On the Mechanism of Niobium Electropolishing: Some effects of Gravity and Geometry

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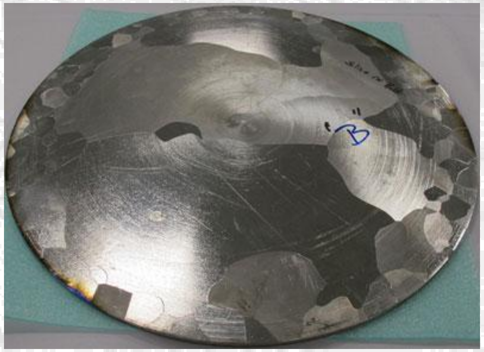

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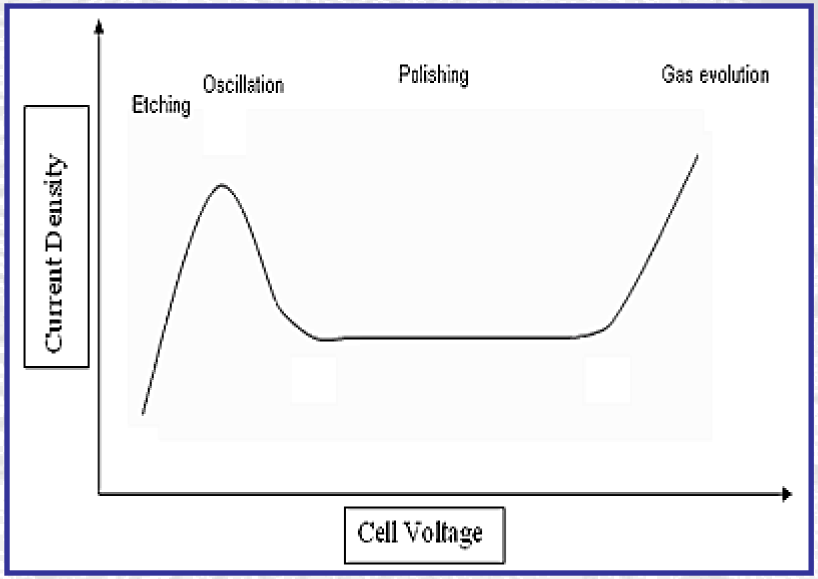
Motivation

- Surface defects like pits, protrusions, and grain boundaries are detrimental to the performance of SRF cavities
- Electropolishing is so far the best technique to get a high quality surface finish
- The electropolishing mechanism for niobium is not very well understood, specially the association of pits with the EBW region
- Interesting to look at the **interface between pure electrochemistry, and its realization in cavity work**

Electropolishing Fundamentals

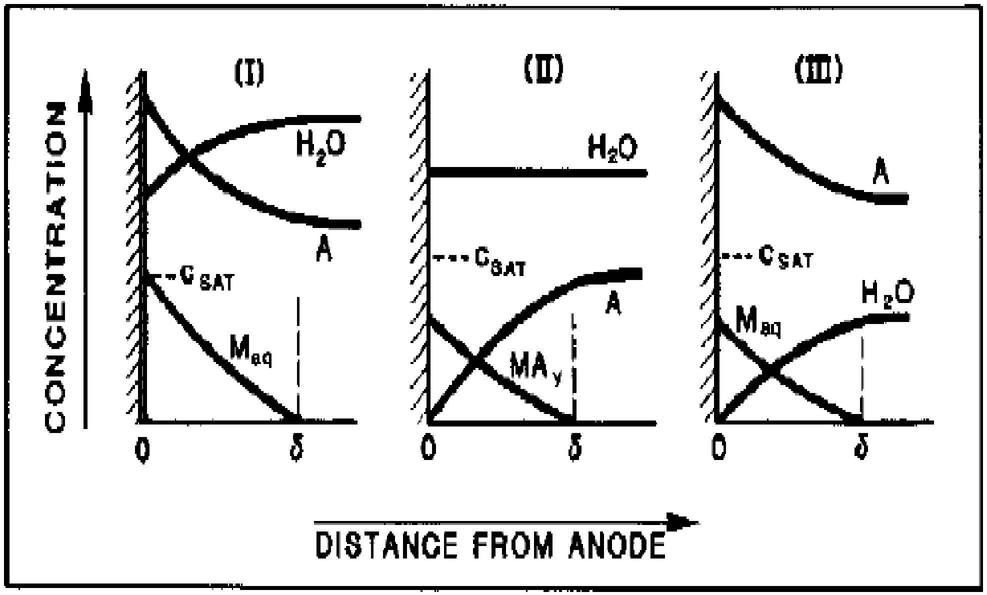
- EP occurs when the metal surface of interest is made anodic (+) in an appropriate solution
- The surface roughness of the finish is much less than that achieved with mechanical polishing
- Polishing is proportional to the local current density ⊥ to the surface of the sample
- The I-V (polarization) curve has etching, oscillation, plateau, and gas evolution regions, EP is carried out in the plateau region
- The current density plateau is observed because of mass transport limitation



A typical electropolishing polarization curve

Possible Mechanisms

Possible mass transport mechanisms[1]



$$i_L = nFD(C_s - C_b)/\delta$$

i_L = Limiting current density

D = Diffusion coefficient of species involved

C_s = Surface conc

C_b = Bulk conc

Salt film – metal ion saturation

Acceptor ion transport limitation

Water transport limitation

1. D.Landolt, Electrochimica Acta, 32,1 (1987)

Probable Reactions Occurring at the Electrodes

At Working Electrode:

Travel to counter electrode and react with e- from Al to form H

Travel to circuit via Nb

(1) Nb oxidizes

$$2\,Nb + 5\,H_2O \rightarrow Nb_2O_5 + 10\,H^+ + 10e^-$$

(2) HF reacts with oxide to give Nb-F species

$$Nb_2O_5 + HF \rightarrow H_2NbOF_5 + HNbF_6 + NbF_5 + 3\,H_2O$$

(3) NbF +sulfuric react

$$NbF_5 + (SO_3,H_2O) \rightarrow NbF_3(SO_3F)_2\,.2H_2O + Nb_2O(SO_4)_4 + S_2O_5F_2$$

Niobium is oxidized to niobium oxide which then dissolves to form niobium fluoride, oxofluoride species, fluorosulfate, oxysulfate and pyrosulfurylfluoride in the presence of sulfuric acid and hydrofluoric acid.

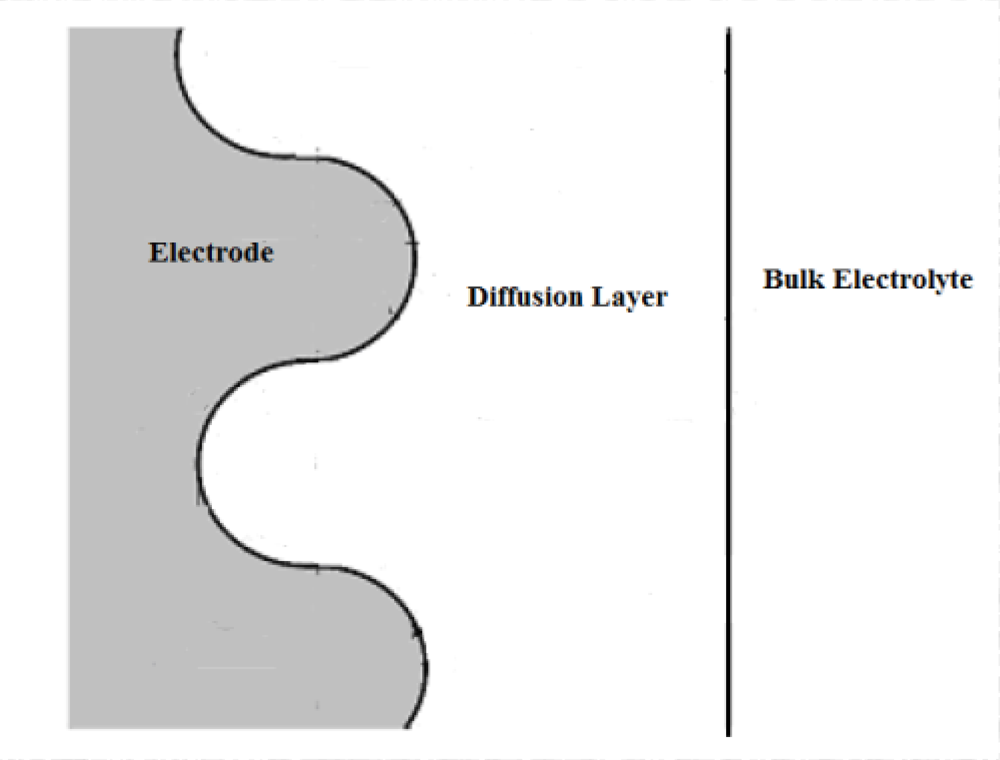
At Counter Electrode:

$$2\,H^+ + 2e^- \rightarrow H_2$$

F.Eozenou, A.Aspart, C.Antoine, and B.Maliki, CARE Report 06-10-SRF. EU Contract number RII3-CT-2003-506395

Electropolishing Effect

In any case, the current flow difference in thick and thin areas causes the polishing occur



$$i_L = nFD(C_s - C_b)/\delta$$

- Diffusion layer thickness (δ) is different over protrusions and valleys.
- Dissolution current density over protrusions is higher than in valley, resulting in leveling effect

Our Schematic Bath for Nb EP

- Working Electrode: High purity polycrystalline Nb (99.999%)
- Counter Electrode: High purity Al (99.99%)
- Reference Electrode: mercurous sulfate electrode (MSE)
- Electrolyte: HF(48%)+ H_2SO_4(96%) in 1:9 vol ratio

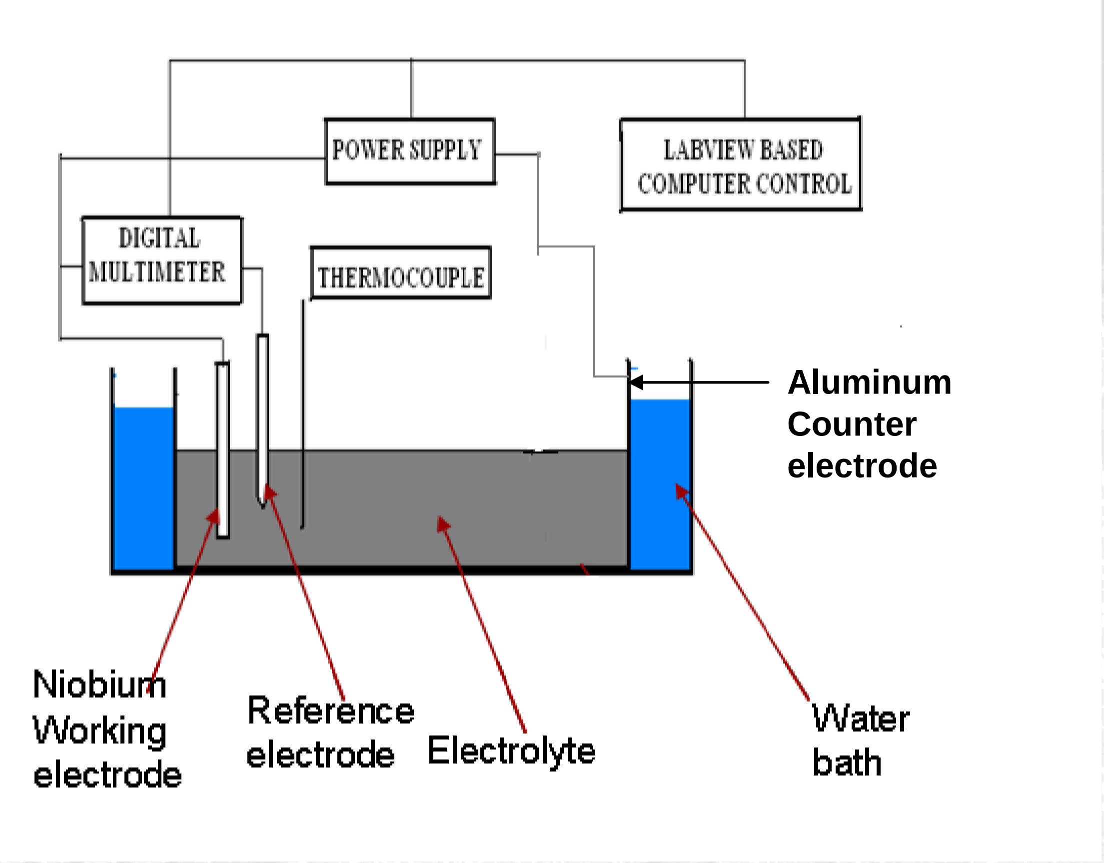
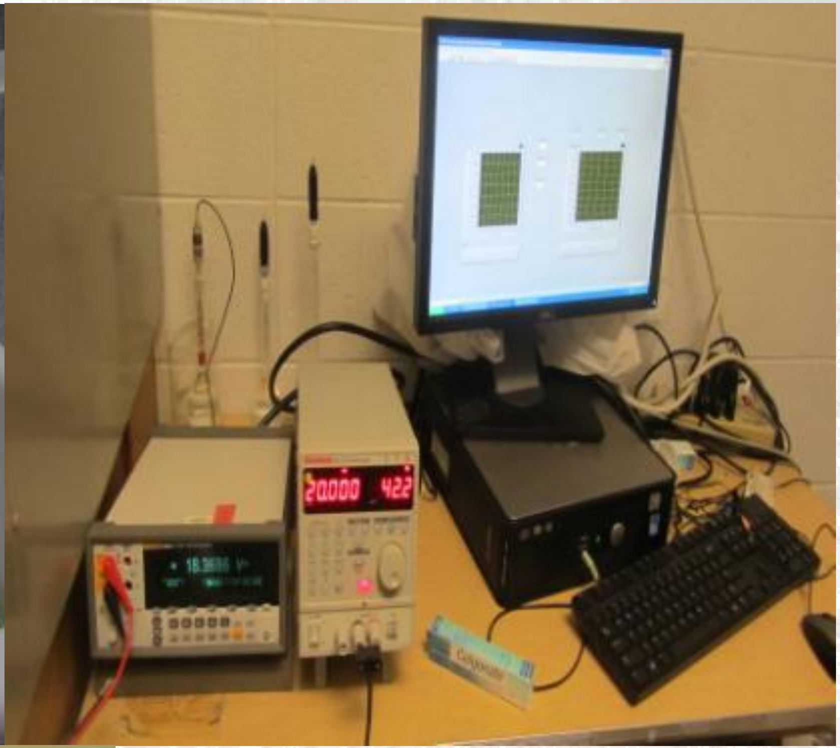
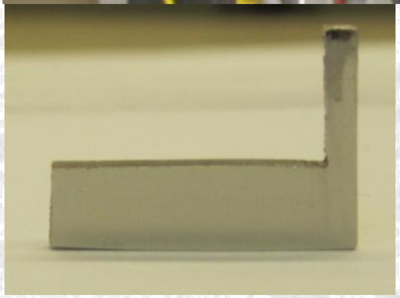
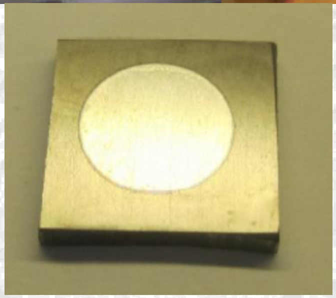


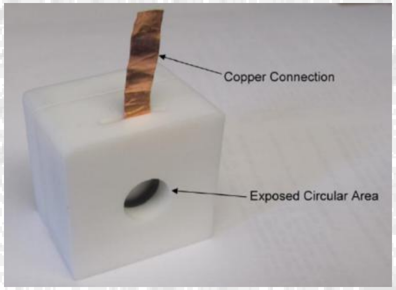
Fig: Schematic of the experimental setup.

Experimental Setup



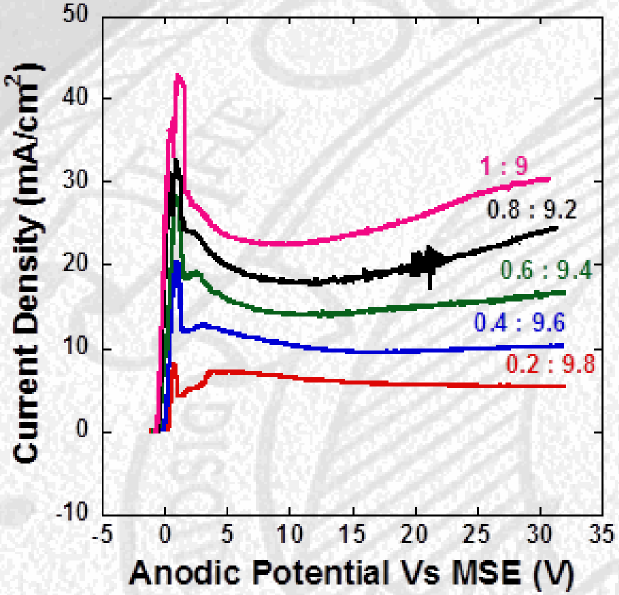






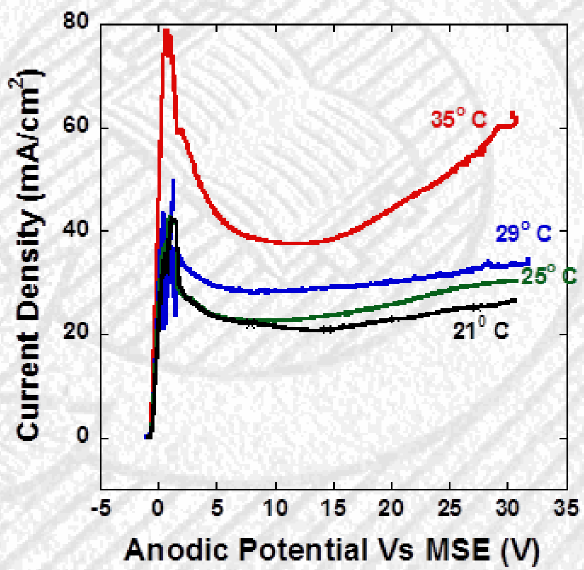
Replicating Acid Ratio/Temperature, and stirring results in our set-up

By know well known effect of acid ratios, T, and agitation

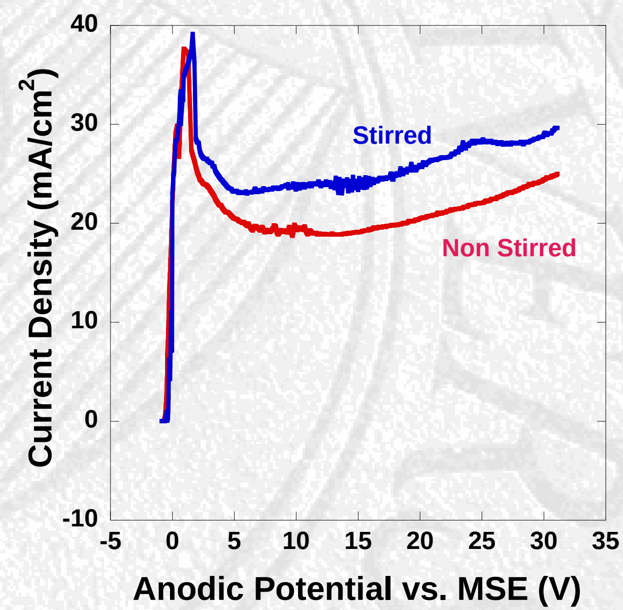


Effect of $HF:H_2SO_4$ ratio

Effect of temperature



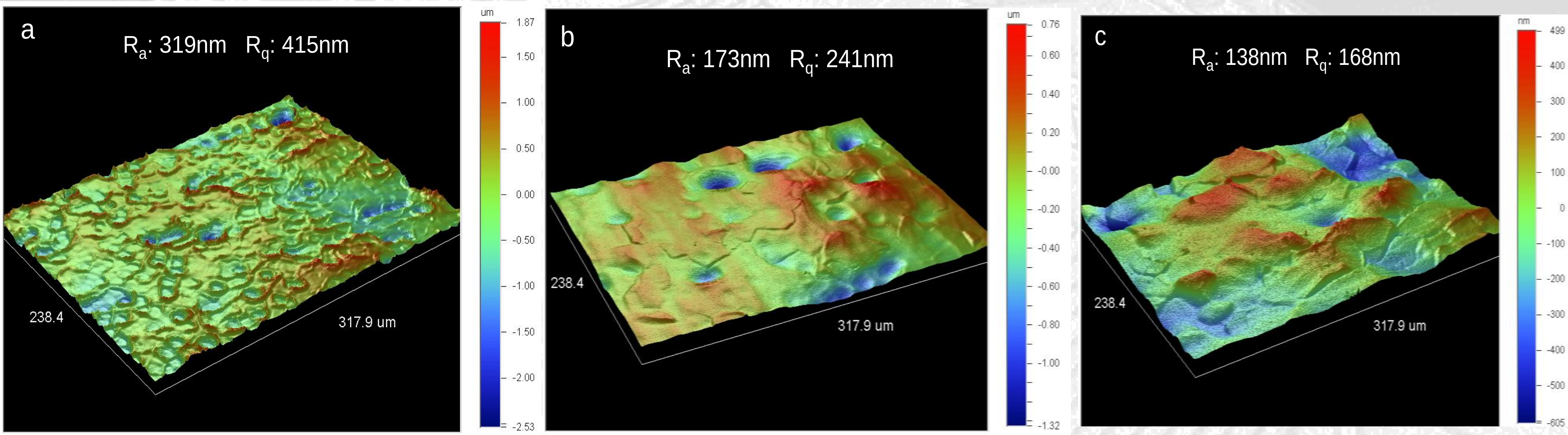
Effect of bath agitation



Note: Effect of $[F^-]$ supports acceptor limited model

Verification of Evolution of surface roughness with EP time

V= 15V, T= 26C, $HF:H_2SO_4 \rightarrow 1:9$



EP time: 2 h EP time: 4 h EP time: 6 h

Surface changes from scalloped appearance after 2 h of electropolishing to a relatively smoother surface after 6 h of polishing.

A novel approach to characterizing the surface topography of niobium superconducting radio frequency (SRF) accelerator cavities
Hui Tiana,b, Guilhem Ribeill a,c, Chen Xub, Charles E. Reecea, Michael J. Kelleya,b,*

PHYSICAL REVIEW SPECIAL TOPICS - ACCELERATORS AND BEAMS 14, 123501 (2011)

Enhanced characterization of niobium surface topography

Chen Xu,[1,2] Hui Tian,[1] Charles E. Reece,[1] and Michael J. Kelley[1,2]

Fluorine diffusion limited mass transport control

- What's controlling process?

Proceedings of PAC09, Vancouver, BC, Canada WE5PFP058

BASIC ELECTROPOLISHING PROCESS RESEARCH AND DEVELOPMENT IN SUPPORT OF IMPROVED RELIABLE PERFORMANCE SRF CAVITIES FOR THE FUTURE ACCELRATORS*

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PHYSICAL REVIEW SPECIAL TOPICS - ACCELERATORS AND BEAMS 13, 083502 (2010)

Evaluation of the diffusion coefficient of fluorine during the electropolishing of niobium

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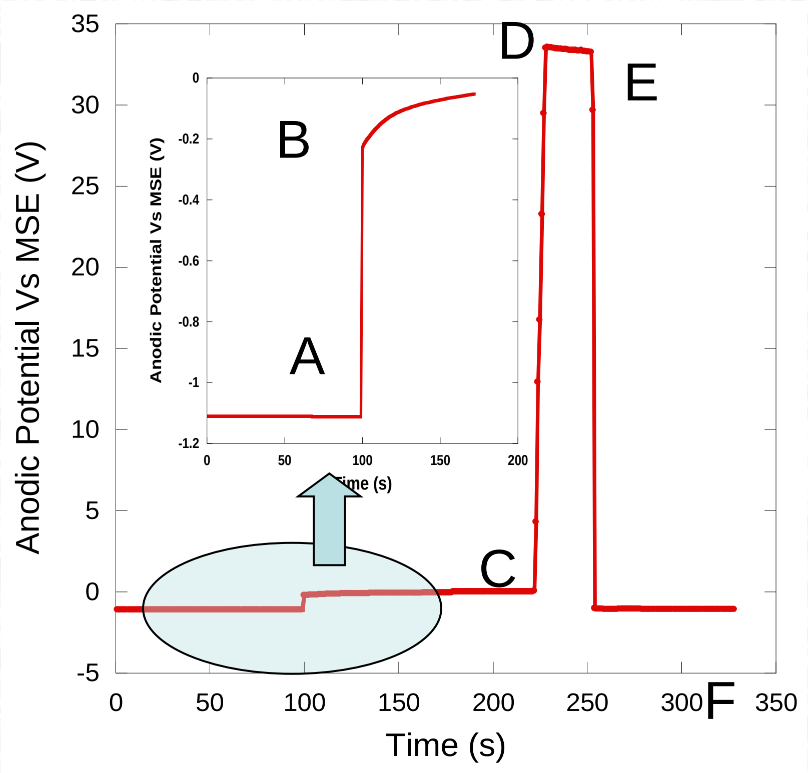
(Received 30 November 2009; published 25 August 2010)

Potential Transients

Galvanostatic experiments help identify EP mechanism.

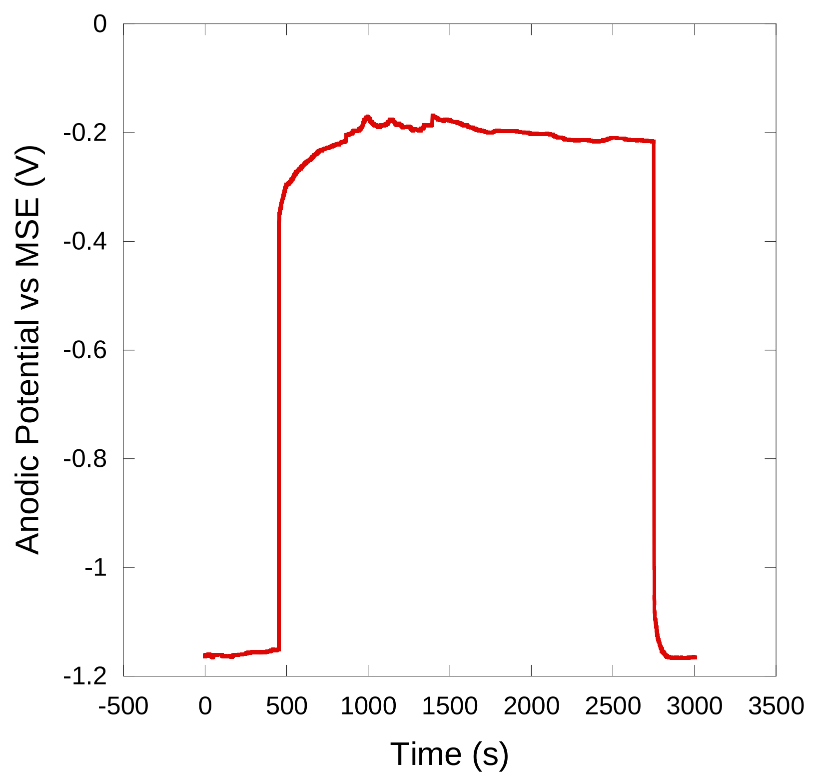
Application of Current at or Above Limiting Current Density Value



- Current switched on at A and switched off at E
- AB: Ohmic overpotential and rapid charging of double layer
- BC: Activation and concentration overpotential
- CD: Potential spike due to fluoride ion concentration going to zero at electrode surface

Potential Transient

Application of Current Below Limiting Current Density Value



- Huge spike in potential not obtained.
- Fluoride ion concentration at surface does not fall to zero.

Potential Transients to Identify the Mechanism Involved

- Sand's equation describes time to reach a particular surface concentration for semi-infinite 1-D diffusion:

$$\sqrt{\tau} = \frac{nF}{2i} C^{o}_{acceptor} \sqrt{\pi D_{acceptor}}$$

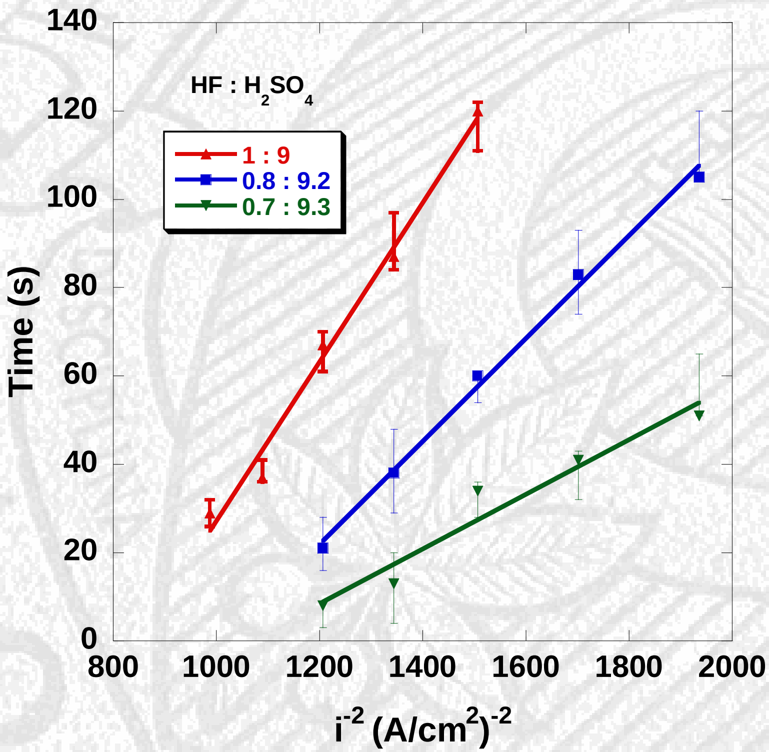
τ - transient time at which potential spikes

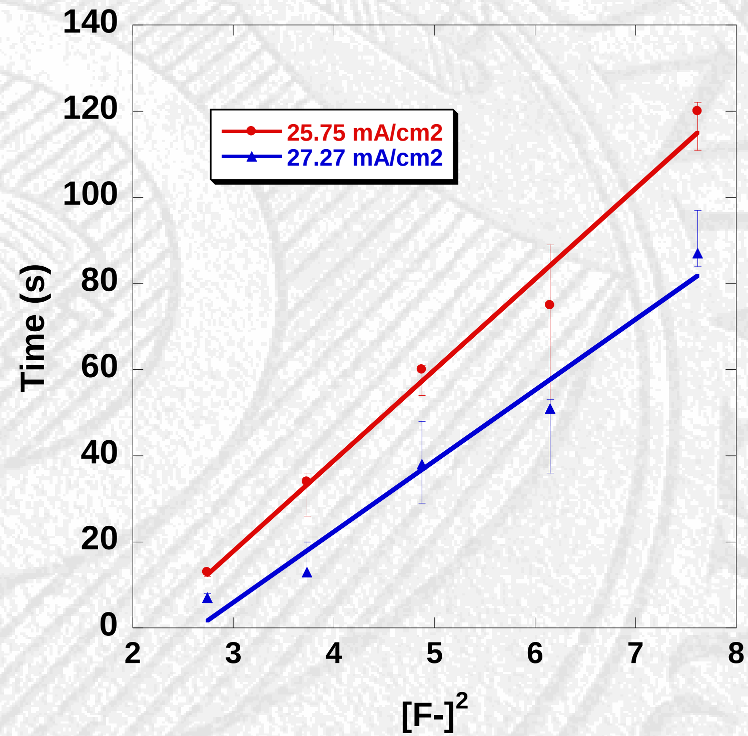
$C^{o}_{acceptor}$ - concentration of acceptor species in bulk electrolyte

$D_{acceptor}$ - diffusion coefficient of acceptor species

Effect of Current Density and Acceptor Ion Concentration on the Induction Time

$$\sqrt{\tau} = \frac{nF}{2i} C^{o}_{acceptor} \sqrt{\pi D_{acceptor}}$$

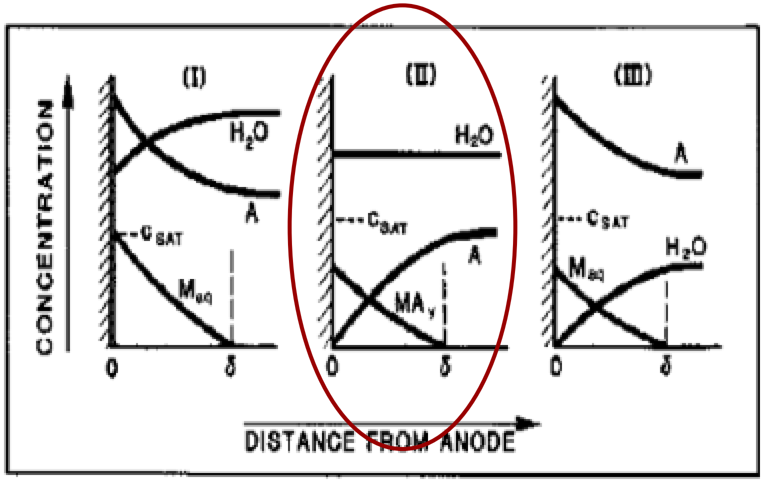




- Expected dependencies observed consistent with acceptor mechanism

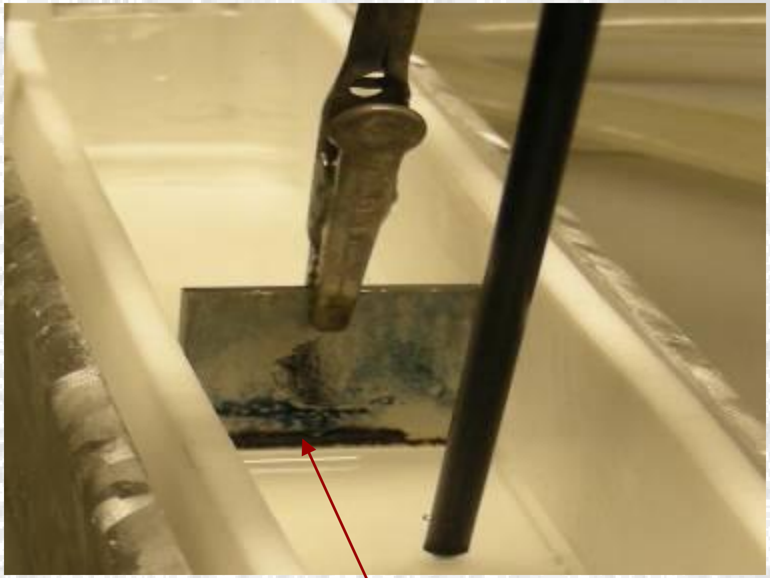
Evidence of Possible Gravity-driven Convective Effects

- Visual evidence of some form of viscous layer formation.
- Bluish-green colored layer which vanishes as soon as the power supply is turned off.



Evidence of the presence of surface film while Niobium electropolishing

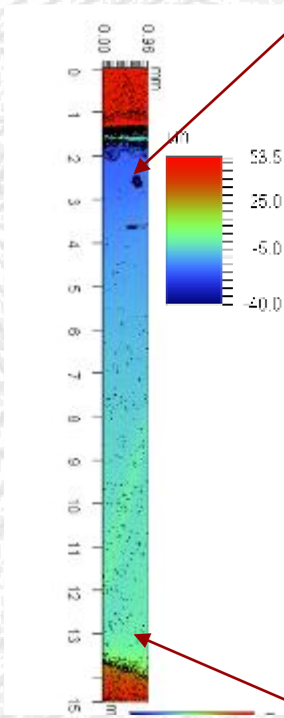
- A mass transport limited current plateau is necessary for electropolishing to take place
- There are evidences of some form of film formation on the surface through which there is diffusion limited transport of ions involved in polishing mechanism
- The surface film formed is soluble and dissolves in the electrolyte on switching off the current



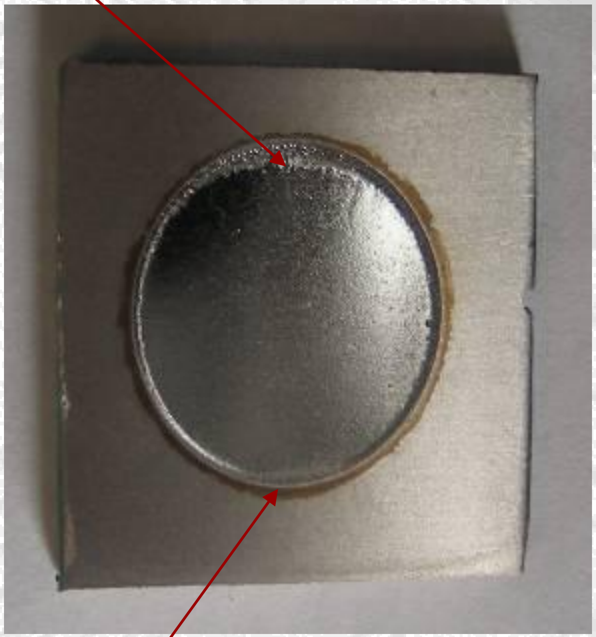
Surface Film formed during electropolishing

Evidence of the presence of surface film while niobium electropolishing

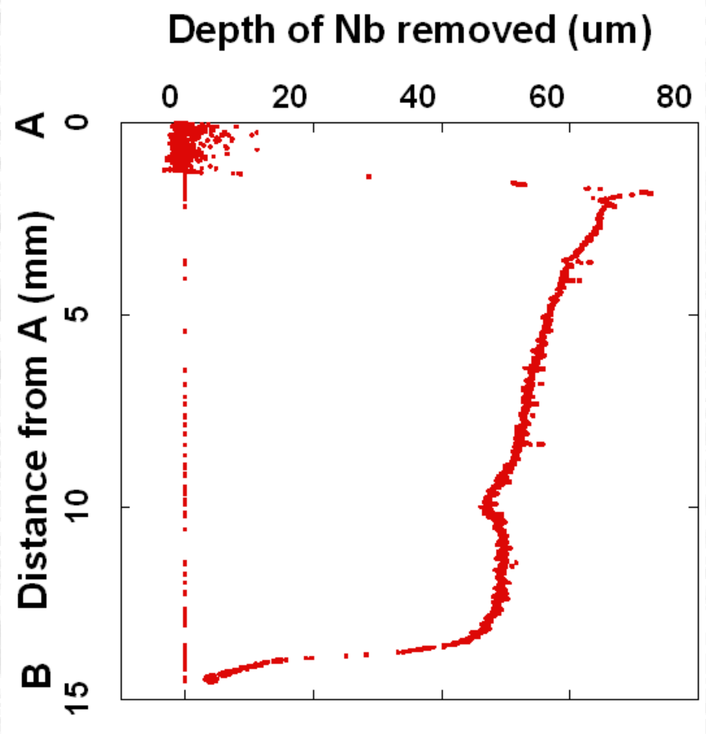
- There is an effect of gravity on the film
- Thinner film at the top of the sample because of hydrodynamics
- Higher dissolution rate at the top of the sample

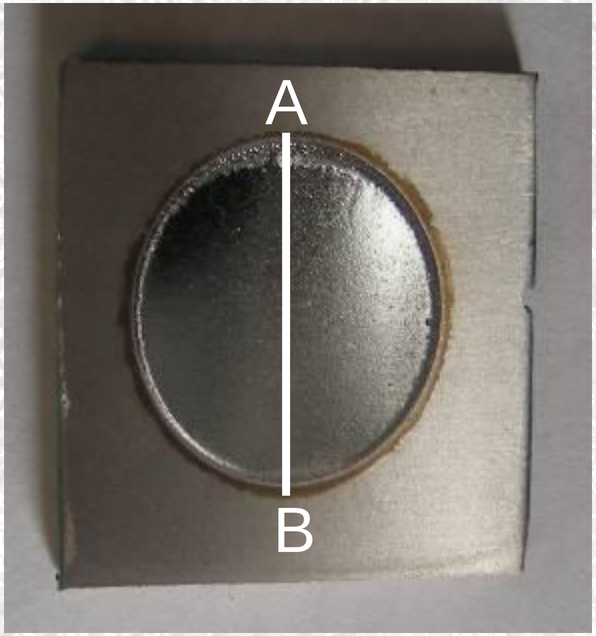


0.96mm by 15 mm



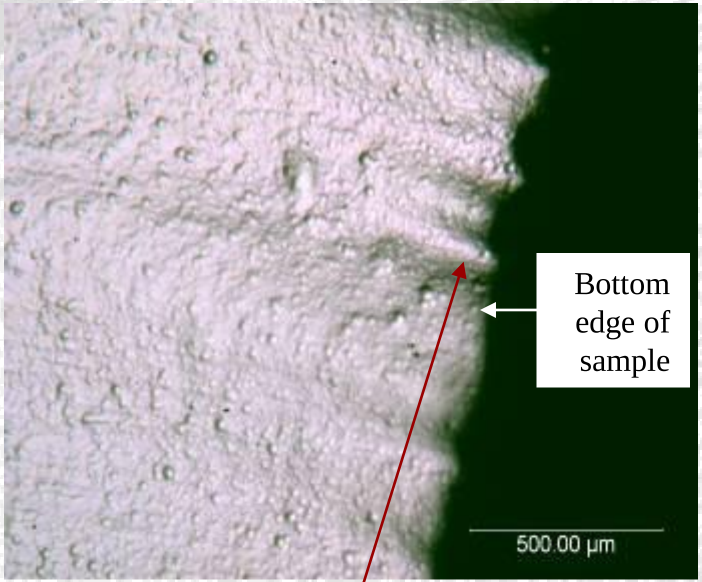
Evidence of Possible Gravity-Convective Effects



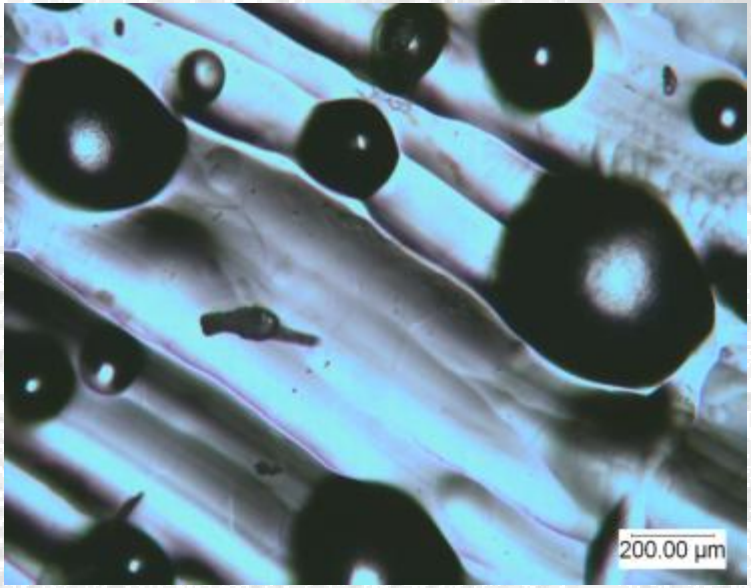


- Natural, gravity driven convection results in thinner diffusion layer at top of sample, hence higher dissolution rate

Evidence of Possible Convective Effects



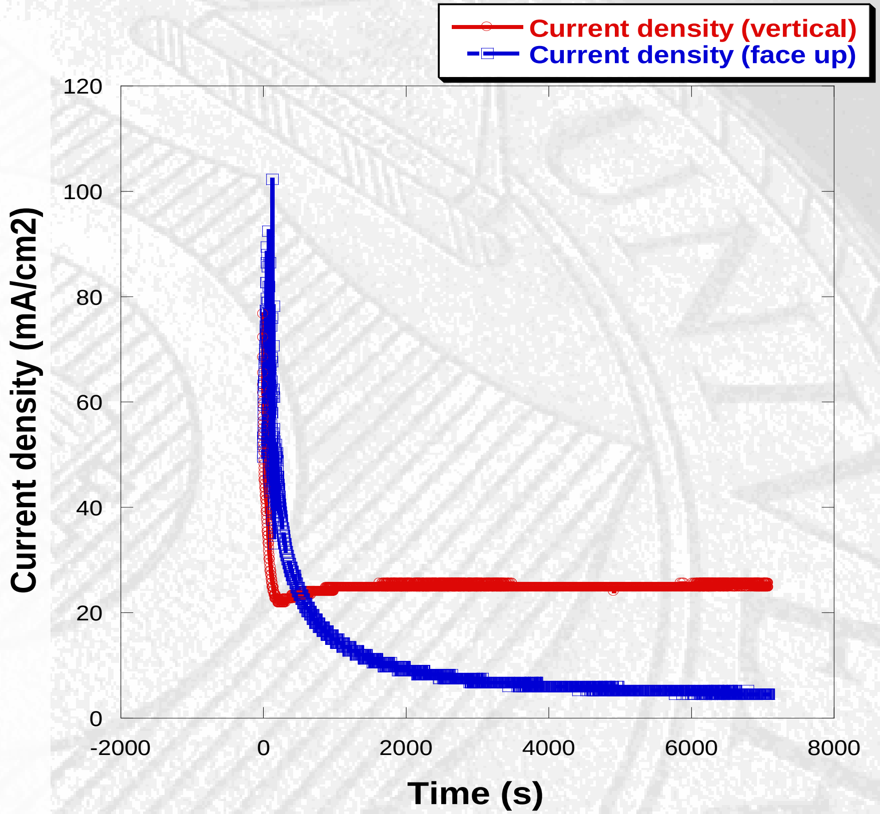
Ridges close to bottom edge of sample due to convection caused by dissolution products (sliding of the film under gravity)



- Pits at surface of flag electrode that was facing down.
- Possibly: Gravity + convection of film prevented the formation of a stable film and hence pitting instead of electropolishing
- Selective dissolution resulted in pitting

Surface film, gravity, convective effects and EP rate for EP "face up" and vertical Flag

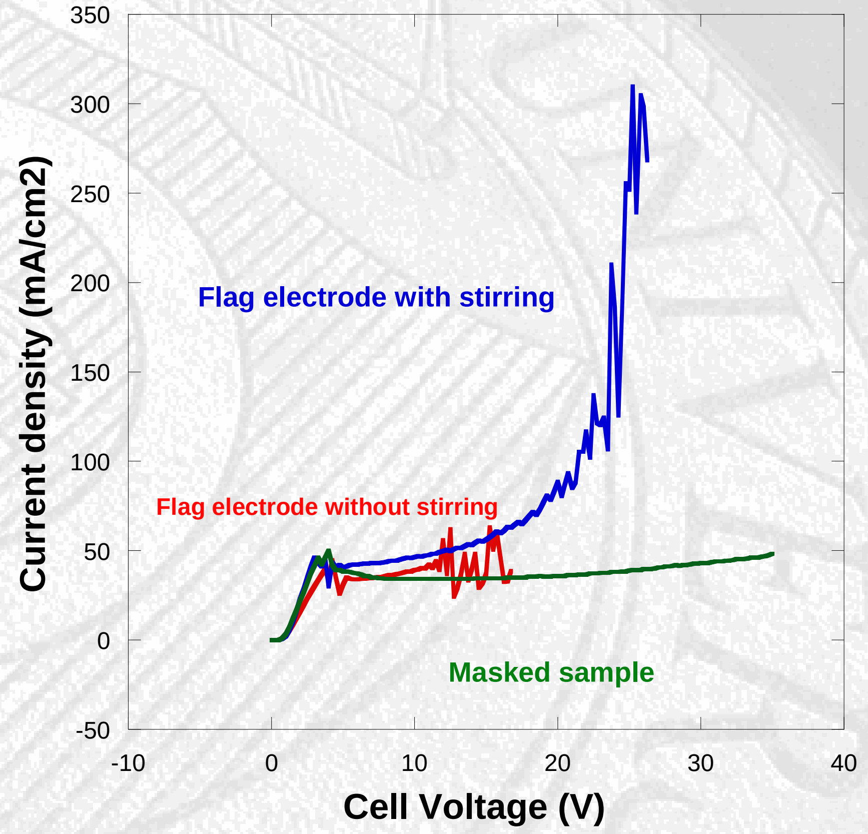
- EP rate should depend on film thickness
- Film is weakly held on and may be affected by gravity
- SO –current density vs time was measured for a films only exposed to the EP bath on top and bottom surfaces, respectively
- The face up configuration (blue) had a very low current density and polishing rate (thick film)
- The vertical configuration (red) had a relatively high current density and polishing rate



I vs *t* for EP done at 15V for 2 hours at 26^{o}C

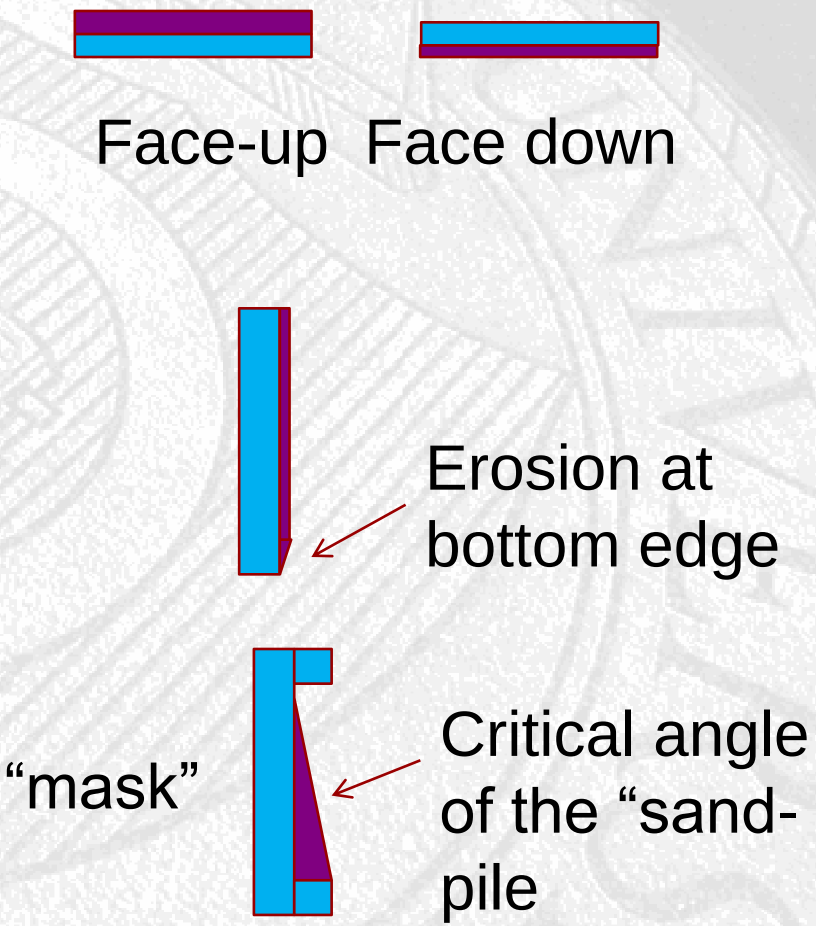
Surface film and polarization curve instability ("noise") during niobium electropolishing of VERTICAL flag

- Film thickness increases with the applied potential till it falls under its own weight
- Formation and re-dissolution of the film causes current oscillation – may well be chaotic (in the physics sense)
- Stirring causes the film to remain thin, weight could be supported till relatively higher potential
- No oscillations in case of electropolishing of masked sample due to controlled hydrodynamics at the surface



Surface (viscous) film, gravity, and EP rate for EP “face up” and “face down”

- Assume weakly adhering surface film
- Gravity assist in “face up” mode leads to thick films
- Gravity “attack” in “face down” mode leads to thin films
- Un-masked vertical films may show preferential attack at bottom edges
- Masked vertical films extra support for film at bottom edge



How will this play out in a cavity as it is polished?

- Will topology of the surface be an issue in any gravity and convection moderated effects?

HYDRODYNAMIC THERMAL MODELING OF 9-CELL ILC CAVITY ELECTROPOLISHING AND IMPLICATIONS FOR IMPROVING THE EP PROCESS *

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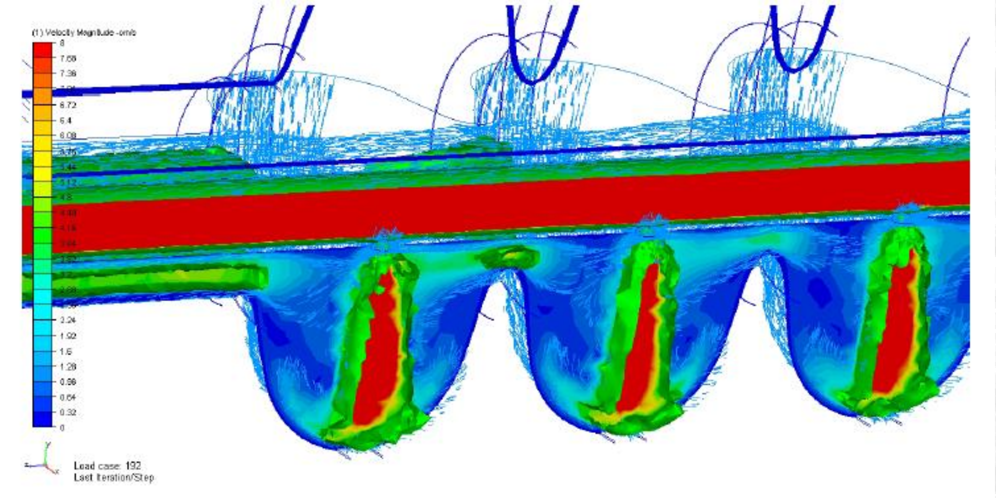

Summary-Conclusions

- Set up made for EP under very controlled temperature conditions
- Standard Temperature, acid, surface roughness results demonstrated with our set-up
- Galvanostatic experiments suggest that mechanism controlling EP of Nb is transport of fluoride ions to surface.
- Natural convection and gravity effects seem to be present – how important are these?

Ongoing work

- EP for Nb samples with welds
- As-received and samples with weld bump removed
- Samples of both types in different orientations and convection conditions to investigate possible film/gravity effects
- Localized EP across the welded regions and the HAZ