

Hui Tian, Charles E. Reece

Thomas Jefferson National Accelerator Facility, Newport News, VA 23606, USA

## Abstract:

Future accelerators, such as the envisioned international linear collider (ILC), require unprecedented cavity performance, which is strongly influenced by interior surface nano-smoothness. Electropolishing (EP) is the technique of choice being developed for high-field SRF cavities. Previous study shows that the EP mechanism of Nb in H<sub>2</sub>SO<sub>4</sub>/HF acid electrolyte proceeds by formation and dissolution of a compact salt film under fluorine diffusion-limited mass transport control [1]. We pursue an improved understanding of the microscopic conditions required for optimum surface finishing. The temperature-dependent viscosity of the standard electrolyte has been measured and, using a rotating Nb disk electrode, the diffusion coefficient of fluorine was measured at a variety of temperatures from 1°C to 50°C. In addition, data indicates that electrode kinetics is becoming competitive with the diffusion limited mass transport and increase dramatically with temperature. These findings are expected to guide the optimization of EP process parameters for achieving controlled, reproducible and uniform nano-smooth surface finishing for SRF cavities.

## Current –Limited Plateau Is

### The Result of Mass-transport Limitation[2]

Mass transport 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

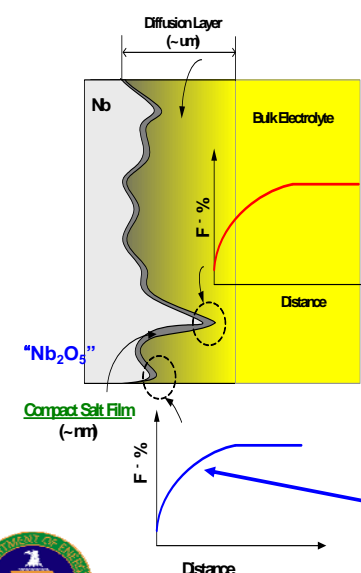
$$J_i(x) = -D_i \frac{\partial C_i(x)}{\partial x} - \frac{z_i F}{RT} D_i C_i \frac{\partial \phi(x)}{\partial x} + C_i v(x)$$

Diffusion, movement of mass transport limited species by a gradient of chemical potential (i.e. concentration gradient  $\frac{\partial C_i(x)}{\partial x}$ )

Convection, natural convection driven by density gradient and forced convection, such as rotating disk electrode (RDE).

Migration, movement of ions driven by a gradient of electrical potential ( $\frac{\partial \phi(x)}{\partial x}$ ).

## The Diffusion-Limited Access of Fluorine To The Salt Film Produces Best Polishing[1]



Sulfuric acid tends to anodize the Nb under polarization potential producing the "compact salt film"- "Nb<sub>2</sub>O<sub>5</sub>".

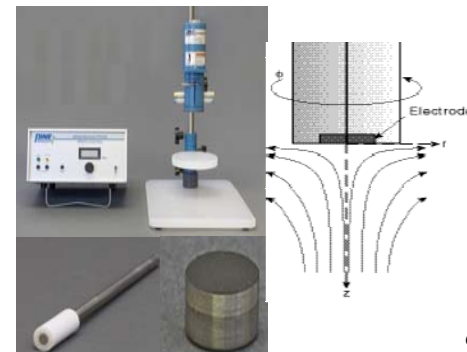
HF acid tends to dissolve the Nb oxide under kinetic control with the "at the surface" concentration of fluorine

F<sup>-</sup> concentration "at the surface" is limited by how fast it diffuses through the electrolyte (~diffusion layer).

The local gradient in fluorine concentration produces the desired polishing action.

Local temperature, flow (stirring) & electrolyte composition affect the local fluorine gradient.

## Determination of the Limited Species Diffusion Coefficient by Rotating Disk Electrode(RDE)



### "Levich equation" [3]

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

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

$$n=1$$

$$F = 96470 \text{ coulomb/mole}$$

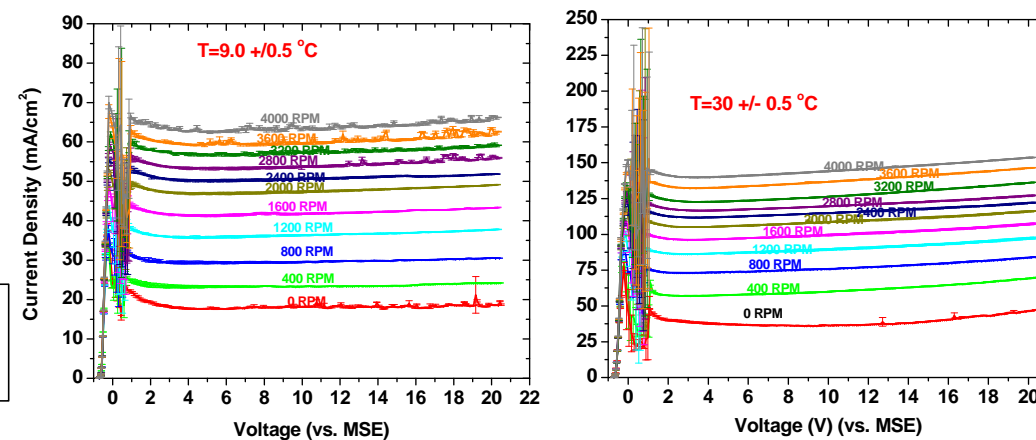
$D$ : diffusion constant for fluorine

$\nu$ : kinematic viscosity

$\omega$ : rotation speed of the electrode

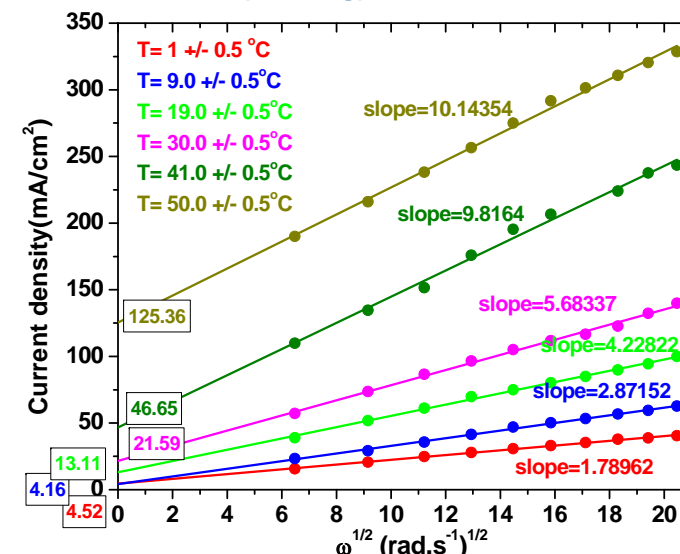
$c$ : bulk fluorine concentration ~ 2.67 mol/l

## I-V Curves of Nb with RDE at Different Temperatures 1°C, 9°C, 19°C, 30°C, 41°C, 50°C



The limiting current density of all of temperatures studied demonstrates a clear dependence on diffusive mass transport.

## Surface Reaction (Etching) vs. Mass Transfer Rate Control.

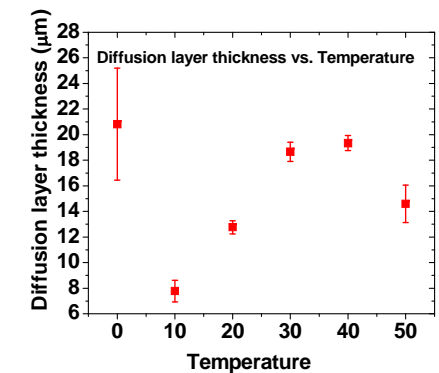
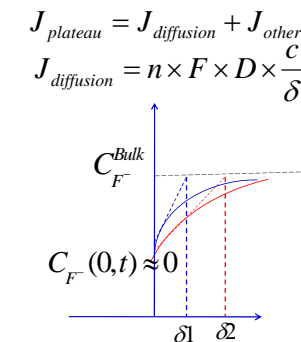


Evidence that an electrode kinetics process proceeds in parallel with the diffusion limited mass transport. The second process is essentially independent of mass flow condition and polarization potential, and strongly depends on temperature.

## The Diffusion Coefficient of Fluorine & The Diffusion Layer

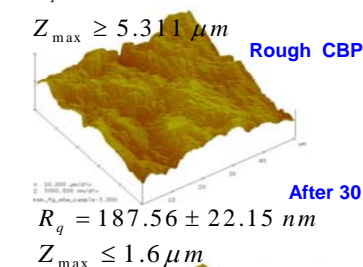
Temperature (°C)	Dynamic Viscosity (cP)	Diffusion Coefficient (cm²/sec)
0	40.7	2.69 E-08
9	34.2	4.44 E-08
19	26.3	8.77 E-08
30	20.8	1.29 E-07
41	18.1	2.83 E-07
50	16.5	2.90 E-07

The electrolyte viscosities were measured with a Brookfield DV-II+PRO digital viscometer and the electrolyte density was measured by weighing the electrolyte in a Teflon volumetric flask.

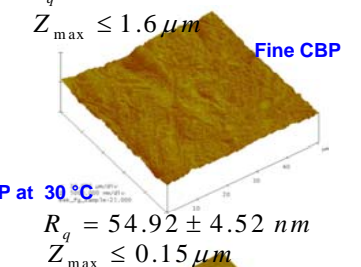


## The Diffusion Limited Mass Transfer Produces the Nano- smooth Surface Finishing

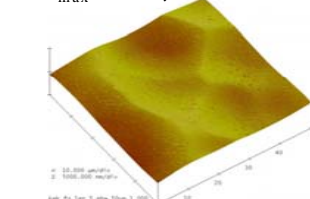
$$R_q = 889.6 \pm 32.55 \text{ nm}$$



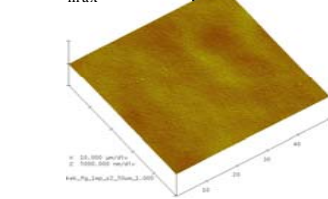
$$R_q = 178 \pm 6.27 \text{ nm}$$



$$R_q = 187.56 \pm 22.15 \text{ nm}$$



$$R_q = 54.92 \pm 4.52 \text{ nm}$$



## Conclusion:

Nb electropolishing was studied using a rotating disc electrode in the standard EP solution under different temperature. The limiting current density demonstrates a clear dependence on diffusive mass transport. However, a parallel electrode kinetics process has been identified, which is essentially independent of mass flow condition and polarization potential, but strongly dependent on temperature. This suggests that high temperature may activate an etching process that recognizes different grain orientations, resulting in a non-uniform surface finishing instead of brightening. The viscosity of the standard HF/H<sub>2</sub>SO<sub>4</sub> electrolyte strongly depends on the electrolyte temperature. The analysis yields effective diffusion coefficient for fluorine on the order of 10<sup>-8</sup>-10<sup>-7</sup> cm².s<sup>-1</sup> under the temperatures studied. This study is expected to improve the fundamental understanding needed to guide the optimization of EP of niobium for SRF cavities.

## References

- [1] H. Tian, S. G. Corcoran, C. E. Reece and M. J. Kelley, J. Electrochem. Soc. 155(2008), p. D563.
- [2] A. J. Bard and L. R. Faulkner, *Electrochemical Methods*, Wiley: New York, 1980.
- [3] V.G. Levich, *Physicochemical Hydrodynamics*, Prentice-Hall, New York, 1962

## ACKNOWLEDGEMENT

This research was conducted at Thomas Jefferson National Accelerator Facility for the Department of Energy under contract DE-AC05-06OR23177

