

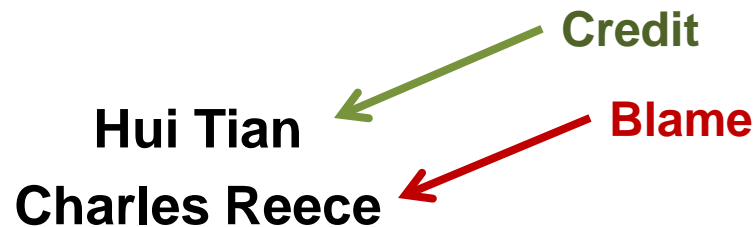
Basic Mechanisms of “Standard” Niobium “EP”

**Hui Tian
Charles Reece**

SRF Materials Mtg, February 2010

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

Basic Mechanisms of “Standard” Niobium “EP”

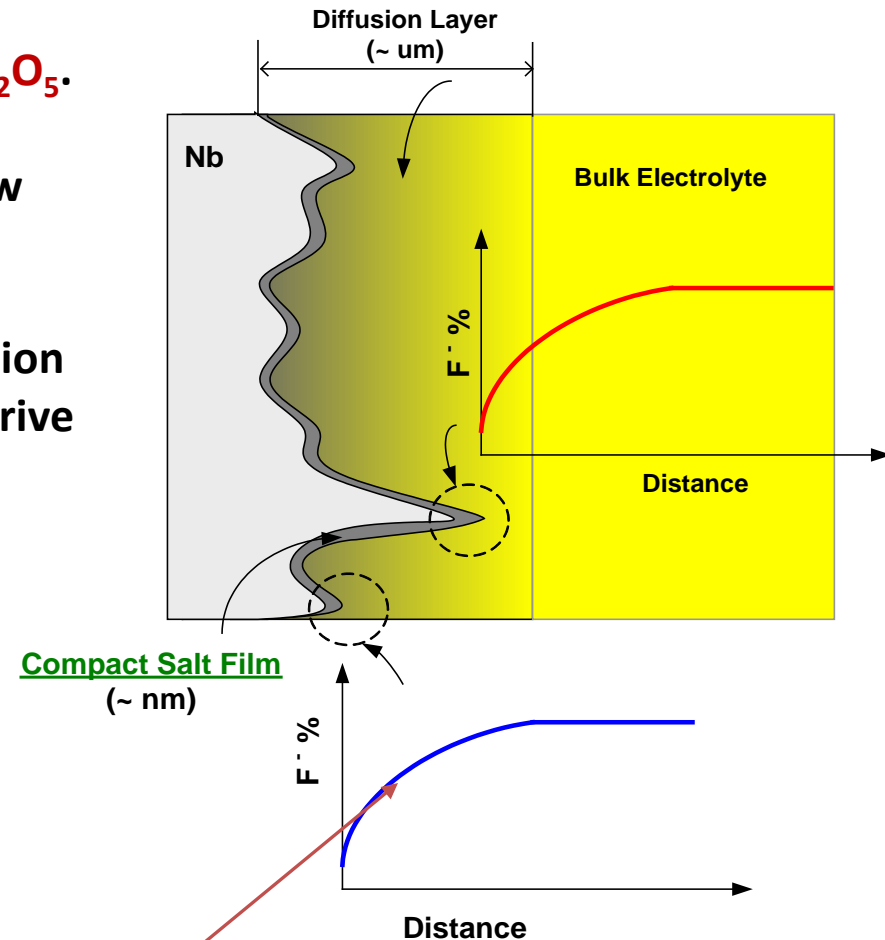


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Past studies show that the diffusion-limited access of F^- to the salt film produces “best” polishing

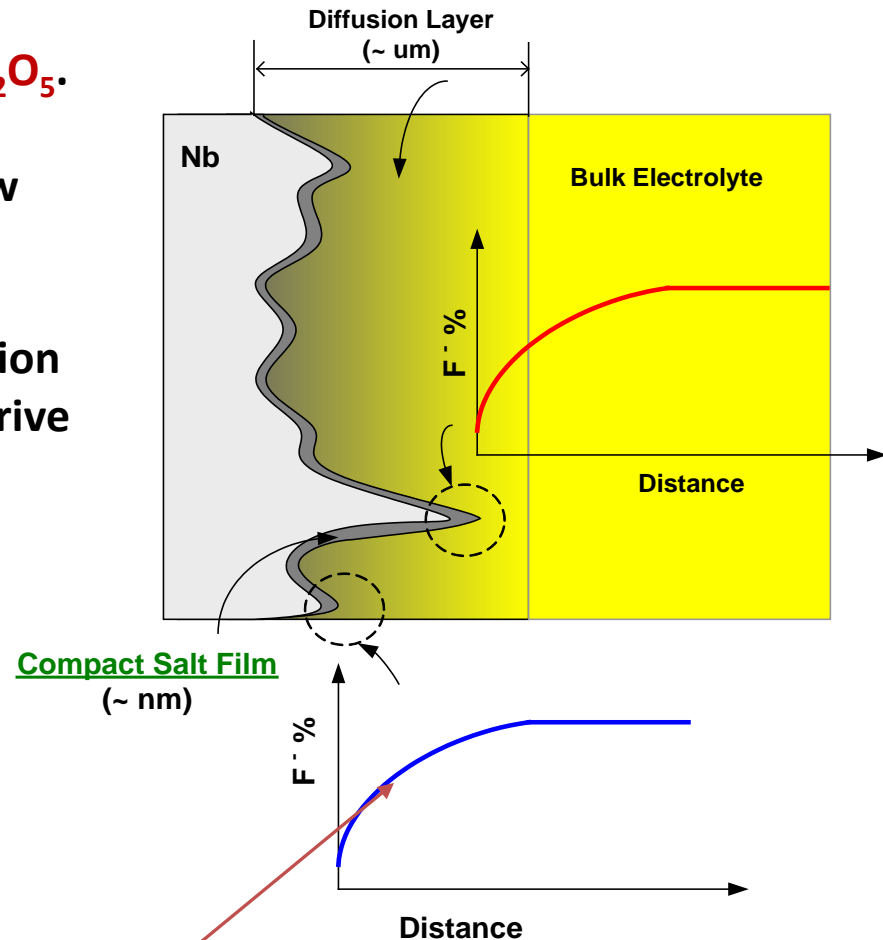
- Anodization of Nb in H_2SO_4 **forces growth of Nb_2O_5** .
- F^- **dissolves Nb_2O_5** .
- These competing processes result in current flow and material removal.
- Above a certain anodization potential, the reaction rate plateaus, limited by how fast fresh F^- can arrive at the surface. (**diffusion-limited**)
- 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



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

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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:

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

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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In ideally static case, only diffusion matters.

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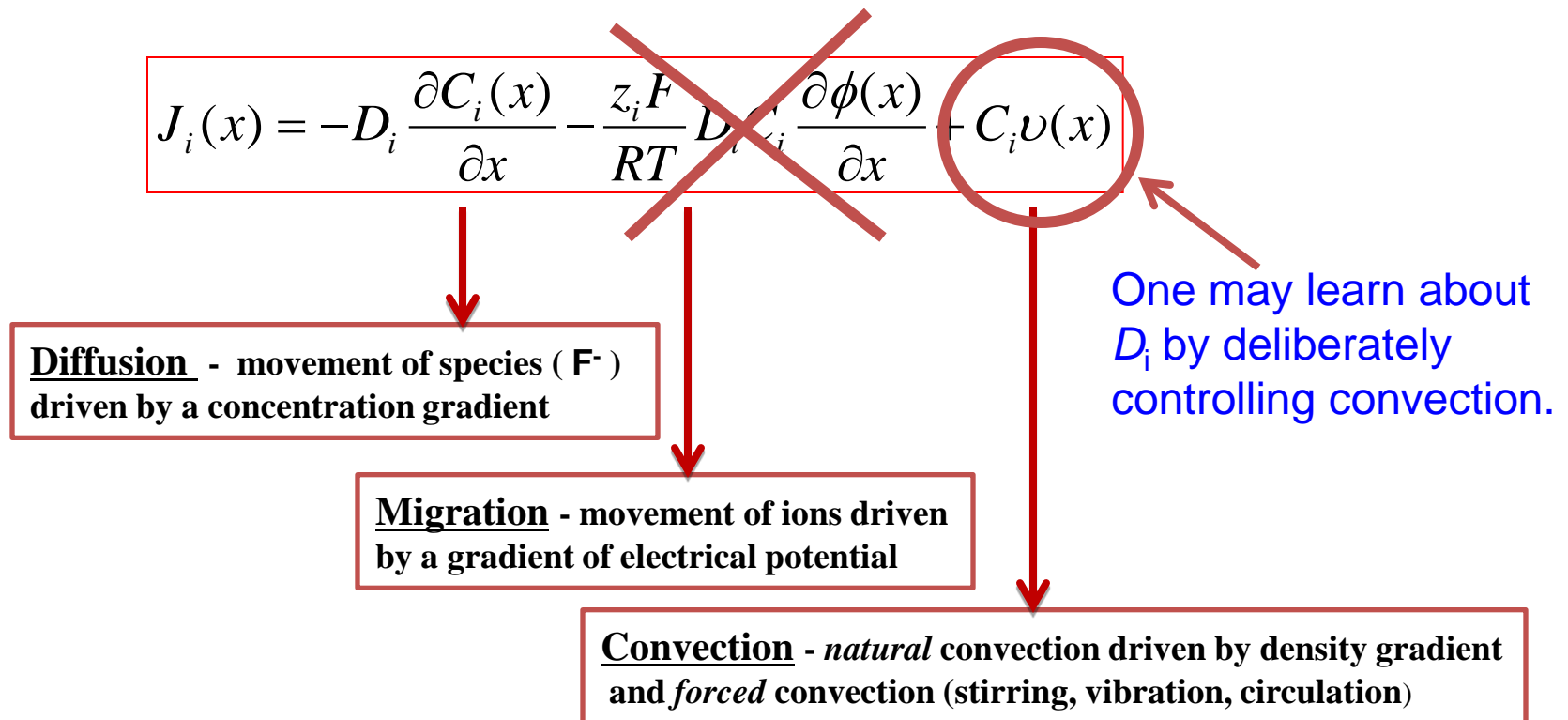
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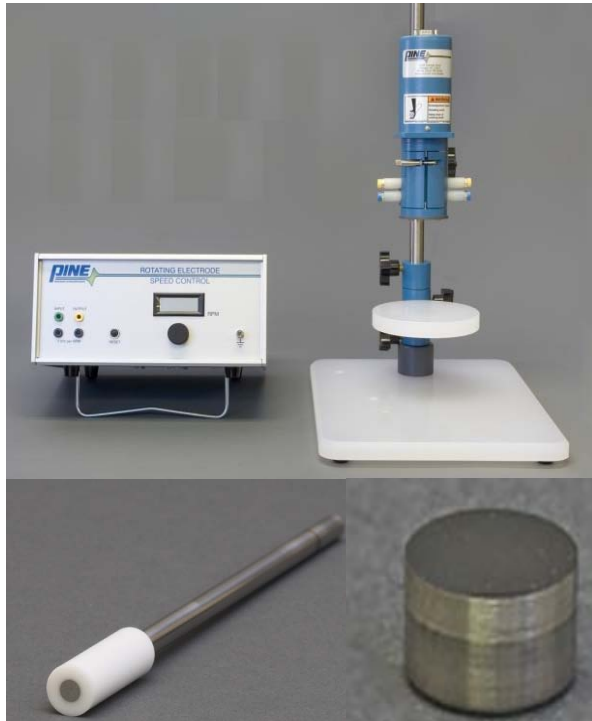
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Determination of the limited species diffusion coefficient by rotating disk electrode (RDE)



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

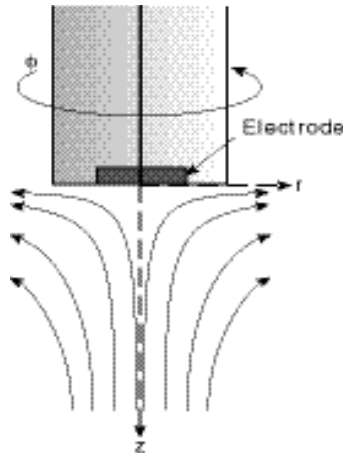
$$J = 0.62nFD^{0.67} \nu^{-0.166} c \omega^{0.5}$$

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

ν : kinematic viscosity

ω : rotation speed of the electrode

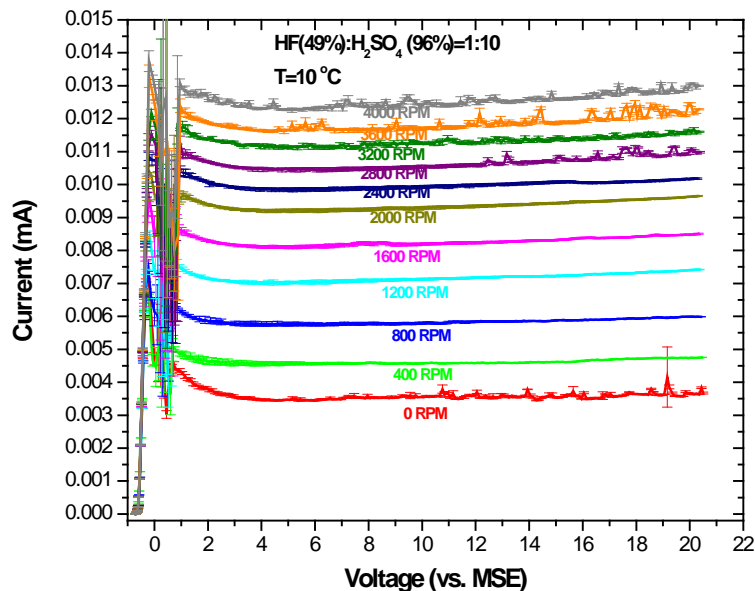
c : concentration of active species



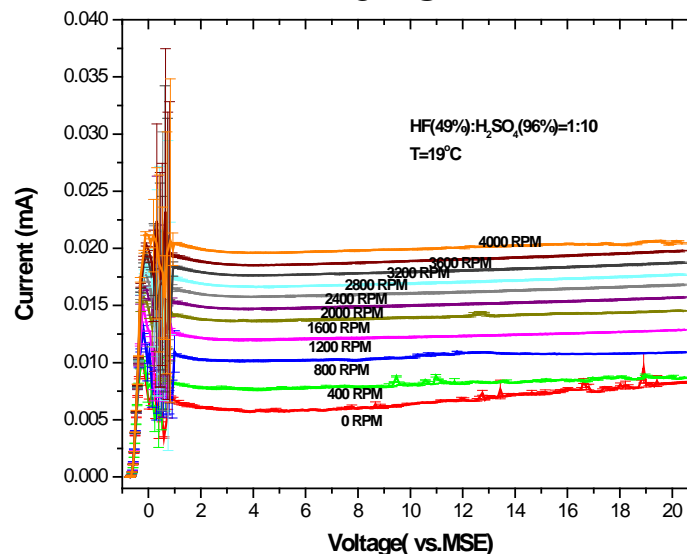
I-V curves of Nb electropolishing at different temperatures with RDE

0 – 4000 rpm

10 °C

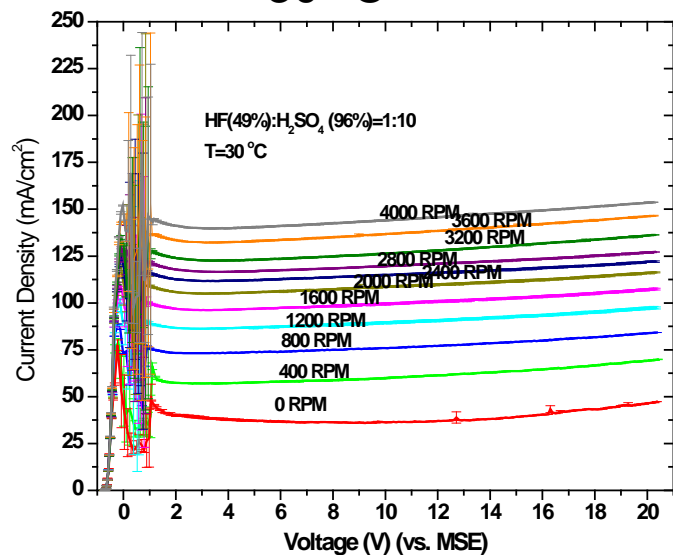


19 °C

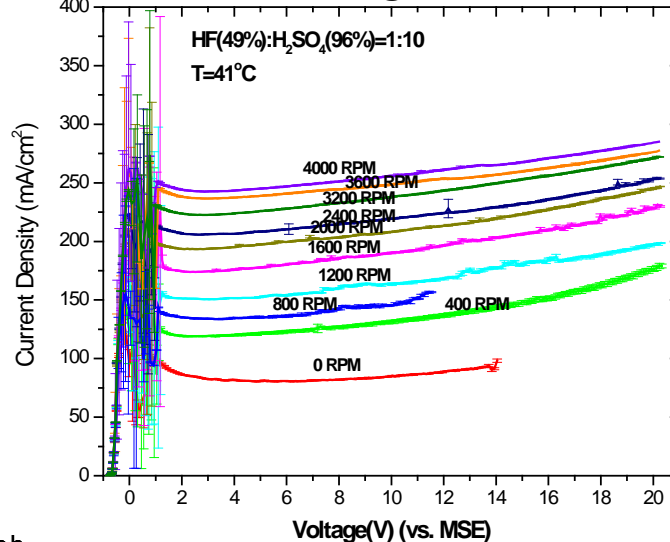


Note only ~20% current rise with 400 rpm, at constant temperature

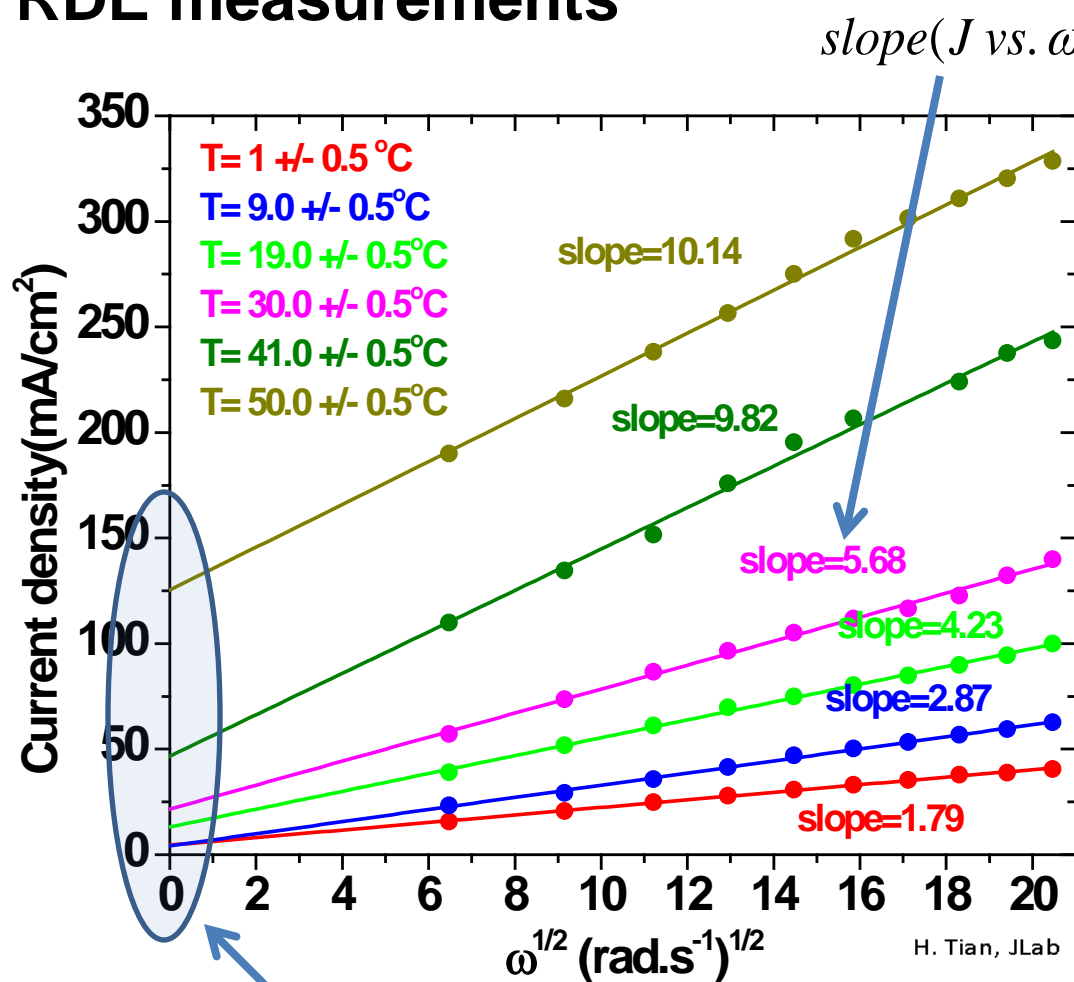
30 °C



41 °C



RDE measurements



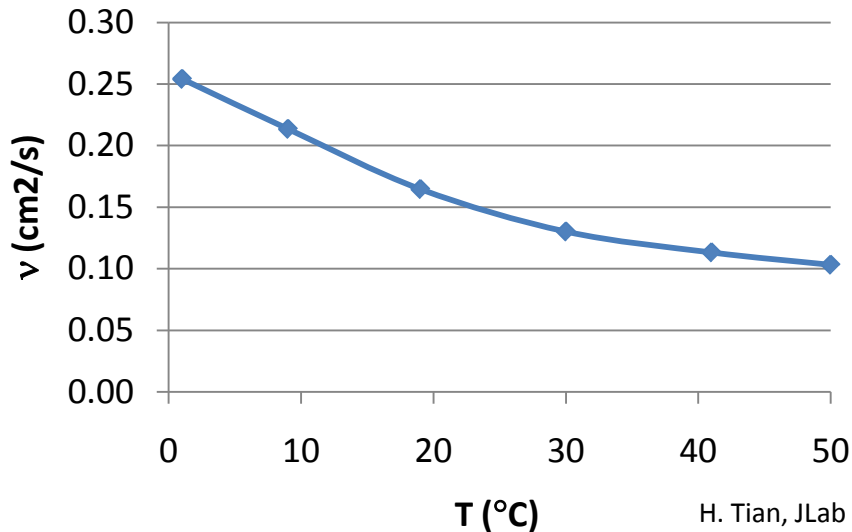
Excellent linear fit provides definitive evidence of a diffusion-limited process. Knowing ν and c yields D .

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

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**

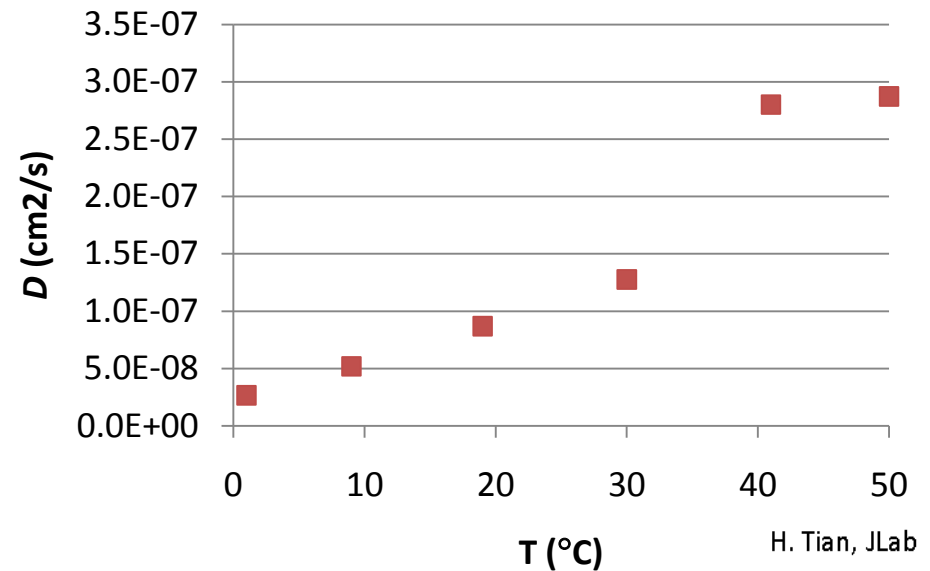


Measured using a
Brookfield DV-II pro viscometer

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

RDE measurements
+ viscosity measurements
+ concentration
determine the Diffusion coefficient

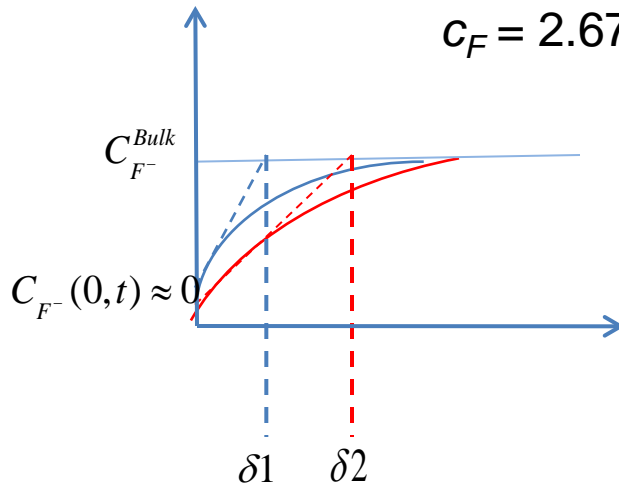
**Diffusion Coefficient of
1:10 HF/H₂SO₄ Electrolyte**




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

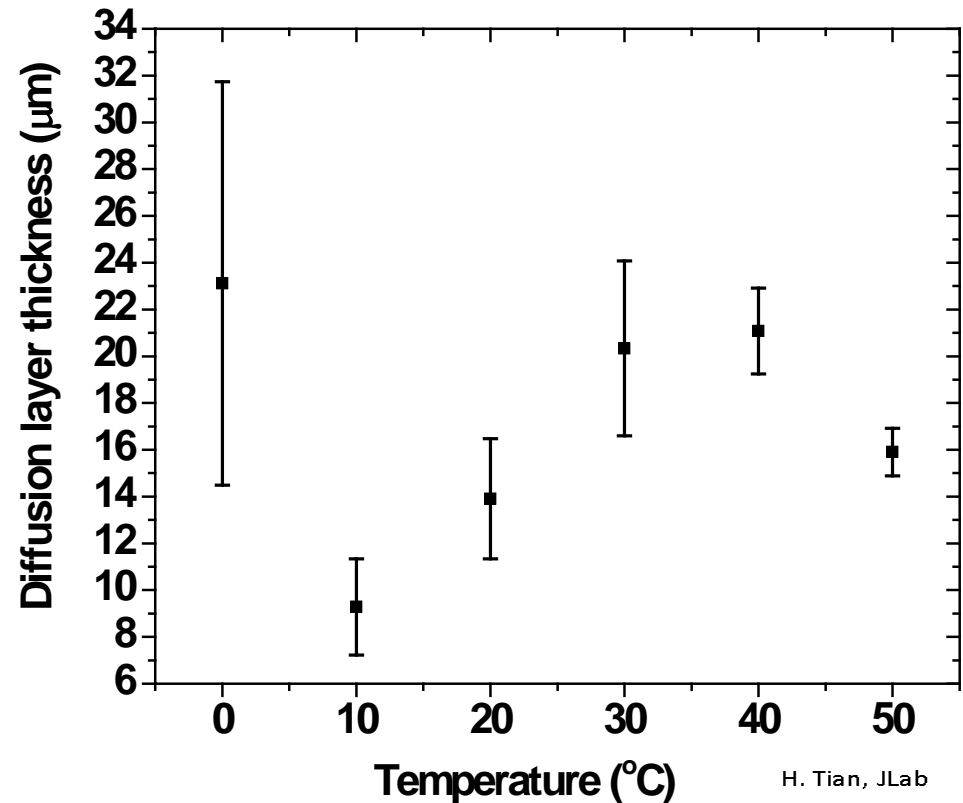
$$c_F = 2.67 \times 10^{-3} \text{ mol/cm}^3$$

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



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.

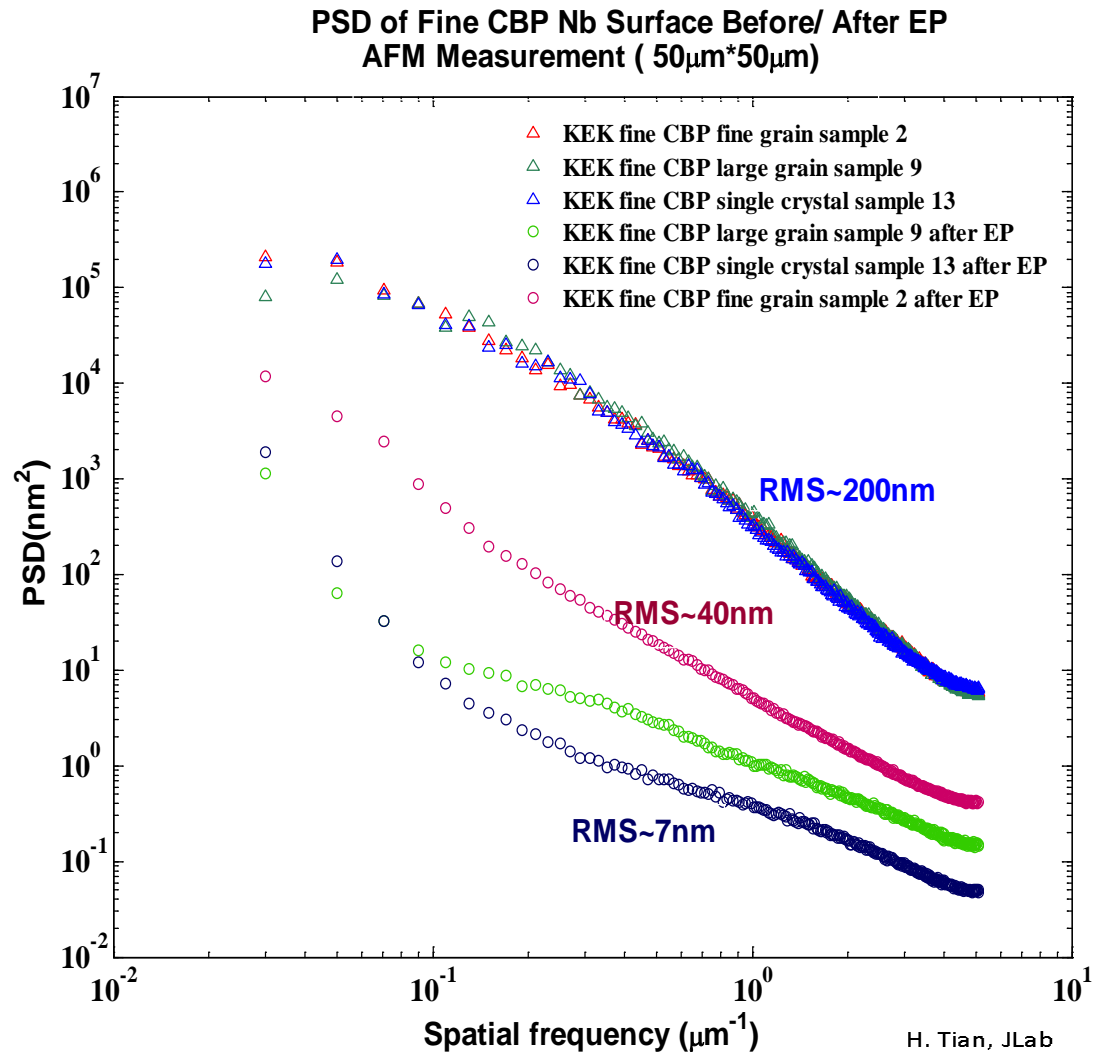


Not all Nb “EPs” the same

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

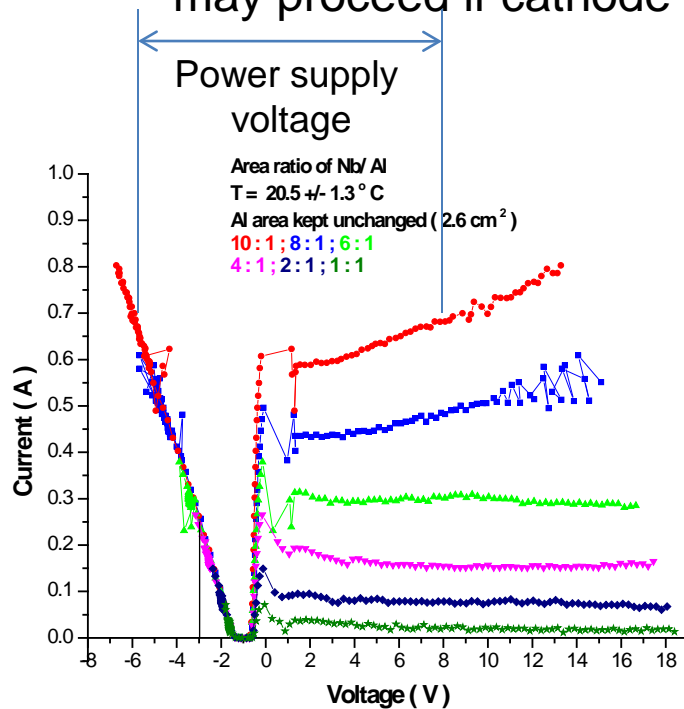


Avoid sulfur production at the cathode

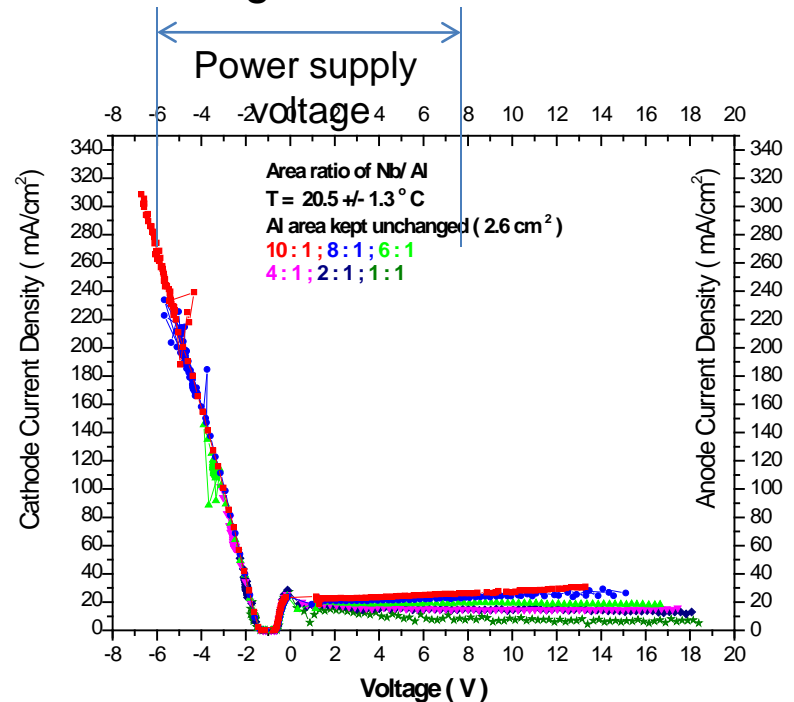
- Most electropolishing applications attempt to maximize the surface area of the cathode to avoid process complications (cost).
- In contrast to this, typical horizontal cavity EP circumstances have a cathode:anode active area ratio of 1:10.
- Result is high current density on the cathode and necessary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



may proceed if cathode overpotential is too high



H. Tian, JLab



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1:10 HF/H₂SO₄ Electrolyte with Nb

If the objective is maximally smooth surfaces:

Implications:

- We should expect the best micropolishing for topographic features smaller than $\sim 15 \mu\text{m}$, 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.
- Reduce sulfur production at the cathode by minimizing cathode current density and improving the reaction kinetics for hydrolysis at the cathode.

Contributors

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Key References:

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