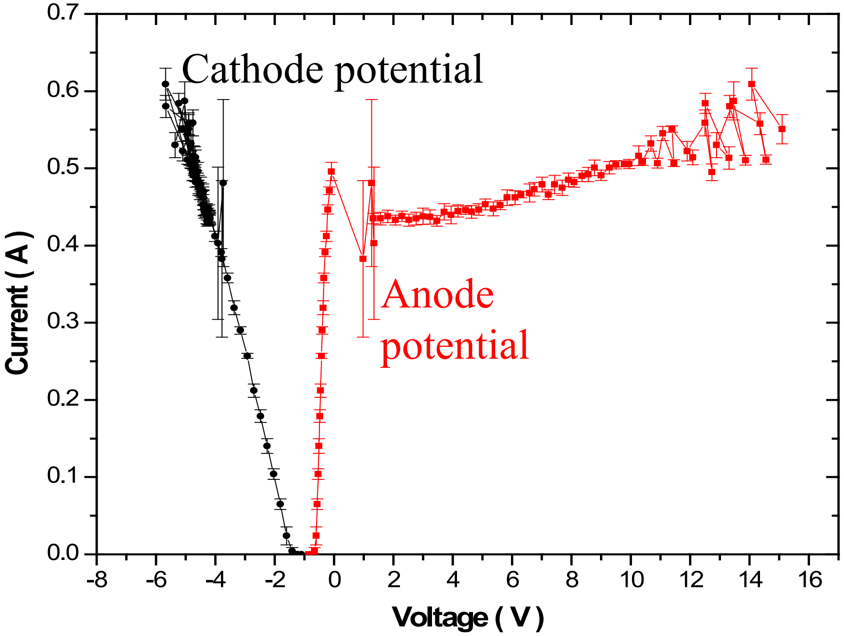
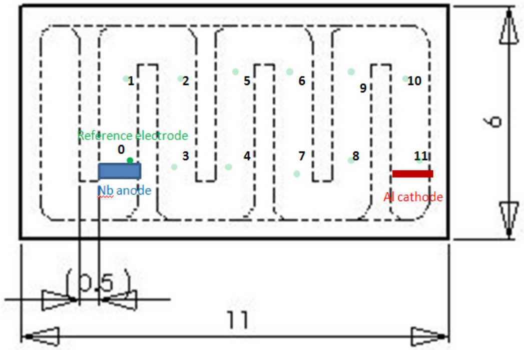
Quantitative EP Studies and Results for SRF Nb Cavity Production

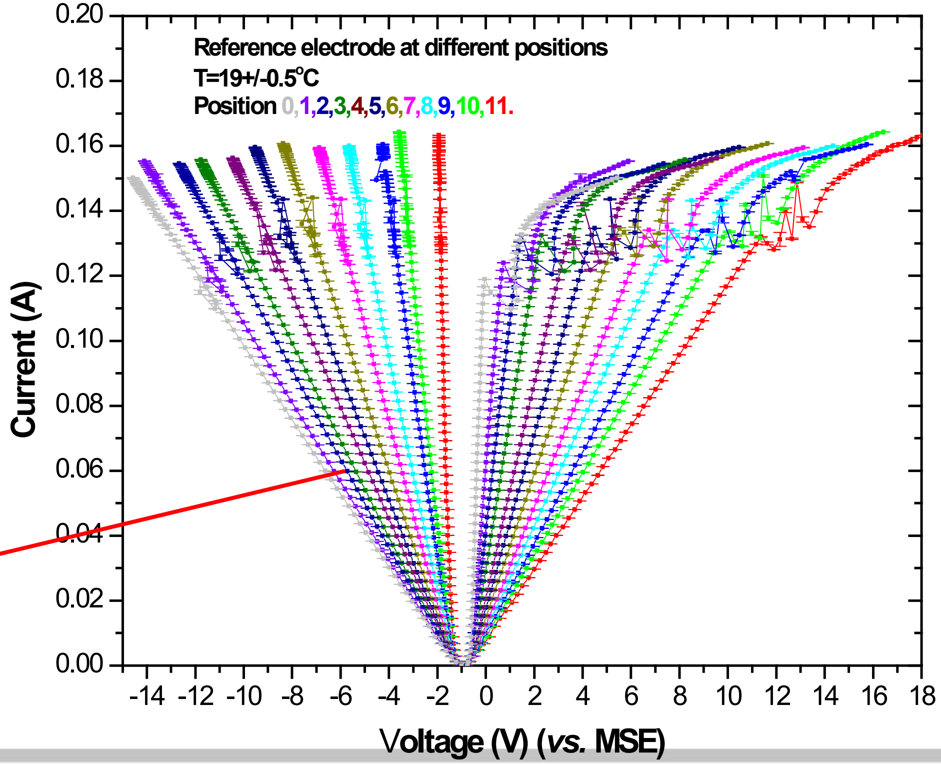
Hui Tian

- **Basic understanding about Nb electropolishing helps to optimize the cavity EP process.**
- **Understanding the scale specific details of surface finishing after EP yield confident process control and optimization.**
- **Recent implications for Nb cavity production achieve promising results.**
- **Future work.**

Understanding Potentials in Electrochemical Cell of Niobium EP





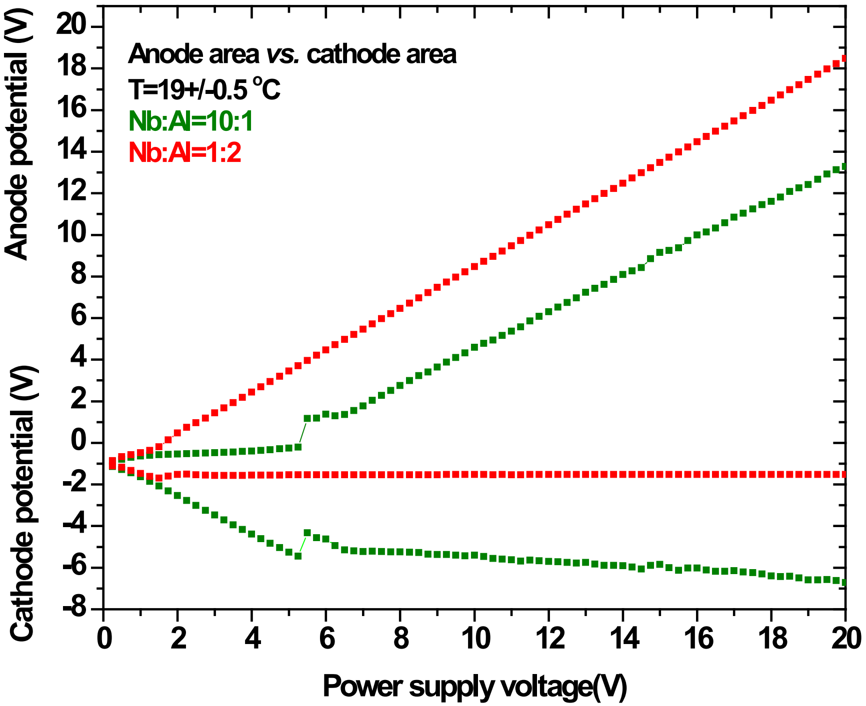


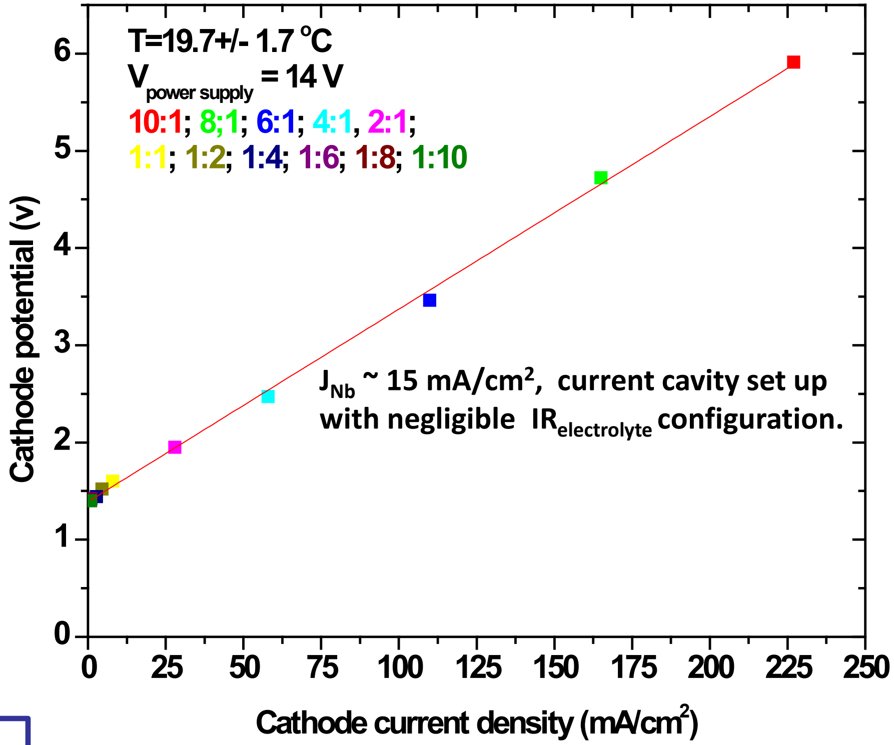
$V_{pwsup}=(V_{anode} - V_{cathode}) + IR_{electrolyte} + IR_{conduct}$

Monitoring I-V_{pwsup} only is inadequate to characterize the local EP effect on Nb.

Separate impacts of individual components in the Nb EP system: V_{anode}, $V_{cathode}$ and $R_{electrolyte}$ (ρ @ 20 C ~ 13 ohm.cm)- those values depend on electrolyte composition, temperature, surface areas of cathode and anode , and geometry.

Large Cathode Surface Area Helps Decrease Cathode Potential





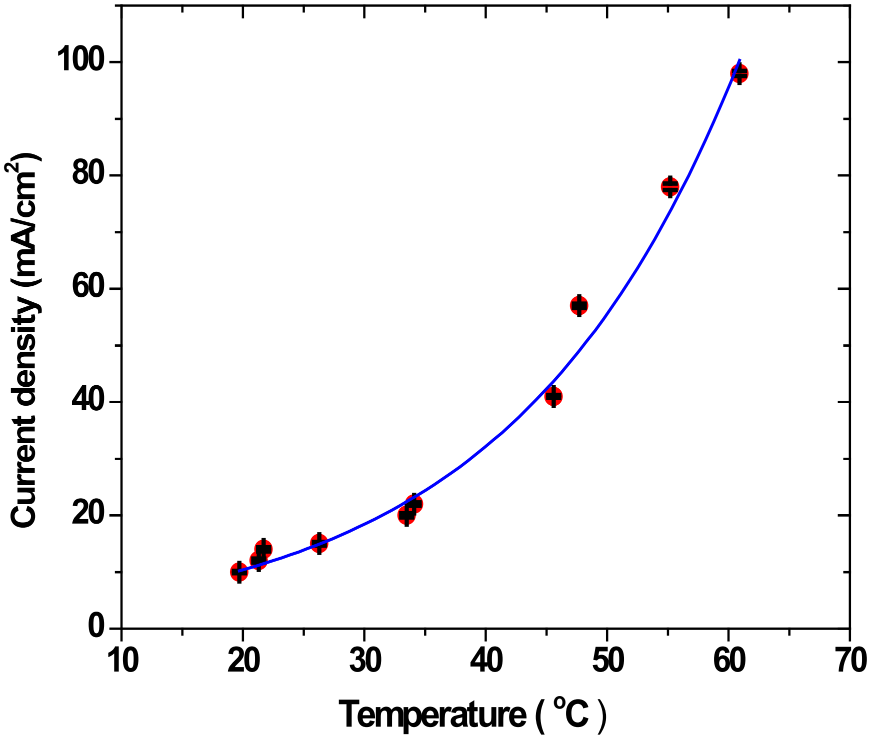
J_{Nb} ~ 15 mA/cm², current cavity set up with negligible $IR_{electrolyte}$ configuration.

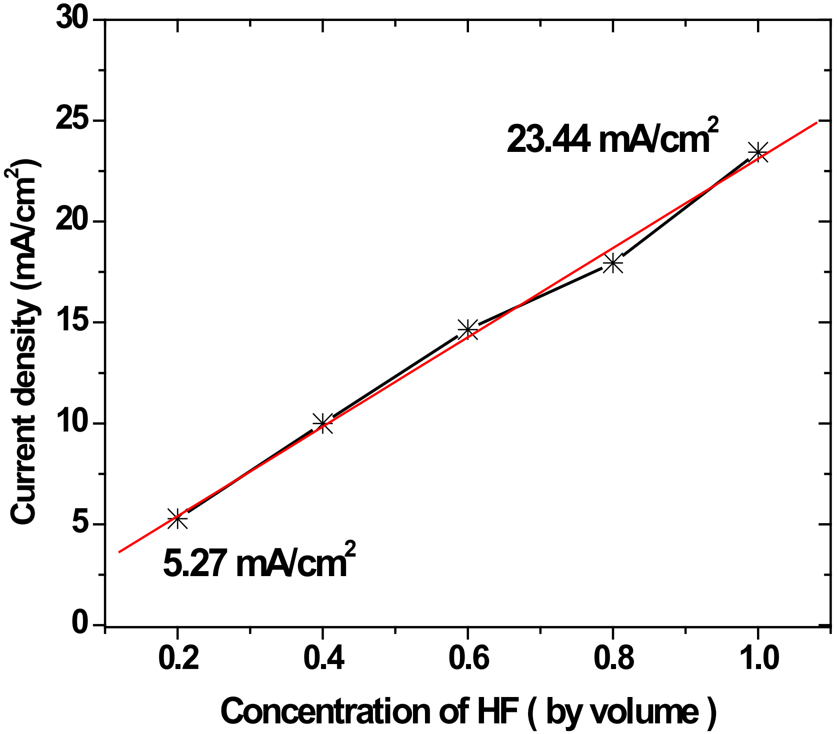
Beside extra power consumption due to low cathode area, high current density on the cathode and high over potential increases sulfur precipitation at the cathode.

"Sulfur Residues in Niobium Electropolishing" , TUPO024, L . Zhao, H. Tian, C. Reece & M. Kelley.

Maximize cathode surface area or use new cathode material for improving hydrolysis at the cathode (less potential drop)

Anode Current Density Strongly Depends on Local Electrolyte Temperature & HF Concentration





The Nb anode plateau current density is directly proportional to the bulk F concentration, increases with temperature, and is independent of the amount of dissolved Nb.

Courtesy of 1) F. Eozénou et al. CARE-report-2008-022-SRF, 2) H. Tian, C. Reece, et al. J. Electochem. Soc. 155(2008), p. D563

Current –Limited Plateau Is The Result of Mass-transfer Limitation

Mass transfer might 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

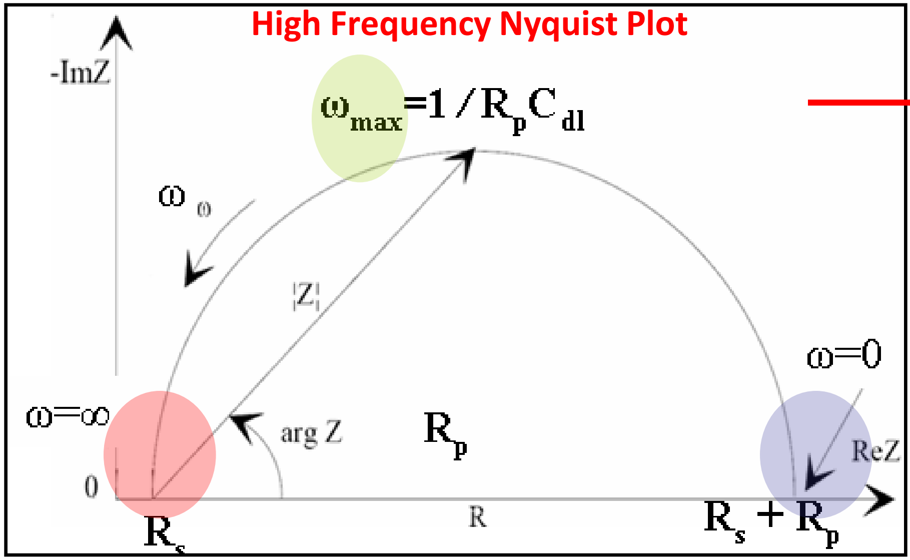
$$\boxed{J_i(x) = -D_i \frac{\partial C_i(x)}{\partial x} - \frac{z_i F}{RT} D_i C_i \frac{\partial \phi(x)}{\partial x} + C_i \upsilon(x)}$$

Diffusion, movement of mass transfer limited species by a concentration gradient

Migration, movement of ions driven by a gradient of electrical potential (for Nb Electropolishing, it is negligible in the plateau region)

Convection, natural convection driven by density gradient and forced convection, such as stirring , vibration, or pumped circulation

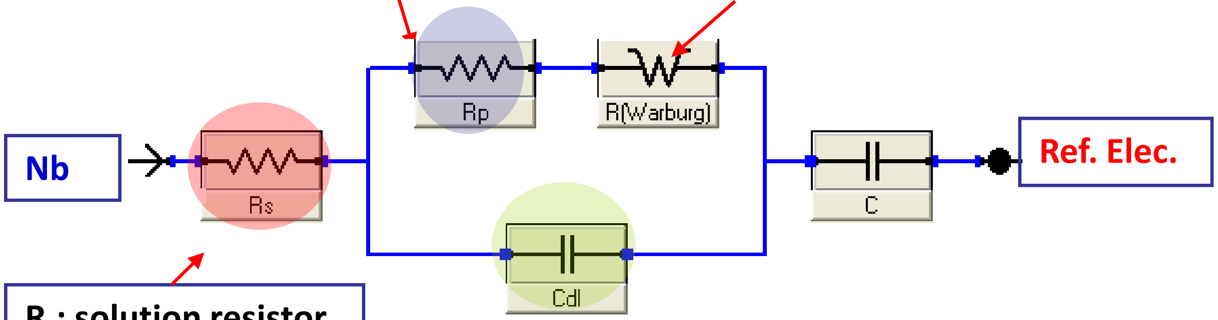
Use Electrochemical Impedance Spectroscopy (EIS) to Determine the Mechanism of Nb Electropolishing


High Frequency Nyquist Plot

$$Z = \frac{R_p}{1+\omega^2 C_{dl}^2 R_p^2} + R_s - j\frac{\omega C_{dl} R_p^2}{1+\omega^2 C_{dl}^2 R_p^2}$$

R_s: electrolyte, temperature.
R_p: temperature, concentration of reaction products, potential. (such as : salt film thickness etc),
C_{dl}: electrolyte, temperature, potential, oxide layer, electrode roughness
R_w: the frequency of potential perturbation

Possible equivalent circuit of Nb-acid interface during Nb EP



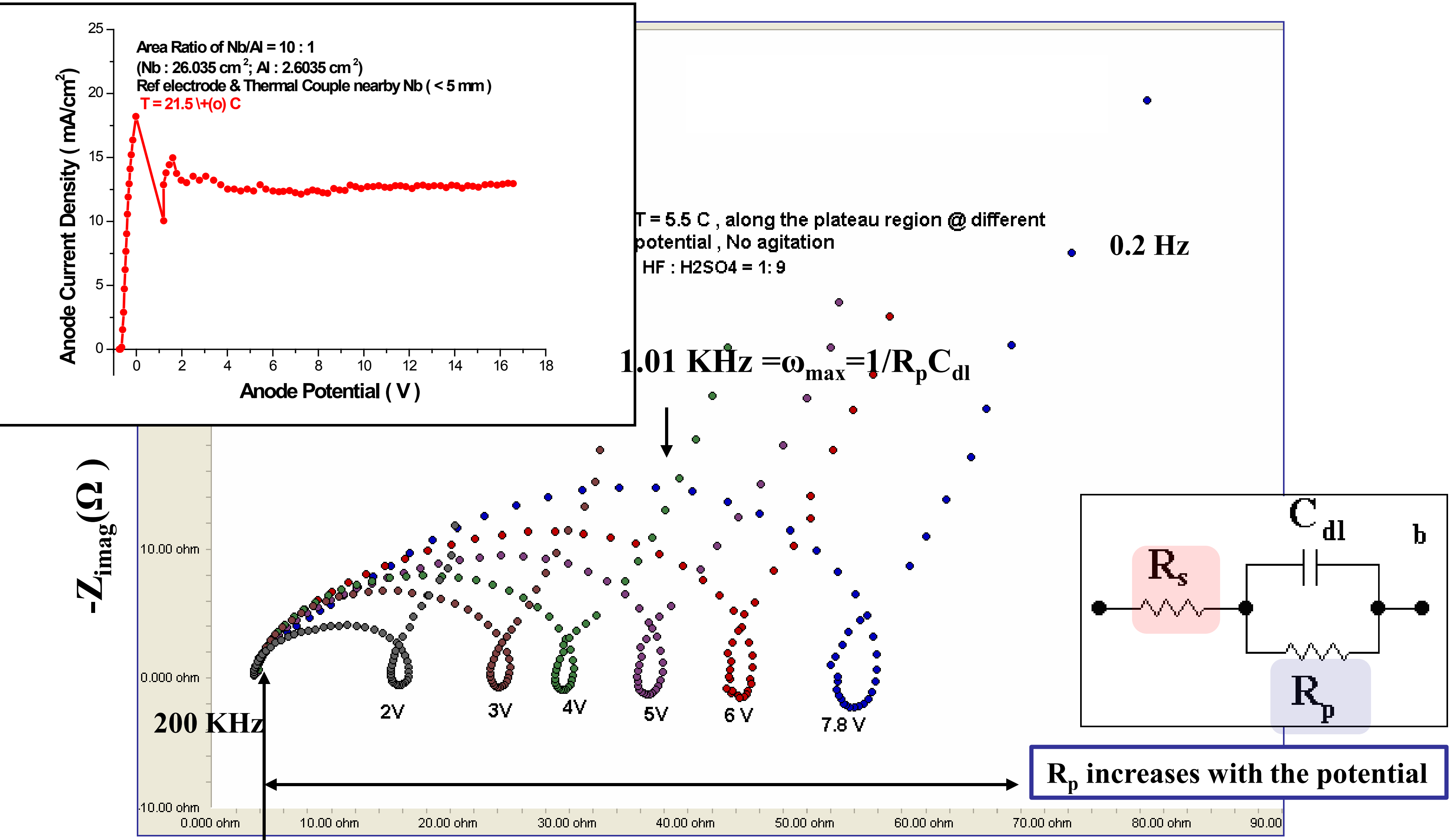
R_p: polarization/charger transfer resistor

$R_{warburg}$: diffusion resistor

R_s: solution resistor

C_{dl} : double layer capacitor of electrode surface

EIS Study Discloses the Mechanism of Nb Electropolishing



0.2 Hz

1.01 KHz $=\omega_{max}=1/R_pC_{dl}$

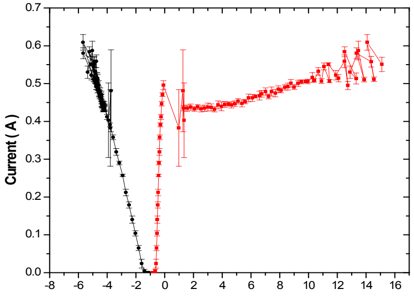
200 KHz

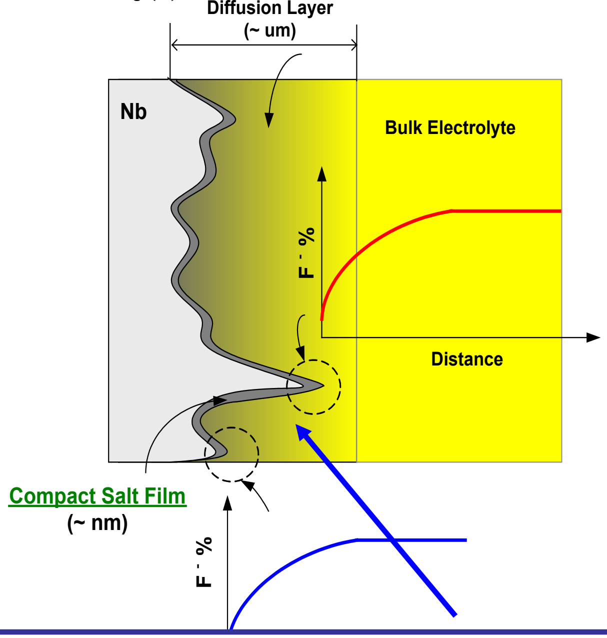
R_p increases with the potential

R_s remains constant

$Z_{real}\ (\Omega)$

The Diffusion-Limited Access of F^- to the Surface Produces Best Polishing





Local temperature, flow (stirring, circulation) & electrolyte composition affect the local F^- gradient.

Anodization of Nb in H_2SO_4 produces Nb_2O_5, but F^- aggressively dissolves Nb_2O_5. These competing processes result in current flow and material removal.

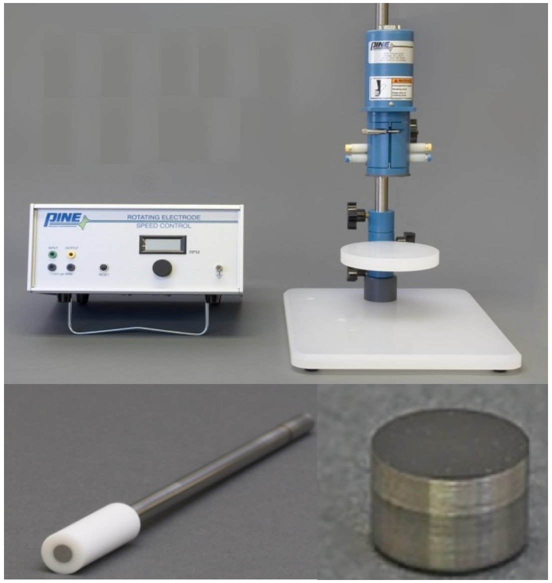
Above a certain anodization potential (establishment of a salt film-Nb_2O_5), the reaction rate is limited by how fast F ions can arrive at the surface: diffusion limited mass transfer control.

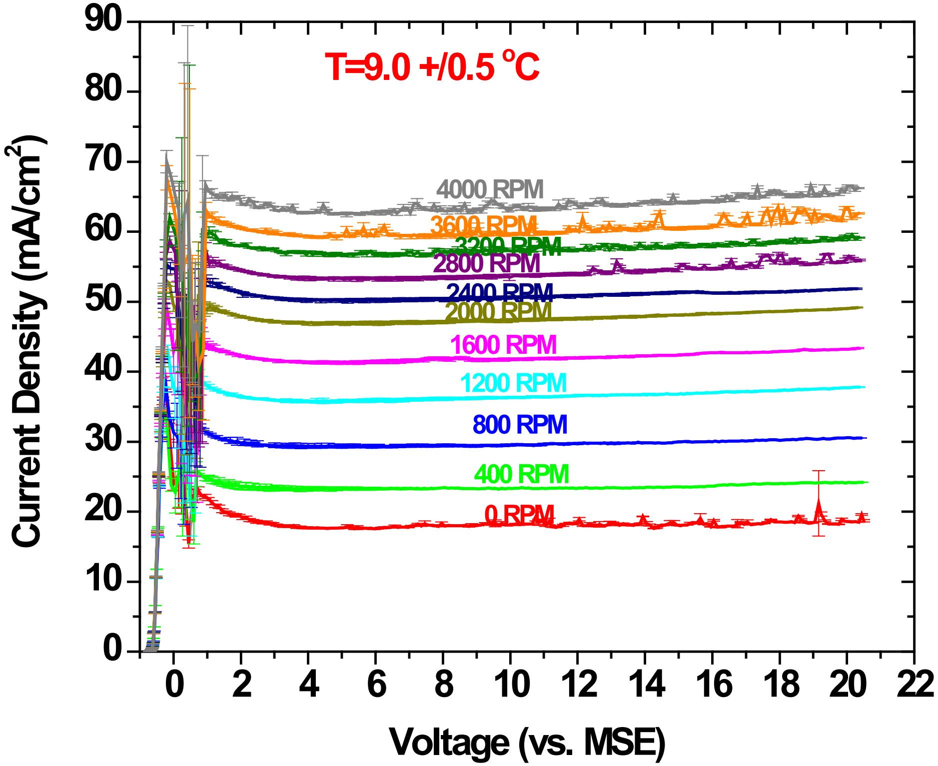
The thickness of the salt film (Nb_2O_5) increases with applied potential (R_p), although the steady-state current does not change: current limited plateau.

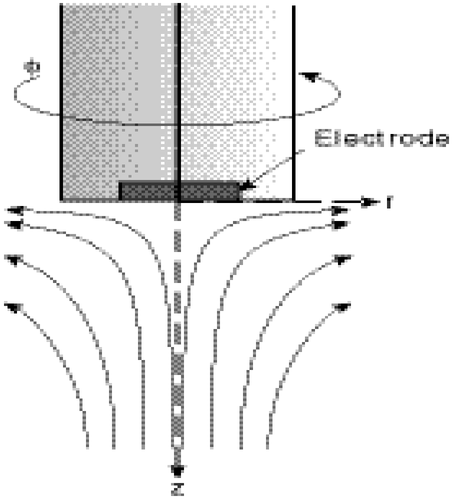
In the diffusion limited mass transfer only circumstance, diffusion is essentially isotropic and independent of the crystallographic orientation and grain boundary of the niobium surface: brightening.

H. Tian, S. G. Corcoran, C. E. Reece and M. J. Kelley, J. Electrochem. Soc. 155(2008), p. D563.

Determination of the Diffusion Coefficient of Rate Limiting Species by Rotating Disk Electrode (RDE)







$$J = 0.62 n F D^{0.67} \upsilon^{-0.166} c \omega^{0.5}$$

Levich equation

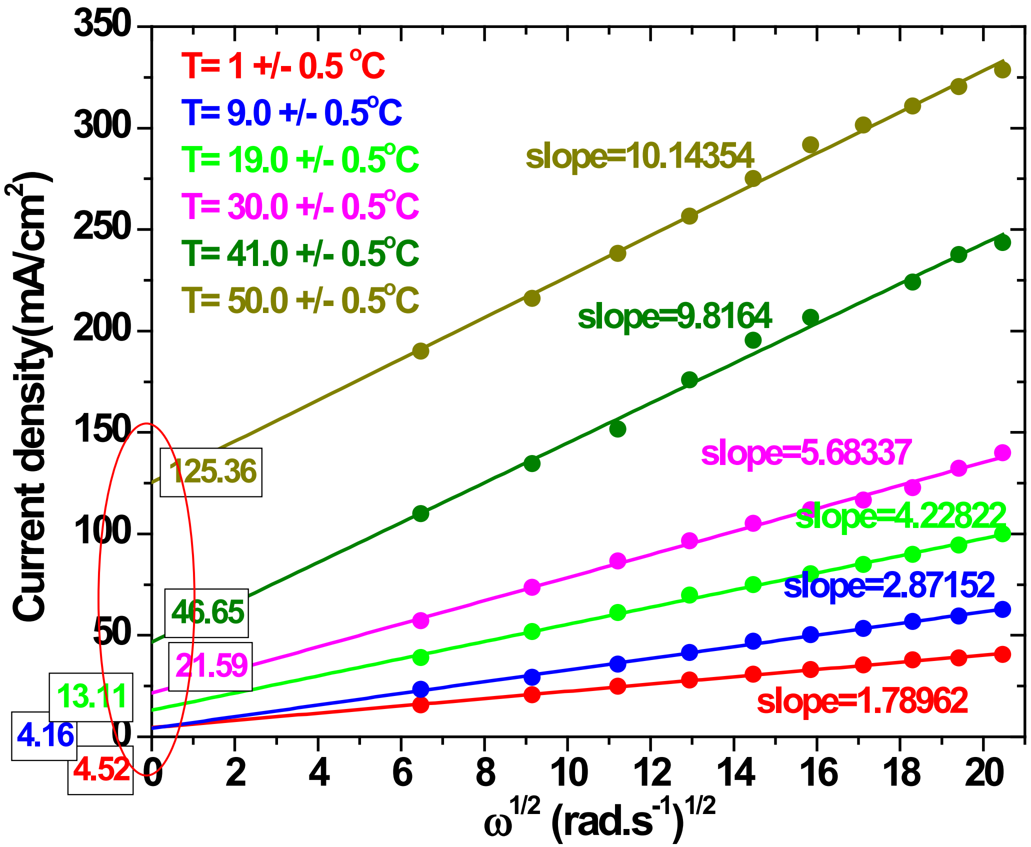
D : *diffusion costant for diffusion limted species*

υ : *kinematic viscosity*

ω : *rotation speed of the electrode*

c : *bulk concentration of diffusion – limited species*

RDE Measurements Indicate a Non-diffusion-limited Kinetics in Parallel and Strongly Depend on the Temperature



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

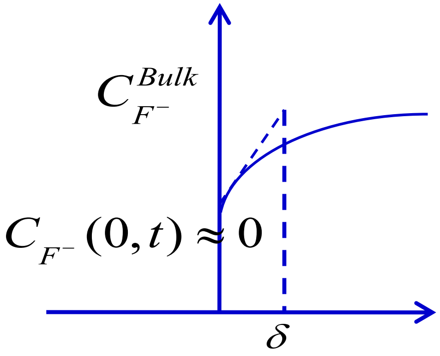
Excellent linear fit provides definitive evidence of diffusion limited process, knowing v and *c* yields *D*.

H. Tian and C. E. Reece, PhysRev-STAB 13, 083502 (2010).

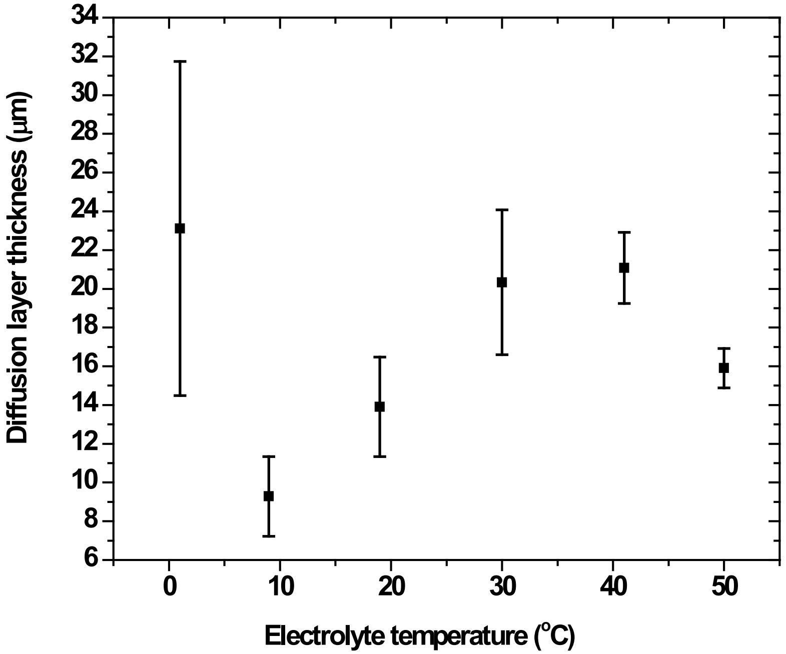
Strong evidence for a temperature dependent kinetics in parallel with the diffusion limited mass transfer process. For best polishing, stay below 20°C.

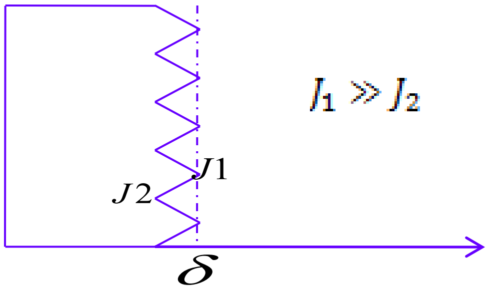
Electrolyte Physical Property and Diffusion Layer Thickness at Different Temperatures

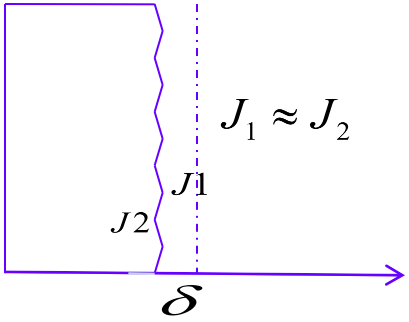
Temperature (C)	Dynamic Visosity (cP)	Diffusion Coefficient(cm²/sec)
0	40.7	2.7E-08
10	34.2	4.4E-08
20	26.3	8.8E-08
30	20.8	1.3E-07
40	18.1	2.8E-07
50	16.5	2.9E-07



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







There exists a F ion concentration gradient within the ~12 µm (20°C) away the surface. Preferential dissolution of protrusions on the order of diffusion layer causes enhanced geometrical leveling. On this scale, initial material removal rate will not be blind to crystallography- no brightening.

Implications of basic understanding of EP
Positive Results from Controlled Light EP After BCP

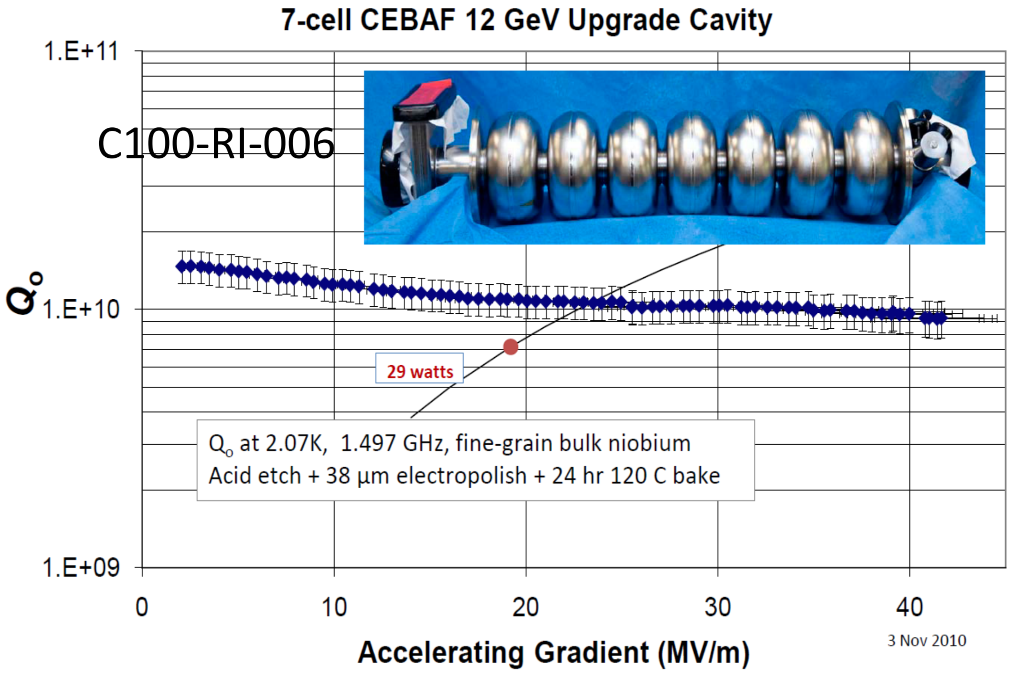
For a well controlled, high reproducibility, efficient, reliable EP process.

✓Control and "minimize" the temperature as much as is practical.

✓Minimize cathode current density, and over-potential (increase cathode surface area, improve reaction kinetics for hydrolysis).

✓Start with surfaces that are consistently smooth below the scale of diffusion layer thickness, such as CBP (if objective is maximally smooth surfaces with minimum chemistry).

✓Manage hydrogen bubbles and other forced or natural convection for maintaining a controlled local surface flow dynamics .

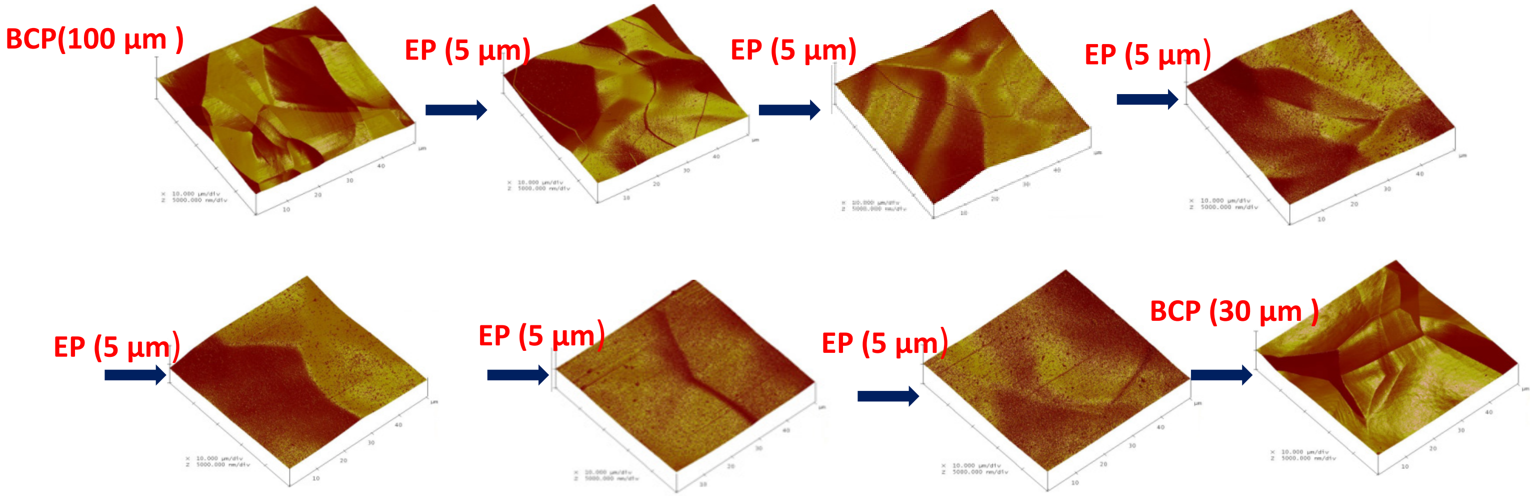


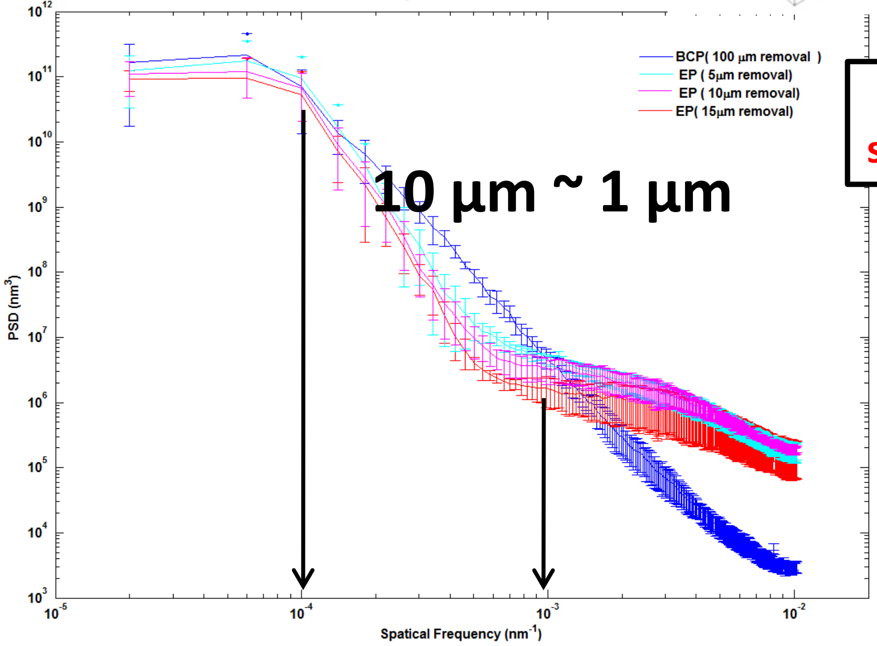
Q_o at 2.07K, 1.497 GHz, fine-grain bulk niobium
Acid etch + 38 µm electropolish + 24 hr 120 C bake

12 GeV Upgrade Project adopts it as an alternated baseline for the 80 cavities, the on-going production progresses steadily.

"Preparation and Testing of the SRF Cavities for the CEBAF 12 GeV Upgrade", TUPO 061, *A. Reilly, T. Bass, A. Burrill, K. Davis, F. Marhauser, C.E. Reece and M. Stirbet.*

Scale-Specific Nb Surface Topographic Evolution During EP



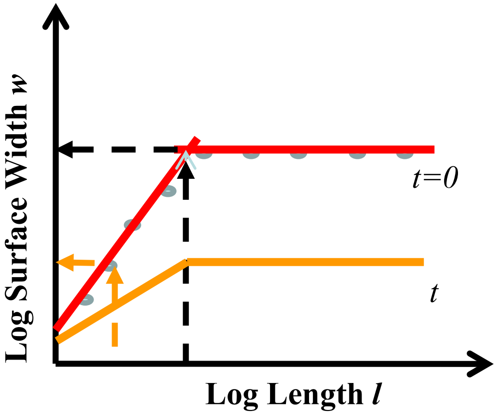


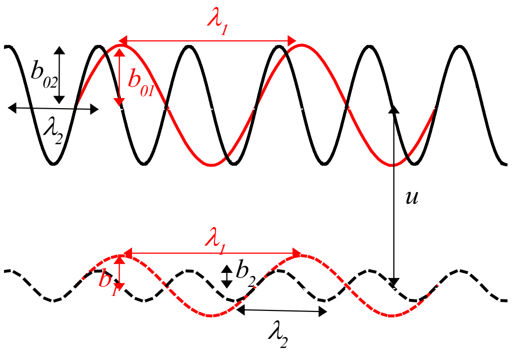
EP is conducted at 14 volts, 20 C with 15 mA/cm2 same condition as Jlab 12 Gev cavity production.

Short duration EP modifies the surface feature with wavelength from 1 µm ~ 10 µm-which might be important for SRF performance improvement.

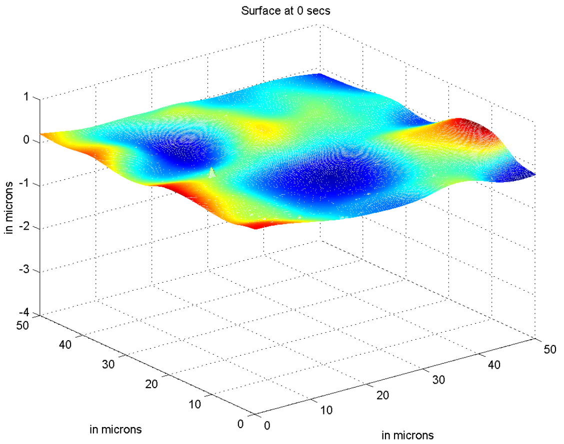
"Characterization of scale-dependent roughness of niobium surfaces as a function of surface treatment processes detailed information", THPO046, C. Xu, H. Tian, C. Reece & M. Kelley .

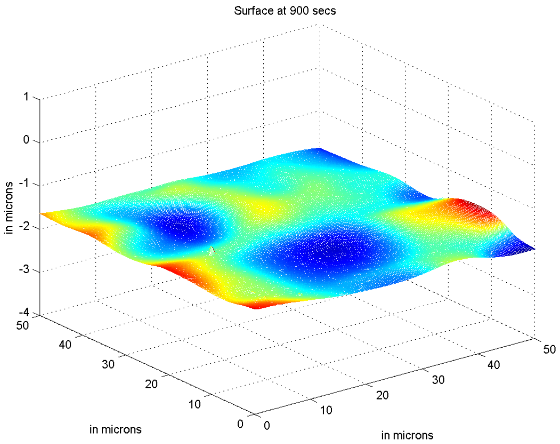
Simulations of the Nb Surface Morphology Evolution During Electropolishing

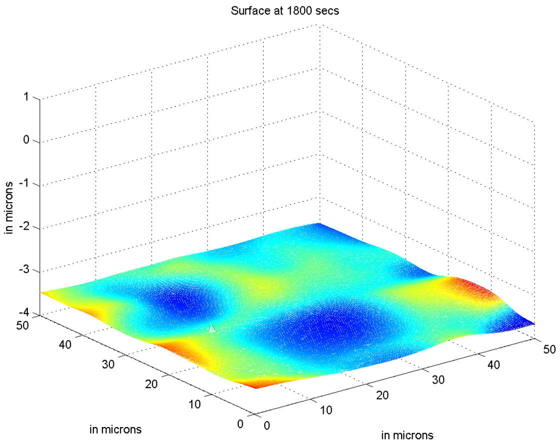




The morphology evolution of Nb surface during the electropolishing is described using a combined approach of scaling analysis and predictions of the electropolishing theory. Establishing the parameters of Nb EP process and the resulting surface smoothening.


Surface at 0 secs

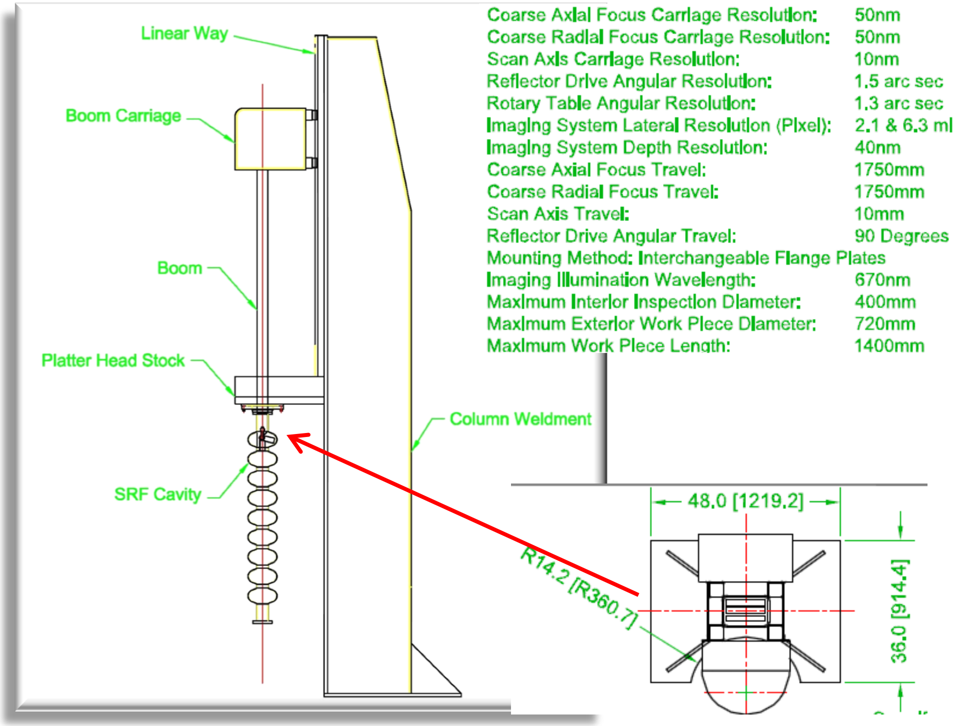

Surface at 900 secs


Surface at 1800 secs

Characterize the topographic transformation function sufficient to gain predictive power over topography as a function of EP time.

"Detailed Nb Surface Morphology Evolution During Electropolishing for SRF Cavity Production" THPO038, H. Tian, C. Reece , Nikhil Dole and Stanko Brankovic .

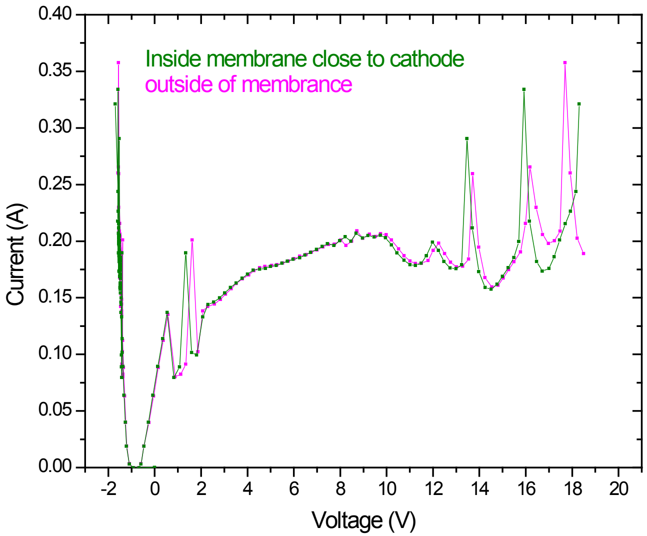
Closing the Loop from Sample Analysis to Single/Multicell Cavities with Internal Cavity Profilometry

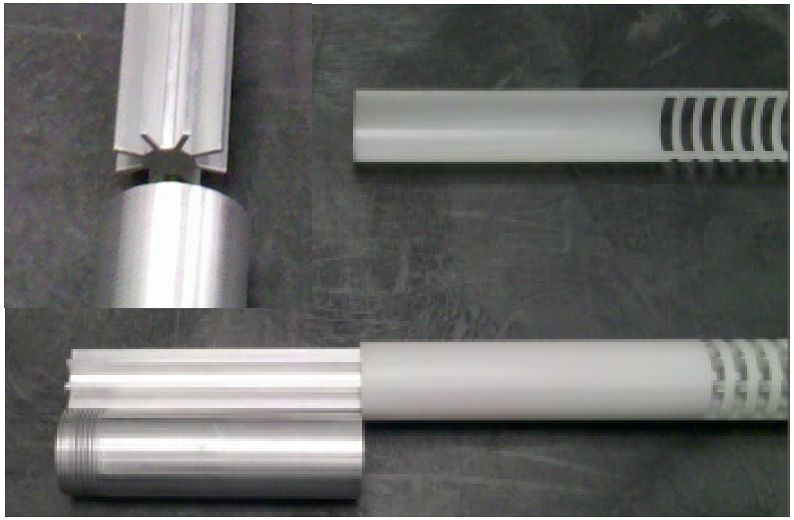


Coarse Axial Focus Carriage Resolution:	50nm
Coarse Radial Focus Carriage Resolution:	50nm
Scan Axis Carriage Resolution:	10nm
Reflector Drive Angular Resolution:	1.5 arc sec
Rotary Table Angular Resolution:	1.3 arc sec
Imaging System Lateral Resolution (Pixel):	2.1 & 6.3 microns
Imaging System Depth Resolution:	40nm
Coarse Axial Focus Travel:	1750mm
Coarse Radial Focus Travel:	1750mm
Scan Axis Travel:	10mm
Reflector Drive Angular Travel:	90 Degrees
Mounting Method: Interchangeable Flange Plates	
Imaging Illumination Wavelength:	670nm
Maximum Interior Inspection Diameter:	400mm
Maximum Exterior Work Piece Diameter:	720mm
Maximum Work Piece Length:	1400mm

Microdynamics internal optical inspection system will be commissioned in this August.
Enable detailed analysis of surface evolution as a function of EP parameters applied to single /multi-cell cavities.
Track specific features/limiting defects through processing, serves as a qualitative and <u>quantitative</u> defect inspection and 3-D surface mapping tool.

Incorporating Lessons Learned into Development of an Integrated Cavity Processing (ICP) System





✓Hydrophobic PTFE membrane proves efficiently blocking hydrogen bubbles created at cathode, and maintains electropolishing process.

✓Spline shape cathode increases cathode area, the introduction of circulation inside of membrane protected cathode drives out hydrogen bubbles without agitation near cavity surface.

✓Commissioning a new, unused cavity chemical processing tool for present VEP studies, and planning to integrate HPR, ultrasonic detergent cleaning, and protected drying in this system in the near future (ICP) -reduce costs and assure appropriate process control -future ILC-like applications

✓ New Jlab infrastructure will be ready for such a tool next year

Our strategy (first step):

1. CBP for consistent, reproducible surface finish and removal of "damage" layer.
2. Minimal (10~20µm) , controlled, low-touch labor EP to expose clean, smooth, crystalline surface.

References:
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7)C. Reece and H. Tian, Proceeding of LINAC2010, Tsukuba, Japan THP010.
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9)C. Wagner*, J. Electrochem. Soc.,* 101, p.225 (1954).
10)F. Family, T. Vicsek, J. Phys. A 18, L75 (1985).

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