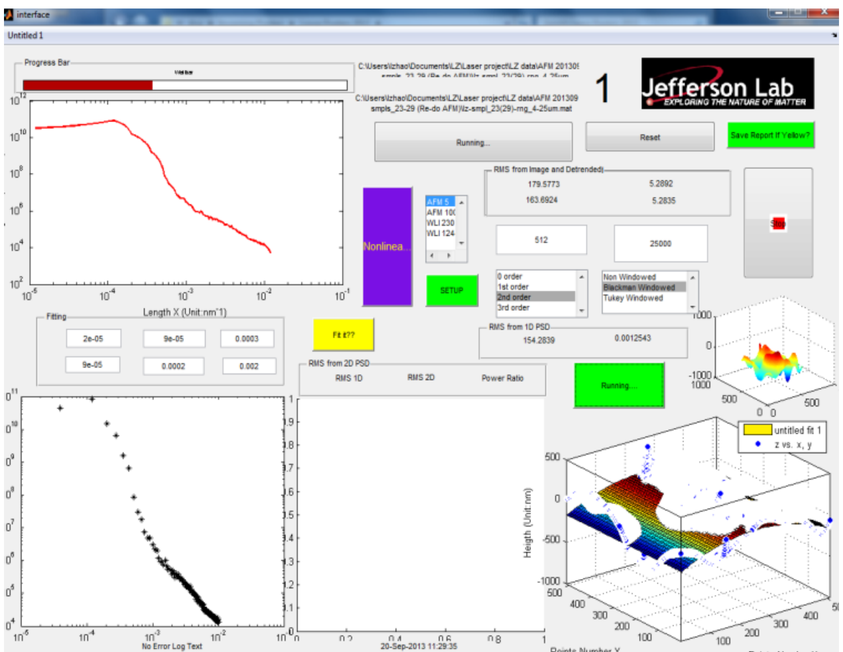

$$J = n \times F \times D \times \frac{c}{\delta}$$




There exists a $F^-$ concentration gradient within the **10-20 µm** away from the surface.

On this scale, peaks are dissolved much faster than valleys.

# Topography characterization



Chen Xu

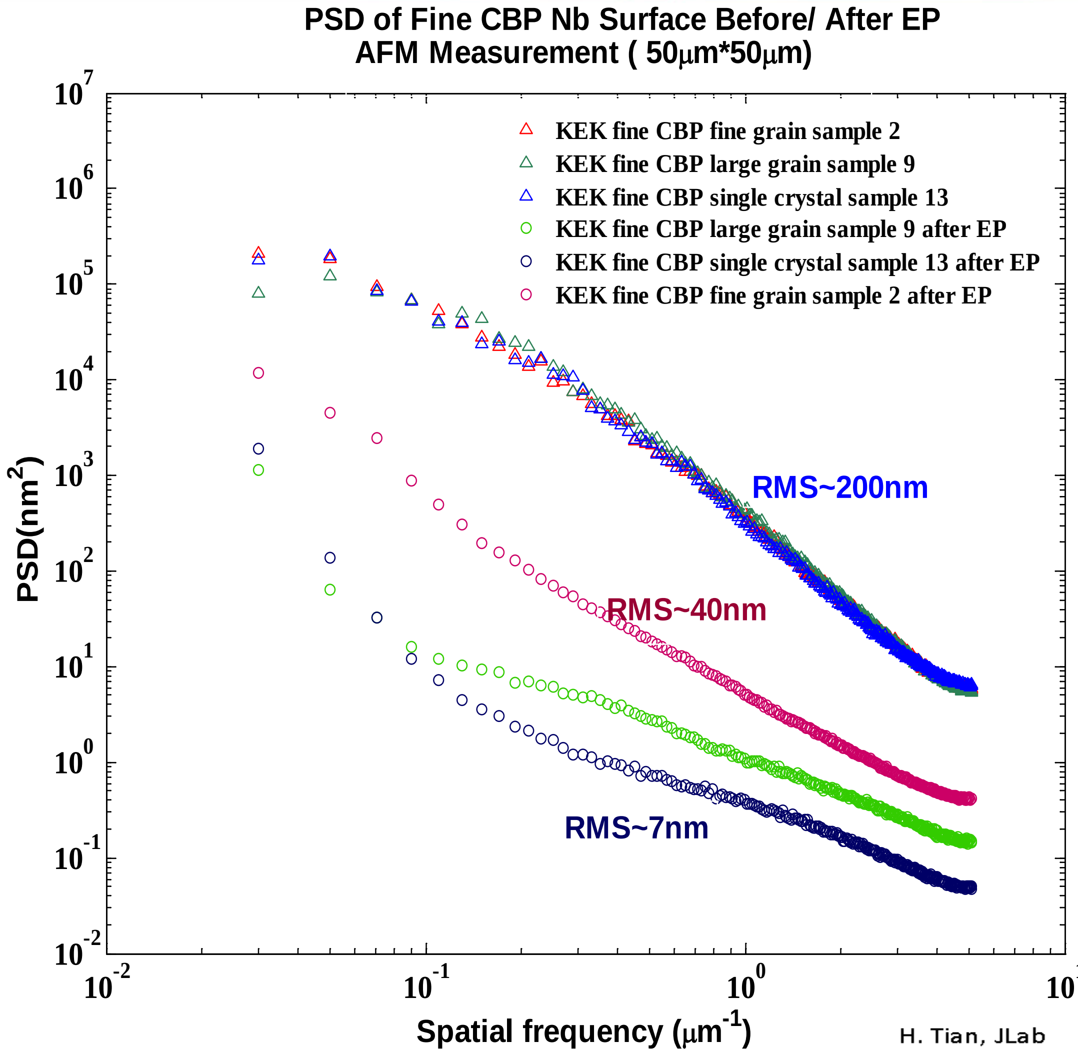
- Hirox optical microscope, Phenom SEM
- Atomic force microscopy (AFM)
  - Tapping mode
  - RMS roughness ($R_q$), height variation of peaks/valleys
- Power spectral density (PSD) of surface height
  - Customized program
  - 2nd order detrending
  - Blackman window
  - Width variation of peaks/valleys
  - Quantitatively describe sharp features

# Not all Nb "EPs" the same

With "standard"1:10 $HF/H_2SO_4$ Electrolyte at 30°C Nb crystallography affects the polishing effectiveness.

With identical starting topography from CBP, given identical 100 min "EP" at 30°C, single-crystal material was significantly smoother.

Evidence for a significant etching activity at 30°C

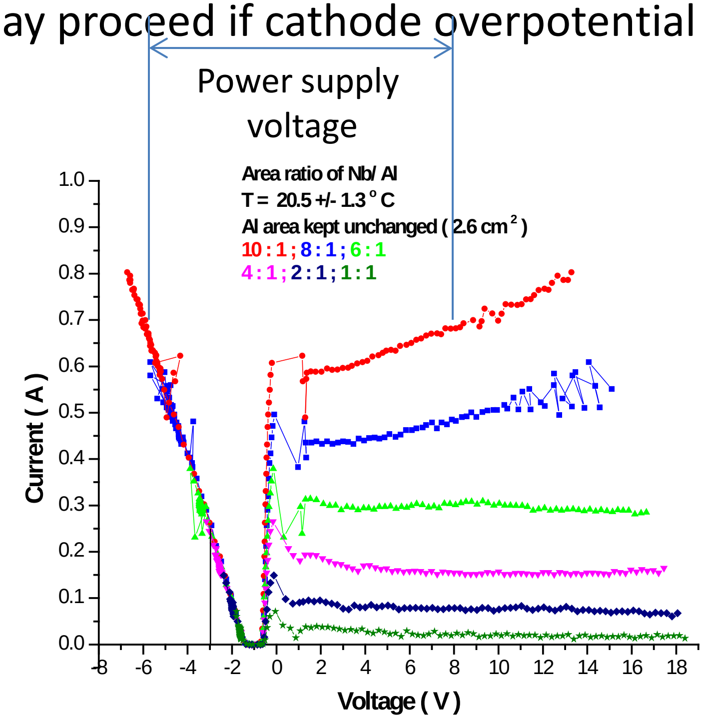


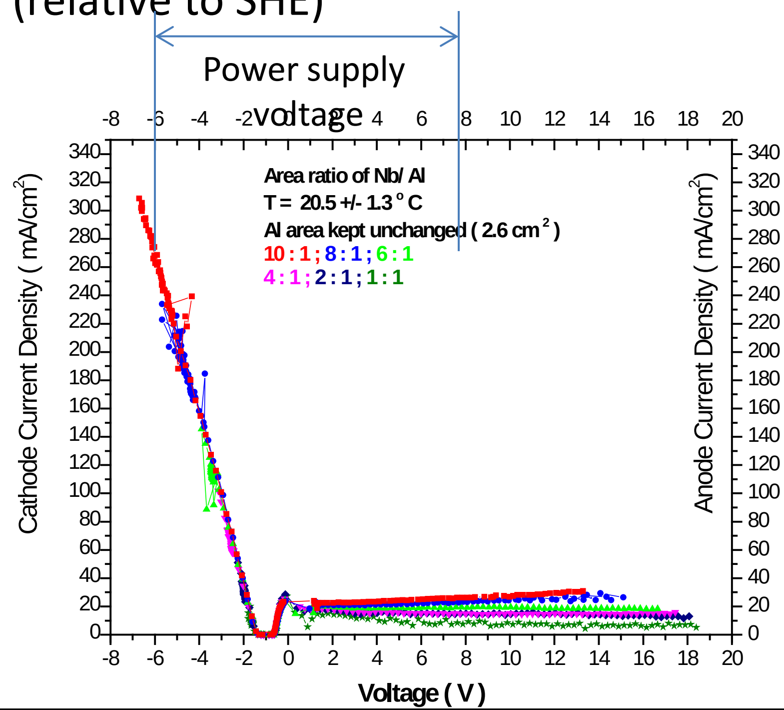
# Avoid sulfur production at the cathode

- Most commercial electropolishing applications attempt to maximize the surface area of the cathode to avoid process complications (cost).
- In contrast to this, typical horizontal cavity EP circumstances have cathode:anode active area ratio of 1:10.
- Result is high current density on cathode and resulting high overpotential on the cathode necessary to drive the current.

**$SO_4^{2-} + 8\,H^+ + 6\,e^- \rightarrow S + 4\,H_2O$**

may proceed if cathode overpotential is >0.45 V (relative to SHE)




H. Tian, JLab

# 1:10 HF/$H_2SO_4$ Electrolyte with Nb

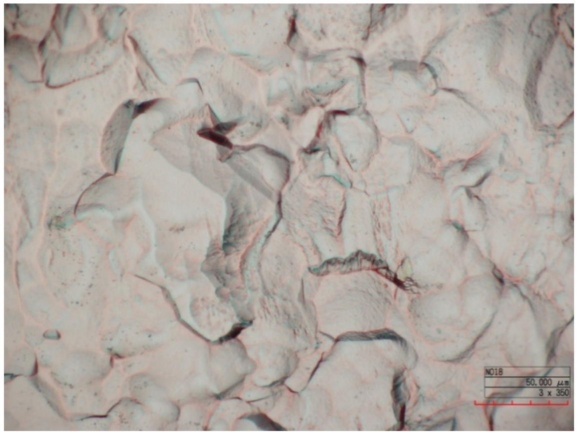
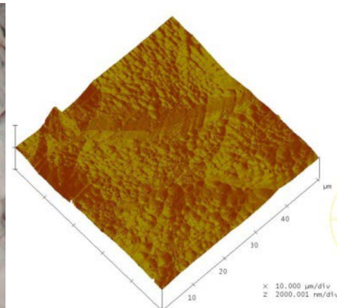
## If the objective is maximally smooth surfaces:

**Implications:**

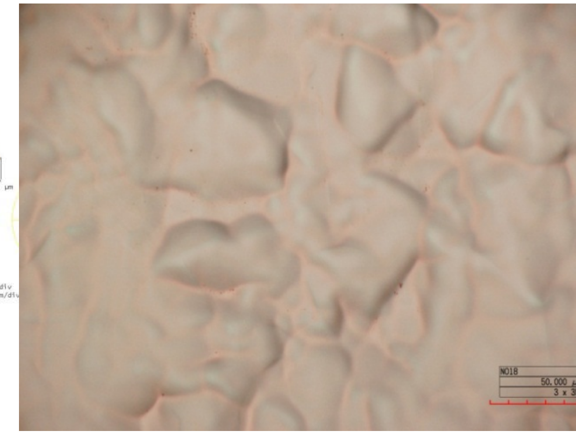
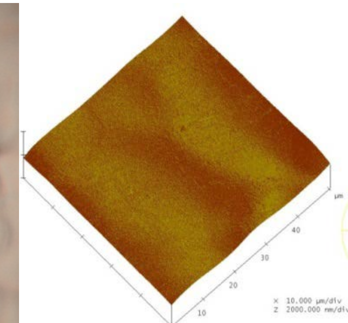
- We should expect the best micropolishing for topographic features smaller than ~ 15 µm, so start with surfaces that are consistently smooth to this scale: CBP?
- This process we call "EP" also has a temperature-dependent etching  process present, even below 20°C.  So, minimize the temperature as much as is practical (process time goes up).
- Reduce sulfur production at the cathode by minimizing cathode current density and improving the reaction kinetics for hydrolysis at the cathode→ maximize cathode surface area

# Optical, AFM - EP topography vs. surface flow rate

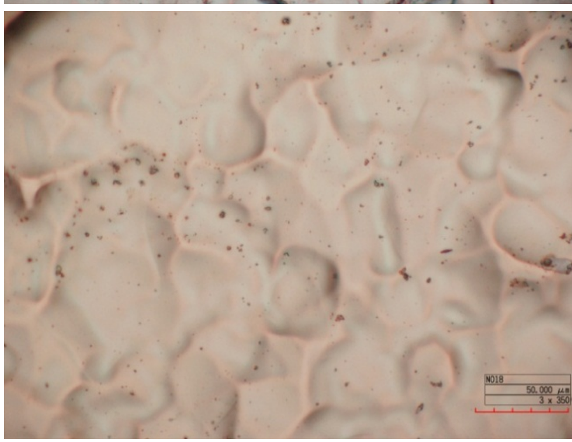
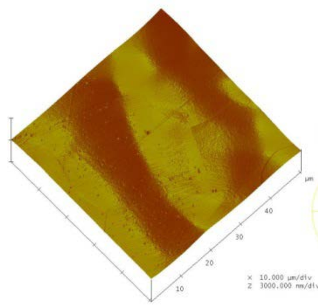
## 14 V, 20-22 °C, 90 minutes, ~40 µm removed

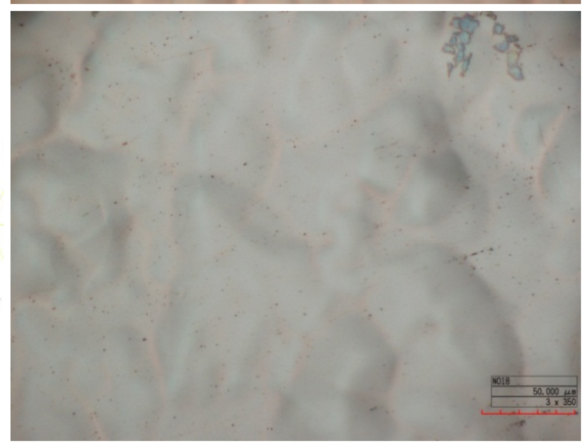
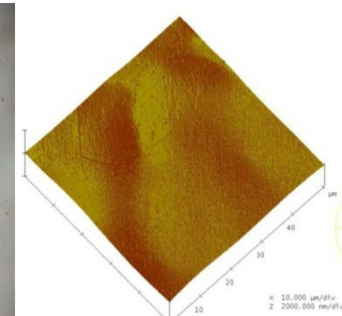
BCP

0.7 cm/s EP

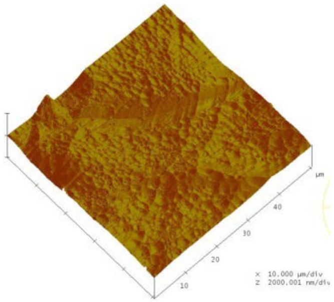
Static EP

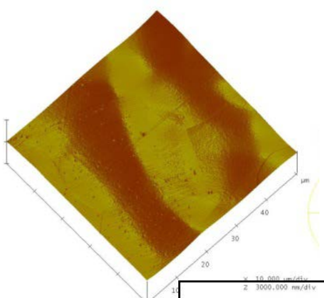
3.7 cm/s EP

# AFM, PSD - EP topography vs. surface flow rate

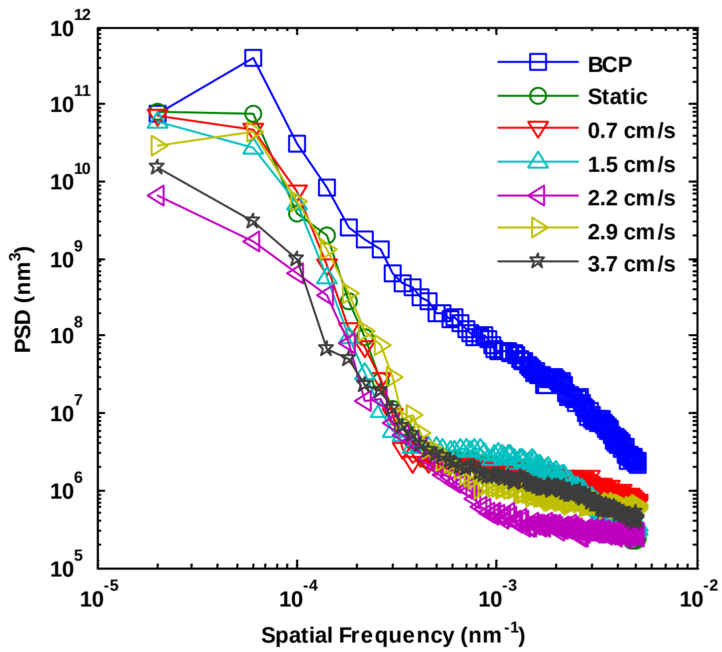
## 14 V, 20-22 °C, 90 minutes, ~40 μm removed

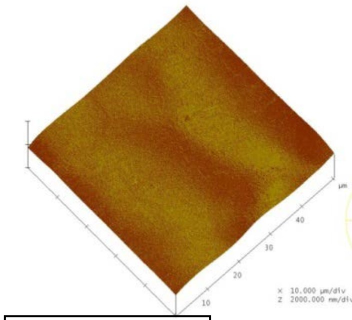


BCP

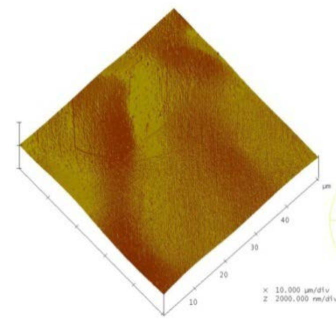


Static EP



0.7 cm/s EP



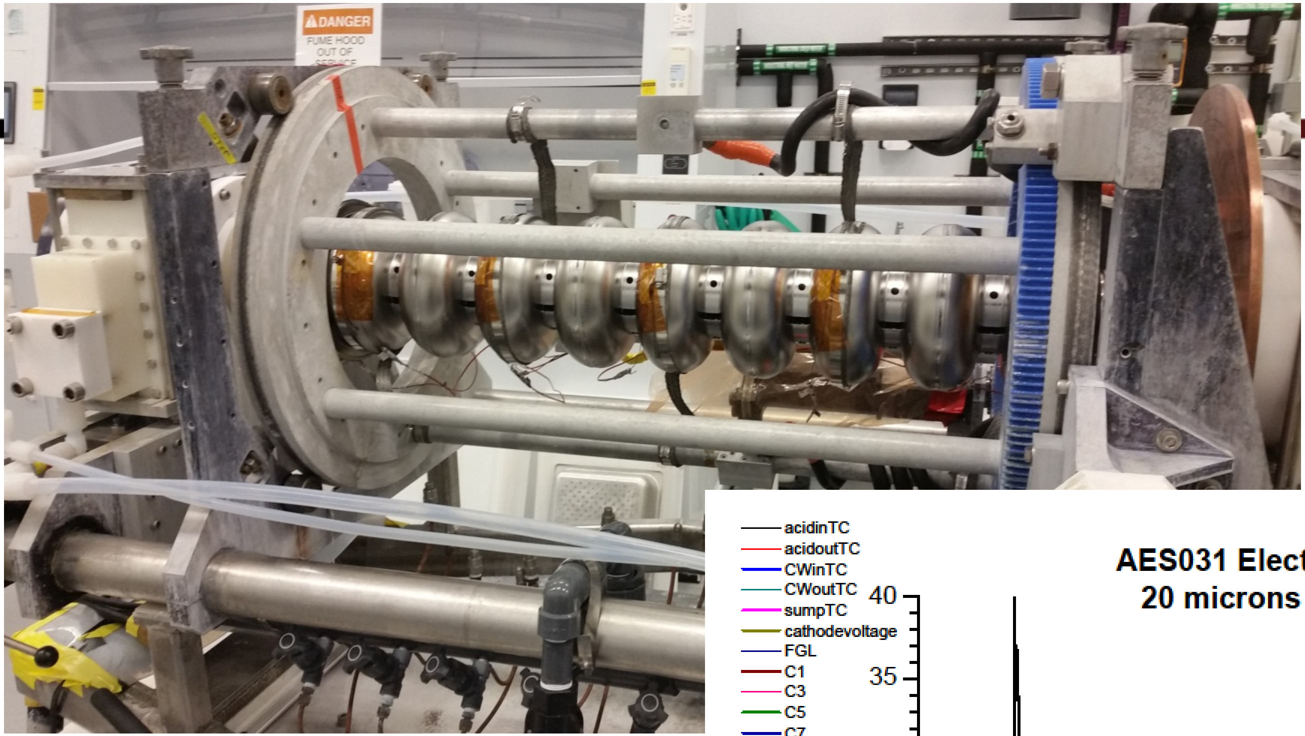
3.7 cm/s EP

# EP Flow-rate Summary

- Within 0-3.7 cm/s range, varying the surface flow rate on niobium shows no clear influence on polishing rate and topography. RMS roughness may be slightly smaller at higher flow rate at micro scale.
- Surface flow is still recommend for cavity production because of possible improvement on micro scale roughness and temperature distribution in the electrolyte.

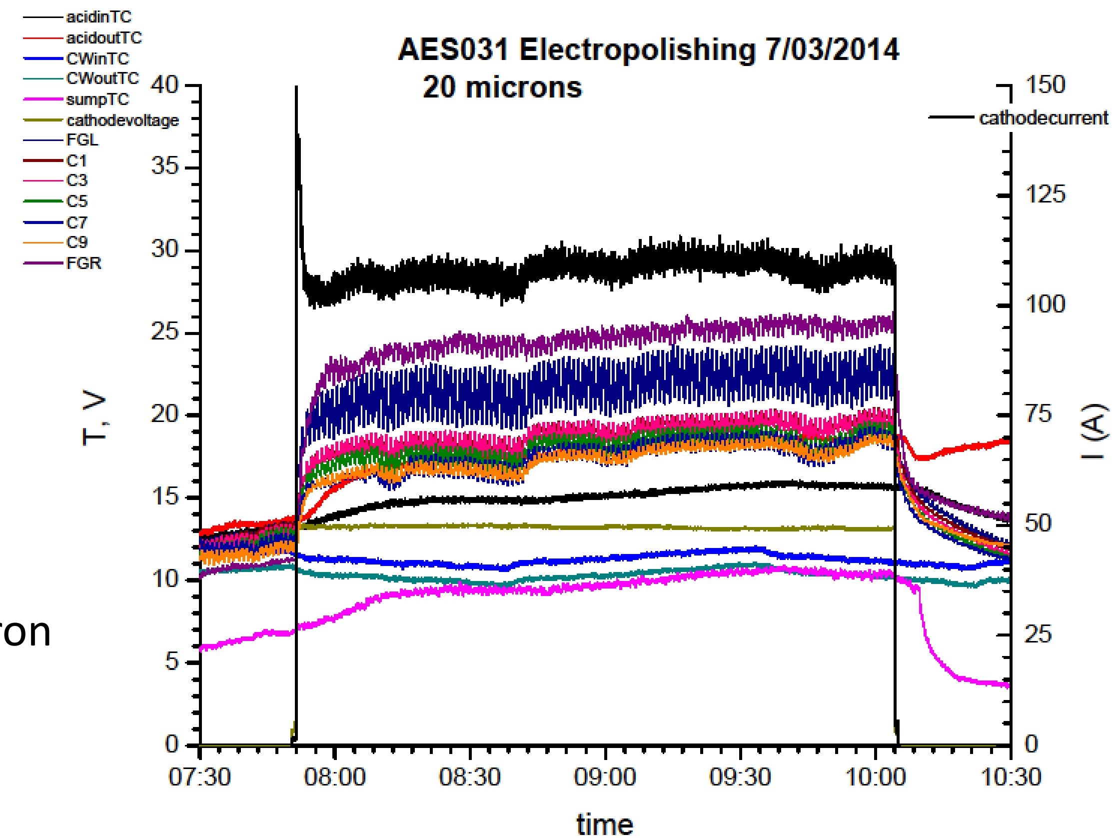
- "Effect of Surface Flow on Topography in Niobium Electropolishing", L. Zhao, M. Kelley, C. Reece, TUP106, 11th Particle Accelerator Conference Proceedings, Mar 28 – Apr 1, 2011, New York

# Cavity Processed for LCLS-II High-$Q_0$ R&D




AES031 receives bulk EP

AES031 final 20 of 120 micron bulk EP



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| | |
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V.G. Levich, *Physicochemical Hydrodynamics*, Prentice-Hall, New York, 1962
H. Tian, Ph.D. Dissertation, Dept. of Applied Science, College of William and Mary, (2008).
C. Xu, Ph.D. Dissertation, Dept. of Applied Science, College of William and Mary, (2013).
L. Zhao, Ph.D. Dissertation, Dept. of Applied Science, College of William and Mary, (2014).

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