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Basic Mechanisms of “Standard” Niobium “EP”

Tutorial in spirit, see published literature for more precise use of language.

Aim

We continue to **deepen our understanding** of what “EP” does to niobium surfaces and apply that knowledge to optimize the process.

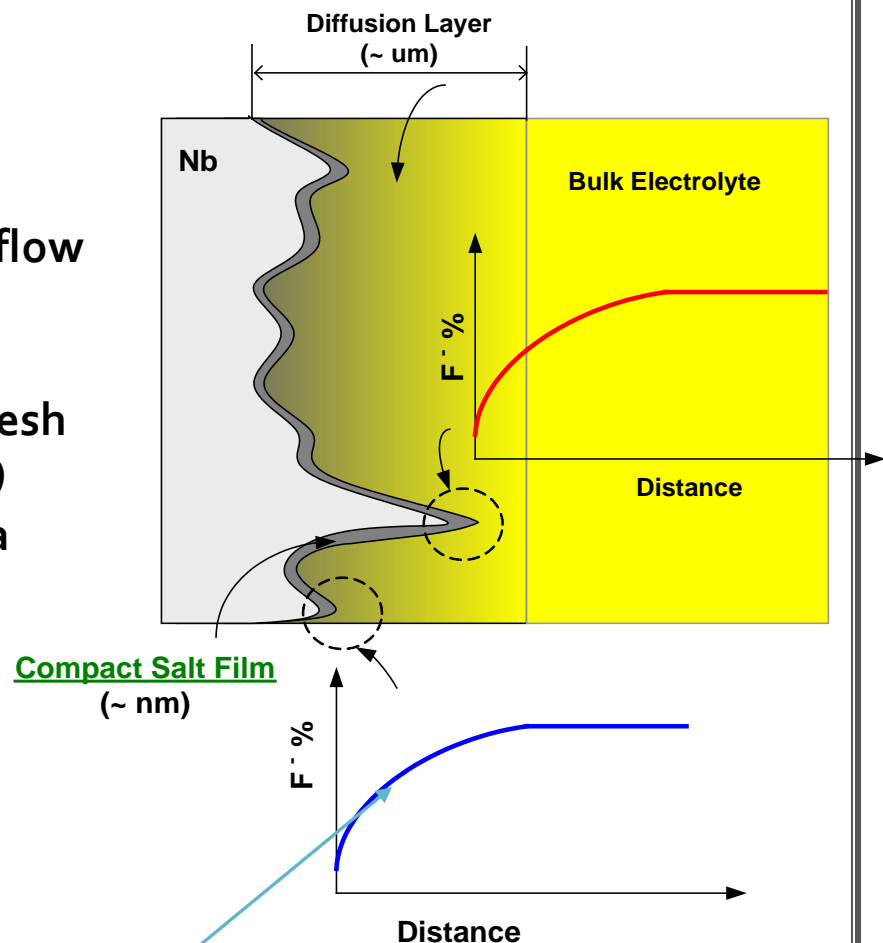
We want to understand the scale-specific details of surface leveling.

We pursue a **reliable, cost-minimized process** for JLab, ILC and other applications.

Diffusion-limited access of F^- to the surface produces “best” polishing

Summary

- Anodization of Nb in H_2SO_4 **forces growth of Nb_2O_5** .
- F^- **dissolves Nb_2O_5** .
- These competing processes result in 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 true diffusion-limited circumstance, material removal is blind to crystallography (avoids crystallographic **etching**).
- The diffusion coefficient **sets a scale** for the most effective leveling

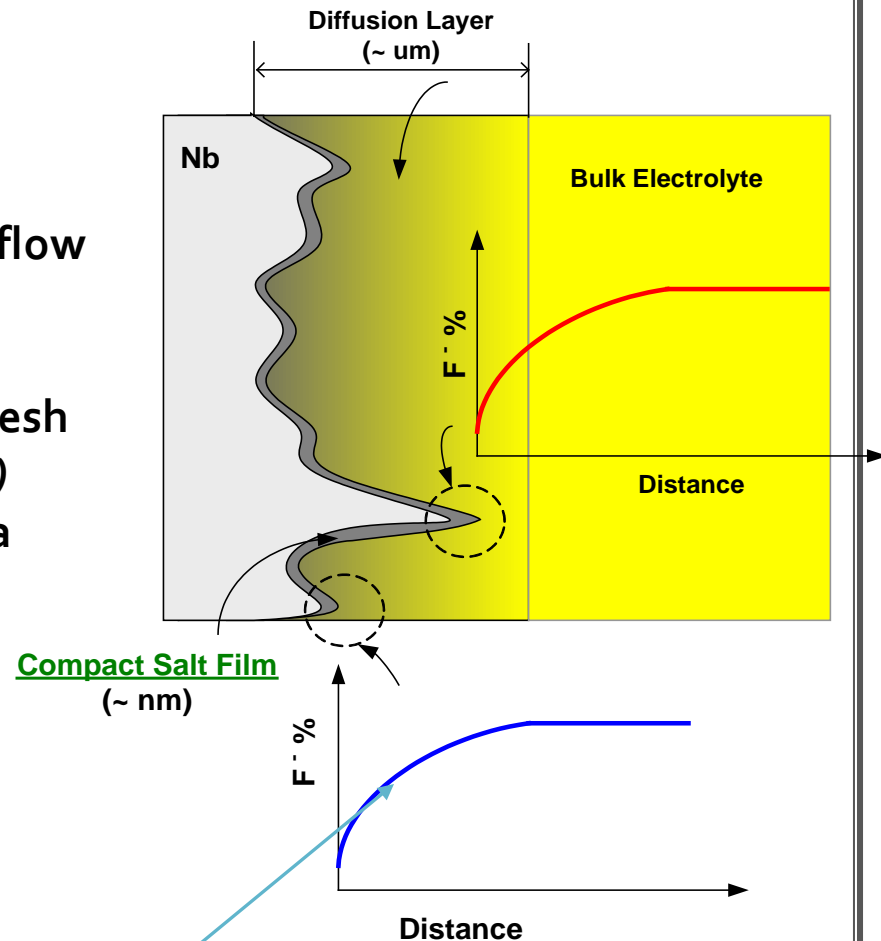


Local temperature, flow and electrolyte composition affect the local F^- gradient

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So we want to understand this diffusion coefficient

We have successfully characterized the

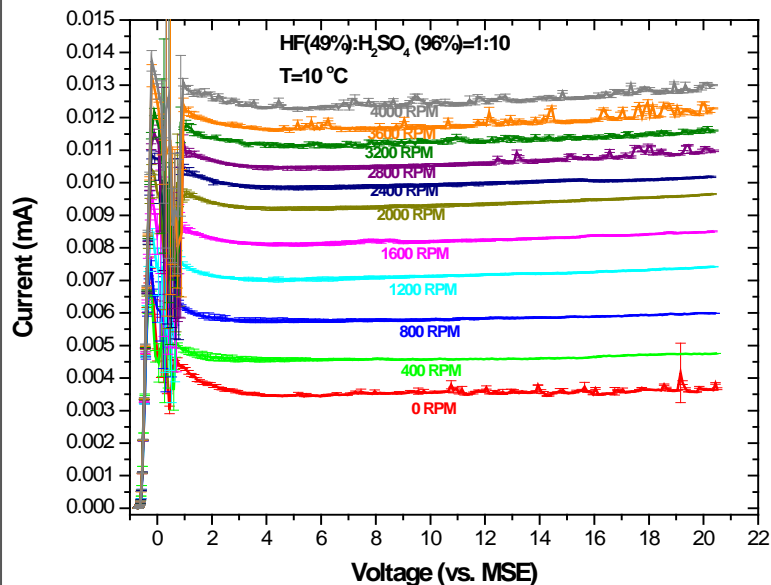
- temperature-dependent **viscosity** of the EP fluid
- **diffusion constant** of F^- in the fluid

This allows us to calculate the **scale** of most effective leveling.

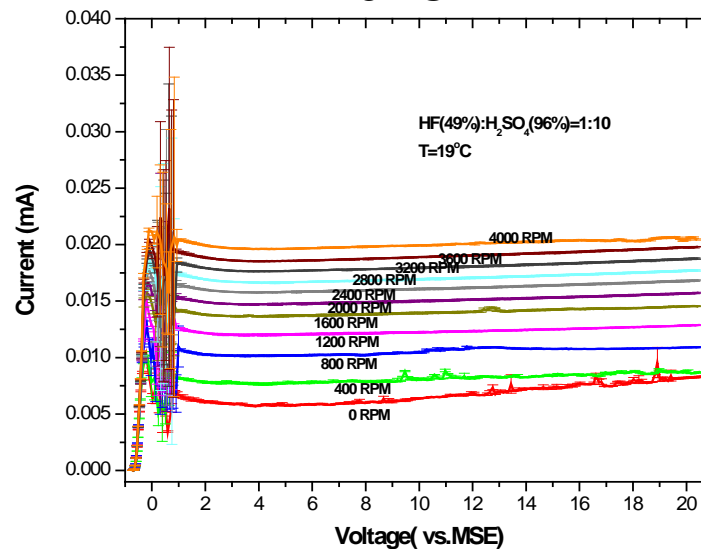
We have also clearly identified that a parallel **etching** process is present at higher temperatures – this works against obtaining the smoothest surfaces, yielding a **reaction rate that is spatially varying with local chemical potential** – grain orientations and lattice stresses.

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

10 °C



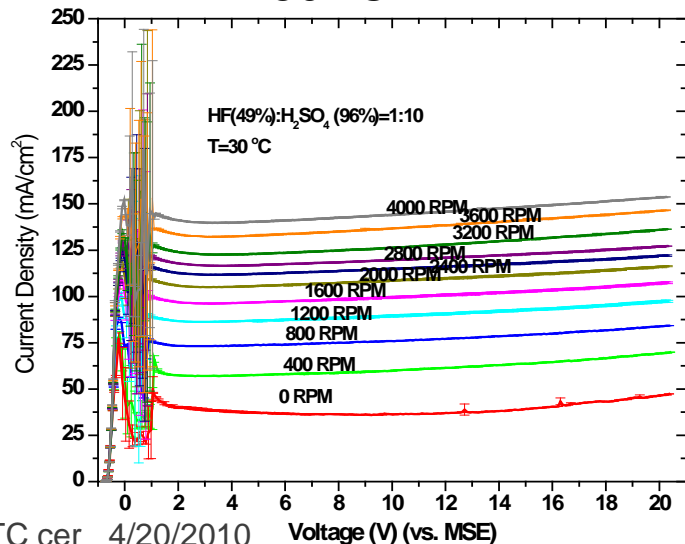
19 °C



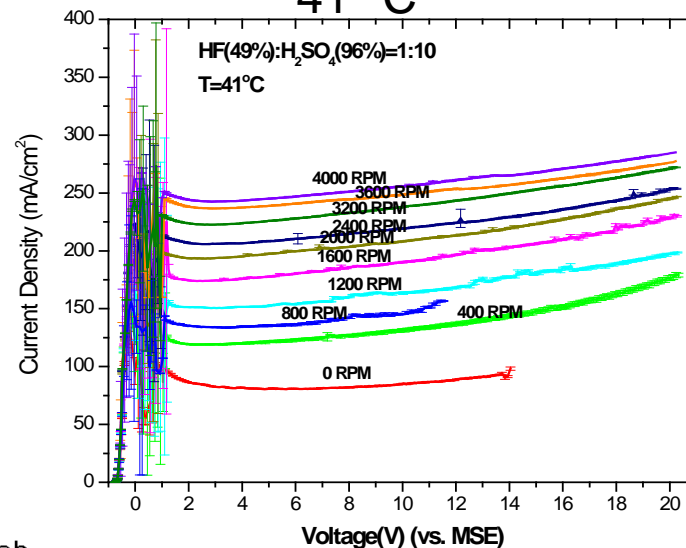
0 – 4000 rpm

Note only ~20% current rise with 400 rpm, at constant temperature

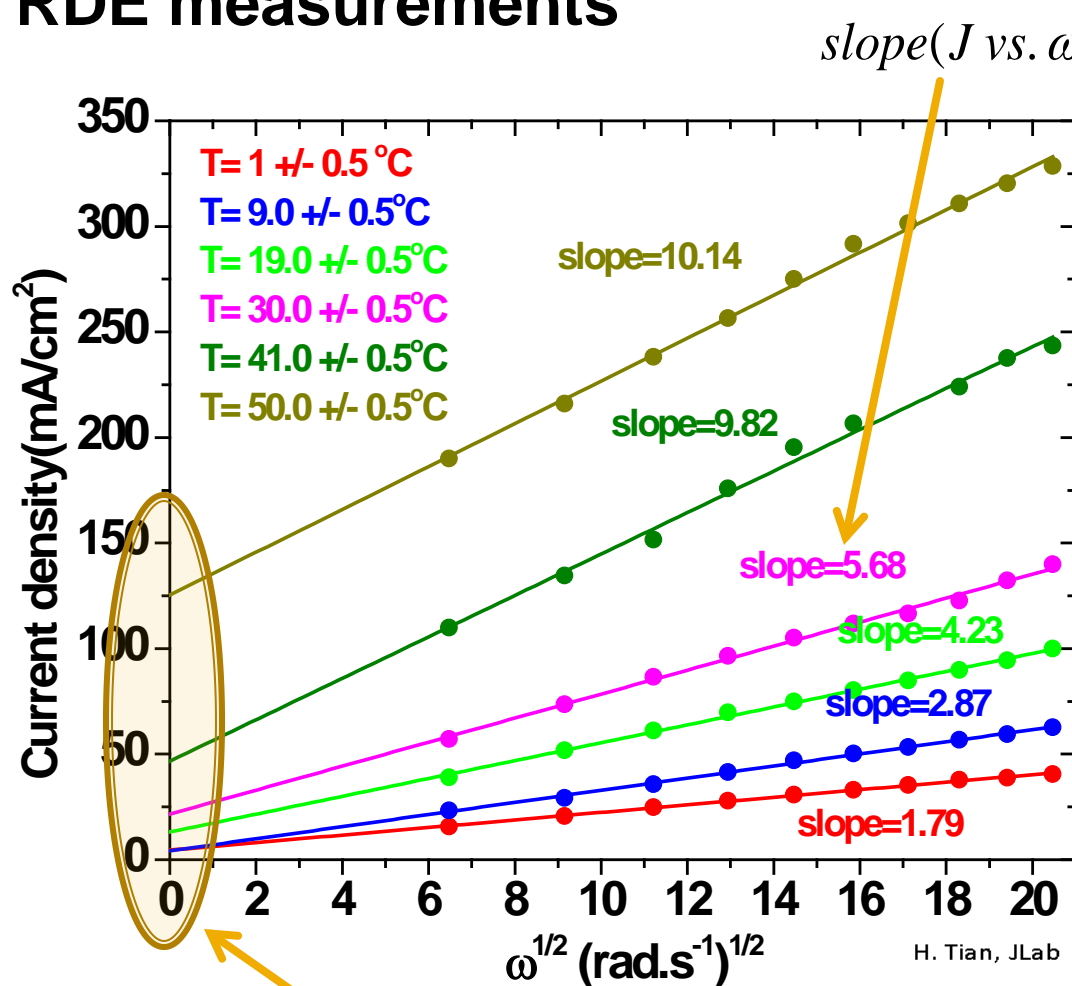
30 °C



41 °C



RDE measurements



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

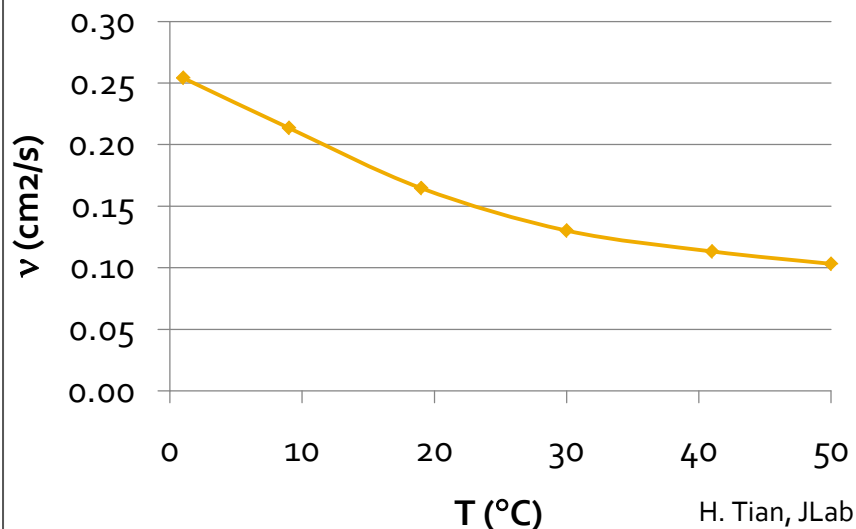
Excellent linear fit provides definitive evidence of a diffusion-limited process. Knowing v and c yields D .

$$c_F = 2.67 \times 10^{-3} \text{ mol/cm}^3$$

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

Determining Electrolyte Physical Properties

Kinematic Viscosity of
1:10 HF/H₂SO₄ Electrolyte

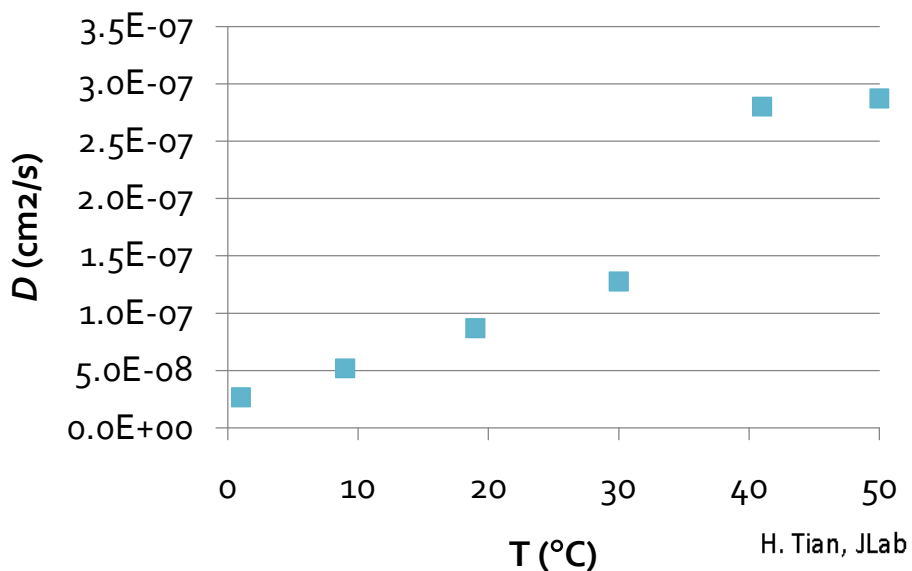


Measured using a
Brookfield DV-II pro viscometer

$$c_F = 2.67 \times 10^{-3} \text{ mol/cm}^3$$

RDE measurements
+ viscosity measurements
+ concentration
determine the Diffusion coefficient

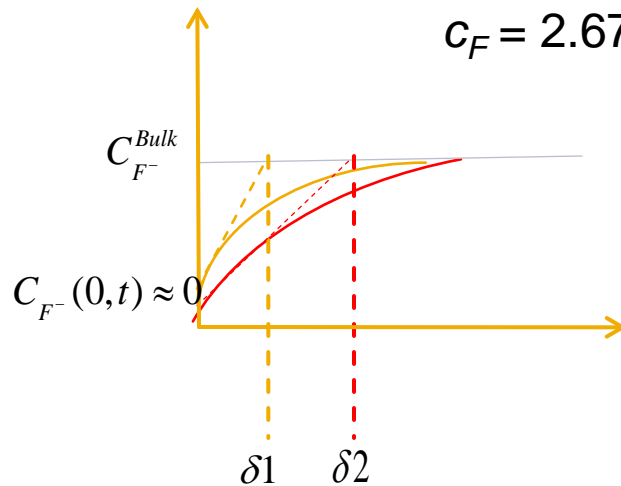
Diffusion Coefficient of
1:10 HF/H₂SO₄ Electrolyte



Estimation of diffusion layer thickness in 1:10 HF/H₂SO₄ Electrolyte at different temperatures

$$c_F = 2.67 \times 10^{-3} \text{ mol/cm}^3$$

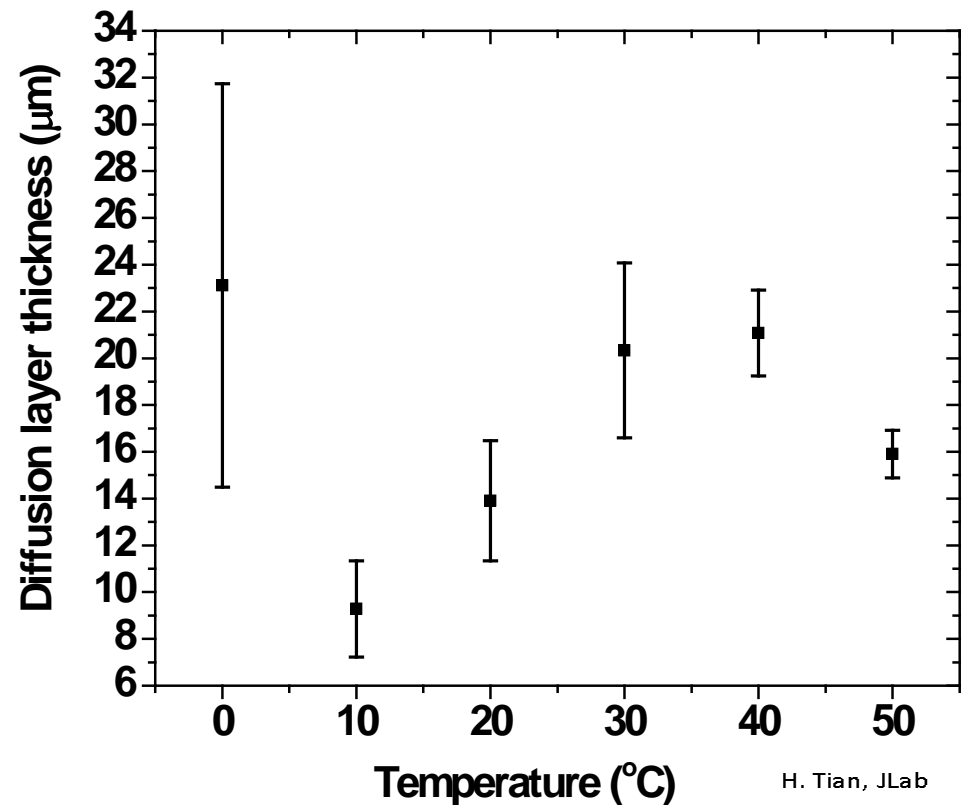
$$J = n \times F \times D \times \frac{c}{\delta}$$



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.



H. Tian, JLab

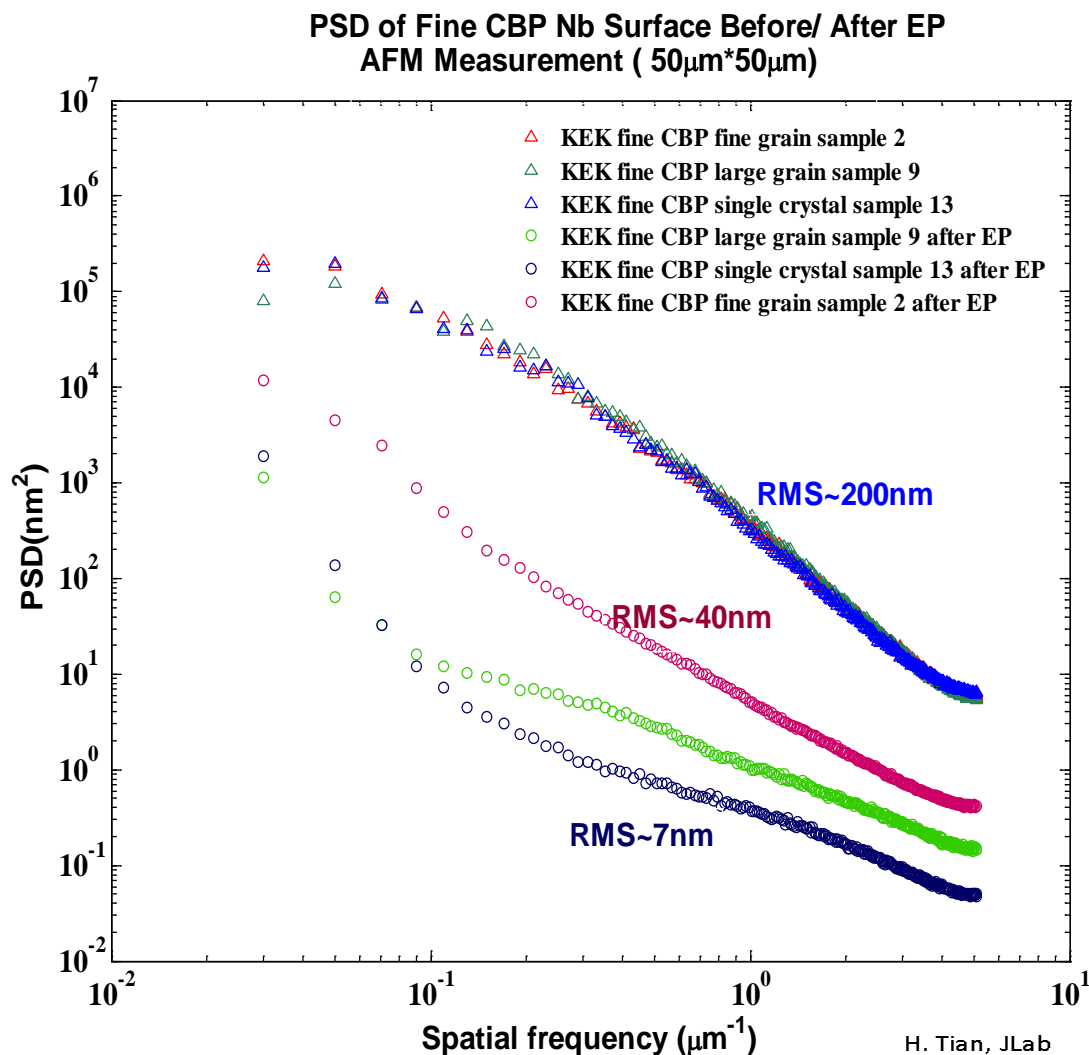
2 μm scale structure should vanish much faster than 40 μm structure

Not all Nb “EPs” the same

With “standard” 1:10 HF/H₂SO₄ 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, consistent with RDE analysis and visual experience.

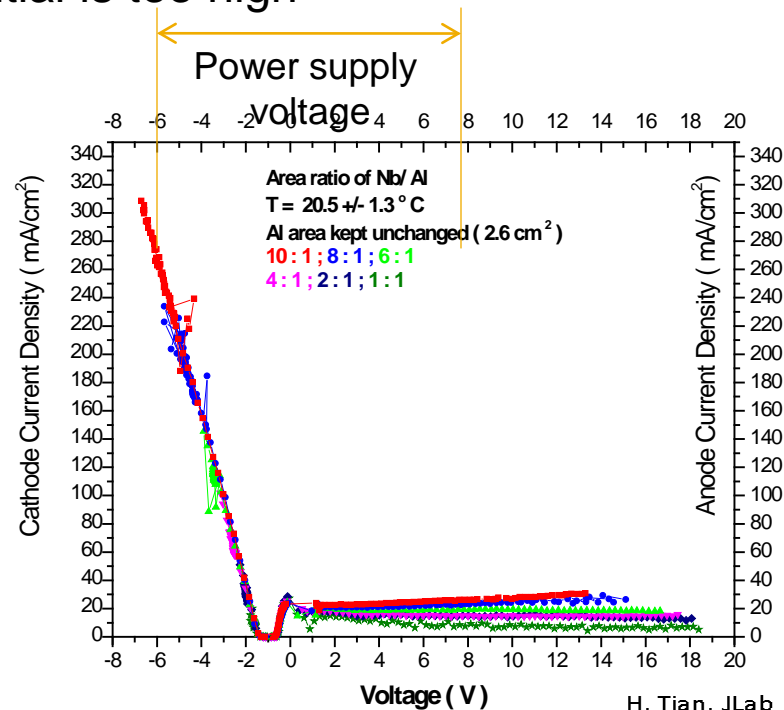
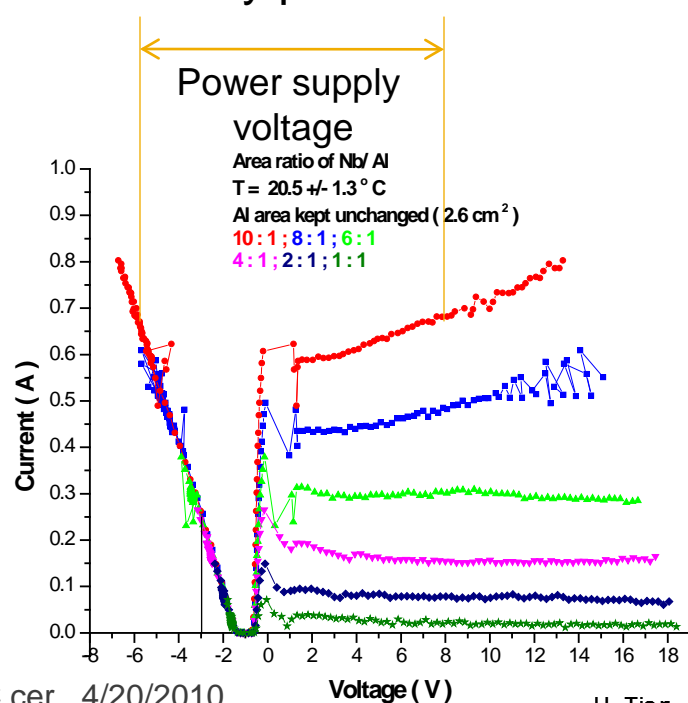


Avoid sulfur at the cathode

- Most commercial electropolishing applications attempt to maximize the surface area of the cathode to avoid process complications (power cost and chemistry).
- In contrast to this, typical horizontal cavity EP circumstances have a cathode:anode active area ratio of 1:10. (Worse if “masking” is applied.)
- Result is high current density on the cathode and necessary high overpotential to drive the current. *This risks driving other chemistry, such as S reduction.*
 - ~5.5 V polarization potential @ cathode to drive 300 mA/cm² ≈ 30 mA/cm² at anode.



may proceed if cathode overpotential is too high



If the objective is maximally smooth surfaces without sulfur particles :

Implications:

- We should expect the best micropolishing for topographic features smaller than $\sim 10\text{ }\mu\text{m}$, **so start with surfaces that are consistently smooth to this scale**: e.g. CBP.
- This process we call “EP” also has a temperature-dependent etching process present. So, **minimize the temperature** as much as is practical (and minimize lattice strains).
- **Reduce or eliminate sulfur production** at the cathode by minimizing cathode current density and **improving the reaction kinetics** for hydrolysis at the cathode.

(1:10 HF/H₂SO₄ Electrolyte with Nb)

Contributors

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Key References:

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