

# NOVEL CHARACTERIZATION OF THE ELECTROPOLISHING OF NIOBIUM WITH SULFURIC AND HYDROFLUORIC ACID MIXTURES\*

H. Tian<sup>+#</sup>, S. G. Corcoran<sup>\*</sup>, M. J. Kelley<sup>+#</sup>, C. E. Reece<sup>+</sup>

<sup>#</sup>Applied Science Dept., College of William and Mary, VA 23187, USA

<sup>+</sup>Thomas Jefferson National Accelerator Facility, VA 23606, USA

<sup>\*</sup>Material Science & Engineering Dept., Virginia Tech, VA 24060, USA

## Abstract

Niobium surfaces are commonly electropolished in an effort to obtain optimally smooth surfaces for high-field SRF cavity applications. We report the first use of controlled electrochemical analysis techniques to characterize electropolishing of Nb in a sulfuric and hydrofluoric acid electrolyte. Through the use of a reference electrode we are able to clearly distinguish the anode, cathode polarization potentials as well as the electrolyte voltage drop that sum to the applied power supply voltage. We then separate the temperature and HF concentration dependence of each. We also report the first use of Electrochemical Impedance Spectroscopy (EIS) on this system. EIS results are consistent with a presence of a compact salt film at the Nb/electrolyte interface that is responsible for the limiting current. Microscopic understanding of the basic Nb EP mechanism is expected to provide an appropriate foundation with which to optimize the preparation of high-field niobium cavity surfaces. The implication of EIS for monitoring Nb surface during electropolishing shows this technology could be potentially used as a source of on-line feedback.

## INTRODUCTION

Electropolishing (EP) is believed to be an effective technique to treat niobium cavity surface for achieving reproducible high performance SRF cavities [1]. Current cavity EP process was inherited from Siemens in the 1970's [2] and was further developed by KEK in collaboration with Namura Plating [3].

Typically, a mixture of hydrofluoric (49%) and sulphuric acid (95 ~98 %) of volume ratio of 1 : 9 was used with a temperature range of 30 °C ~ 40 °C, and a current density 40 ~ 50 mA/cm<sup>2</sup> with applied voltage of 10~20 volts. Nb electropolishing is a common electrochemical process; however, the underlying electrochemical reaction at the Nb-solution interface has not been fully understood.

Previous EP studies have shown that the best polishing condition occurs in the limiting current plateau of the polarization curves. Parameters such as electrolyte temperature, acid concentration, viscosity and stirring have strong effects on the EP process [4]. Some studies conducted on either small samples or half cell tried to

evaluate the influence of each parameter [1, 4]. However, the application of electrochemical techniques are needed for the development of a clear picture of the exact role of each parameter involved during the EP process

Electrochemical Impedance Spectroscopy (EIS) is a proven technique for identifying the active electropolishing mechanism. EIS is a method in which a small variable ac signal is applied to the electrode on top of a controlled dc potential; impedance as a function of frequency is recorded and used to characterize the Nb interface and electrochemical processes [5].

The surface removal of more than 100 μm post fabrication has been used practically for Nb SRF cavities for reproducible high performance through a number of cavity studies; however due to the complex shape of cavity and practical chemical treatment facility, no direct characterization technique has existed to monitor surface changes during cavity production. Studies show that as the roughness was increased, a deviation of the impedance characteristics from the vertical and a decrease in double layer capacitance were observed [6]. This technique might be suitable for use as an on-line feedback mechanism.

In this study, we determine the separation of the power supply voltage into three components: (1) applied potential at the anode-Nb, (2) applied potential at the cathode-Al and (3) potential drop in the electrolyte. These results are used to reveal the local effects of the temperature, solution concentration and flow condition on Nb electropolishing. The electrochemical impedance of the Nb EP process has been measured as a function of potential and flow rate. The mechanism of Nb electropolishing is discussed, and the use of EIS in electropolishing for potential on-line feedback also has been explored.

## EXPERIMENTAL PROCEDURE

### Three-Electrode Set-up

High purity polycrystalline Nb slab was embedded into a Teflon sample holder that precisely controls the reactive surface area. High purity Al with surface area fraction either 0.1 or 0.5 of Nb surface area was positioned with separation from the Nb of about 98 mm, a typical distance between the equator cavity wall and Al tube during cavity EP processing. A saturated mercury-mercurous reference electrode (MSE) was placed 10 mm from the Nb sample. The electrolyte used is a typical mixture of hydrofluoric (49%) and sulfuric acid (95 ~98%) by volume ratio of 1:9. In order to protect the reference electrode from HF

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contamination, the reference electrode was placed in an electrode bridge tube with a Vycor frit. The electrode bridge tube was filled with 1 M H<sub>2</sub>SO<sub>4</sub> as conductive electrolyte. Figure 1 shows the EP cell set up and data acquisition scheme.

The polarization curves were measured at a scan rate of 0.25 volts/sec over range of the potential from 0 to 20 volts (using a Sorensen DCS 33-33E power supply), while the potential between Nb and reference electrode was recorded by a Keithley 6517A electrometer. The current was recorded by a HP 3478A multimeter. The data acquisition system was supported by a customized LabView program.

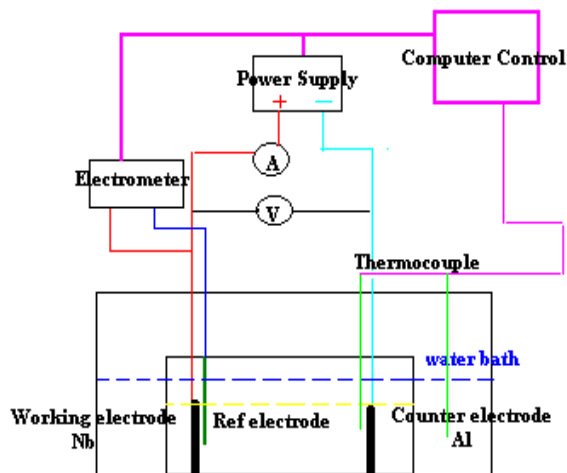


Figure 1: The EP set up and data acquisition scheme.

For clarity, the voltage displayed on the polarization curves in this study is relative to the reference electrode. Prior to the polarization measurement, the electrodes were immersed in the bath at the open circuit for 3 to 5 min. A typical polarization curve is indicated in Figure 2. The anode polarization curve is shown in red and the cathode polarization curve is shown in blue. Several features are noteworthy: the cathode exhibits a well-behaved polarization resistance. We believe that the polarization potential developed across the cathode resistance and the associated power deposition has not been previously identified in the niobium electropolishing configuration. The potential drop across the electrolyte itself is purely resistive, the bath resistivity is measured to be  $\sim 8 \Omega\text{-cm}^2/\text{cm}$  with  $T_{\text{bath}} = 32 \text{ }^\circ\text{C}$  by placing the reference electrode at the different position between anode-Nb and cathode-Al. For a typical cavity polishing condition of 15 V (power supply) with similar materials, the anode polarization potential would then be about 9 V, the cathode about 4 V, and the potential drop in the solution 1 -2 volts.

### Sample preparation

High purity polycrystalline Nb samples with dimensions of 22mm x 22 mm x 4 mm mechanically ground using 1  $\mu\text{m}$  grit refers as "ground" state. "Light BCP" refers to the samples etched in a fresh BCP (1:1:2) bath at room temperature for 20 minutes. As measured by weight loss, 30  $\mu\text{m}$  removal was achieved. The BCP

solution was a 1:1:2 (by volume) mixture of HNO<sub>3</sub> (69%), HF (49%) and H<sub>3</sub>PO<sub>4</sub> (85%).

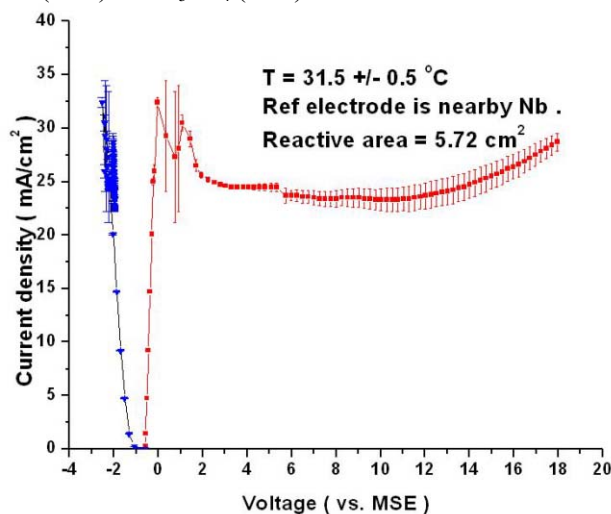


Figure 2: A typical polarization curve of three electrodes set-up for Nb EP process (voltage is relative to the MSE reference electrode).

### Electrochemical Impedance Spectroscopy (EIS)

Electrochemical impedance spectroscopy is a method in which a small AC signal is superimposed on a normal polarization voltage and the resulting current is measured, the measuring instrument processes the current-time and voltage-time measurements to provide the impedance at the different frequencies as the impedance spectrum, typically represented in a Bode plot or Nyquist plot. Figure 3 shows a schematic Nyquist plot and equivalent circuit corresponding to the high frequency part of the impedance diagram, indicating a solution resistance  $R_s$  (the left intercept of the semicircle), the diameter of circle as the polarization resistance  $R_p$  and the effective double layer capacitance  $C_{dl}$ , determined from the angular frequency at the top of the semicircle  $\omega_{\text{max}} = 1/R_p C_{dl}$ . The low frequency phenomena, which for a salt film should yield a vertical line on the Nyquist plot and which for an acceptor limiting electropolishing should exhibit the 45  $^\circ$  Warburg-Nernst impedance signature [7] are difficult to obtain in a polishing system undergoing high rate dissolution, and are therefore not included in Figure 3. The most common method used to analyze EIS spectra is equivalent circuit modeling. The behavior of each element is described in terms of "classical" electrical components, such as resistors, capacitors, inductors, plus a few specialized electrochemical elements (such as Warburg diffusion elements). EIS can be used to identify and quantify these characteristic values and thus characterize the anodic layers and electrochemical process.

In this study, impedance measurements were performed using a potentiostat (Series G 300, Gamry Instruments). The amplitude of potential modulation was 10 mV. Impedance measurements were made in the frequency ranging from 0.2 Hz to 200 kHz.

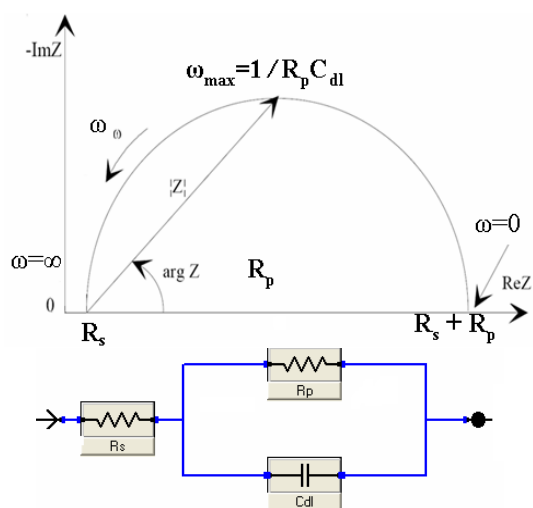


Figure 3: A schematic Nyquist plot and equivalent circuit corresponding to the high frequency part of the impedance diagram.

## RESULTS AND DISCUSSION

### Effect of Temperature

Past EP studies identified that a working temperature of electrolyte 25°C ~ 35°C gave the best gloss on Nb surfaces [3]. In this study, anode polarization curves were determined in a typical freshly prepared mixture of hydrofluoric and sulfuric acid by volume ratio of 1:9 at series of temperature for a static flow condition. The measurements have been done at temperature 54.6°C, 45.6°C, 33.5°C, 26.3°C and 21.3°C in an order with Nb/Al area ratio of 10: 1 as shown in Figure 4. The temperature was recorded by placing a thermocouple within 5 mm of the anode surface.

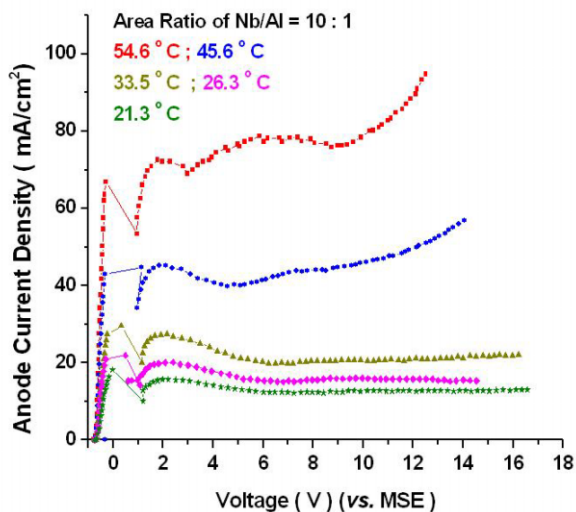


Figure 4: Anode polarization curves measured at the different temperatures.

All anode polarization curves exhibit a limiting current plateau extended from 2 V to 17 V. The anode current density increases exponentially with temperature instead of linearly as previously reported [1]. During the

experiment, we noticed that the temperature difference between a thermocouple within 5 mm of the anode vs. one in the fluid bulk increased from 0.4°C to 6.3°C as the bulk electrolyte temperature increased from 21.3°C to 54.6°C. At the two highest temperatures, the plateau current rises at higher voltages, which we attributed to the local heating. Since same electrolyte was used, HF loss was speculated during the measurements, which causes extra decreasing of measured anode current density and the detailed discussion about effect of HF is reported below. Corresponding to cavity EP process, the electrolyte also serves as the process coolant which will result in unstable temperature [8]. Therefore a non-uniform polishing effect is expected.

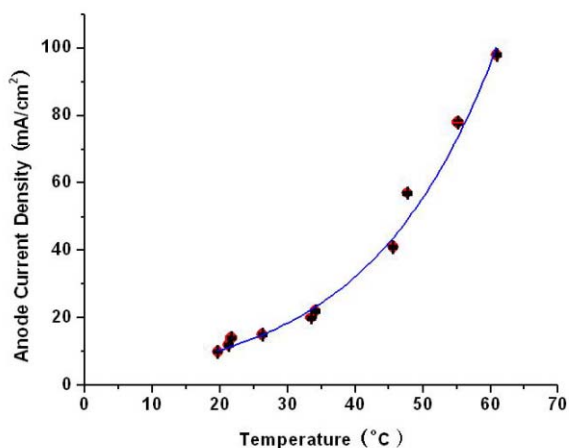


Figure 5: The anode current density increases exponentially with the temperature.

### Effect of HF concentration

The effect of increasing HF above the widely used 1: 9 composition has already been reported by others [1]. We explored decreasing HF concentration from a typical freshly prepared mixture of 1.0 to 0.2 by volume, since HF loss during operation of a processing facility either by evaporation or by reaction may be expected [1].

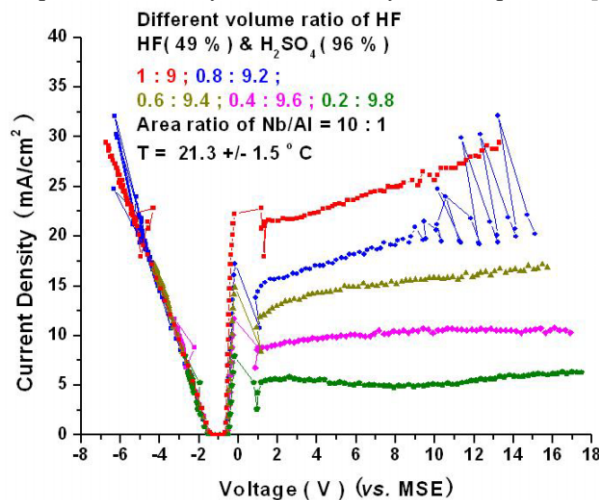


Figure 6: The polarization curves measured at the different concentration HF

We found that at 21°C with the same 10:1 area ratio for a static flow condition, the anode plateau current density fell approximately linearly with decreasing HF content, while the cathode current slope was substantially unaffected, as shown in Figures 6 and 7. This suggests that polishing rate is strongly affected by HF or a species arising from it. The understanding of detailed role of HF involved for Nb dissolution during the EP process requires further electrochemical impedance studies.

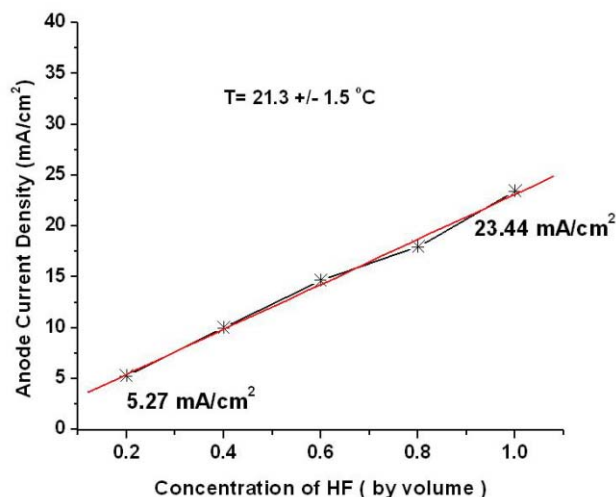


Figure 7: The anode current density increase with HF concentration, 6 V anode polarizations, 21°C.

*Mechanisms of electropolishing*

Electropolishing is a surface finishing process based on anodic dissolution of metal. The polishing phenomenon is characterized by the elimination of micro-roughness (leveling) and the absence of crystallographic and grain boundary attack (brightening) and so as to obtain smooth, bright surfaces [9]. Previously Nb EP studies suggested that the best electropolishing conditions are generally found along the limiting current region. Mass transport limitation of anodic dissolution is believed to be responsible [1, 3].

The study of mass transport mechanism in polishing systems is critic for the optimization of electrolyte formulation and of operating parameters. It has been studied theoretically and experimentally over the past several years. Grimm et al. proposed the duplex salt film model [10-13] and it was further discussed by Matlosz et al. theoretically [13]. The physical picture of this model is that the origin of anodic limiting current is the presence of salt film precipitate, which fixes the metal cations concentration at its saturation value at the salt film/electrolyte interface. The rate of transport of cations across the diffusion layer into the bulk electrolyte limits the anodic dissolution rate. The precipitate itself is composed of two regions: the compact salt film region and porous salt film region. In the compact film region, the precipitate forms a solid dielectric barrier through which the cations are transported by solid-state ionic conduction in the presence of much higher electric field.

In the porous film region, the pores of the precipitate are filled with electrolyte solution at the saturation concentration and mobile charge carriers (anions and cations) transport the current by migration in the electric field in the pores. In some special cases, one may speak of porous salt film model or compact salt film model individually for clearly separating solid state and liquid state effects. Due to the low mobility of the ions for solid state transport, compact salt films are generally considered to have a thickness on the order of 10 nm, while corresponding porous layer has a thickness up to few μm. Matlosz et al. investigated the adsorbate-acceptor model through a complete impedance analysis [14]. Contrary to the salt film model, where the surface concentration is fixed by a saturation value, the limiting current is reached when the concentration of the acceptor species drops to near zero at the anode/electrolyte interface. Due to the absence of a salt film, the transport process is limited by diffusion of acceptor species through the electrolyte diffusion layer.

As mentioned previously, the Nb-electrolyte interface could be simulated as an equivalent circuit, which has polarization resistance  $R_p$ , solution resistance  $R_s$  and the double layer capacitance  $C_{dl}$ . These characteristic values also can be used as the experimental criteria to distinguish mechanisms involved during the Nb electropolishing.

For a compact salt film in which a solid-state conduction process occurs in parallel to capacitive charging of the film, the interface capacitance and the polarization change with applied potential or flow condition. For a porous salt film in which ionic transport occurs in the electrolyte filling the pores of the film, the measured solution resistance varies with applied potential or flow condition. In the case of the adsorbate-acceptor mechanism, the polarization resistance is inversely proportional to the steady-state current density, should decrease with applied flow. Table 1 summarizes the results from the theoretical analyses in the references [14] and [7], which can be used to determine expected trends for targeted experiments aimed at comparing impedance spectra obtained at different steady-state operating conditions. Examples are: a series of impedance diagrams obtained at the different applied potentials along the limiting current plateau, or a series of impedance diagrams obtained at a fixed applied potential along the limiting current plateau but with varying electrolyte agitation.

Table 1: Characteristic features of Nyquist diagram at the high frequency loops.

Characteristic feature @ the high frequency (* C = constant)	Salt Film Models						Adsorbates -Acceptor Model		
	Porous Film			Compact Film			$R_s$	$R_p$	$C_{dl}$
	$R_s$	$R_p$	$C_{dl}$	$R_s$	$R_p$	$C_{dl}$			
Different Potential (↑)	↑	C	C	C	↑	↓	C	C	C
Different Rotation (↑)	↓	↓	C	C	↓	↑	C	↓	C

*EIS study of varying applied potential*

In the limiting current region, a series of Nyquist plot were measured as a function of applied potential for a

static flow condition, as shown in Figure 8. In order to avoid convective diffusion caused by local heating, the solution has been cooled down to 5.5°C. From the impedance diagrams, this is evident that the polarization resistance,  $R_p$  increases with potential as indicated from Figure 9, while the solution resistance,  $R_s$  between Nb and reference electrode remains constant.

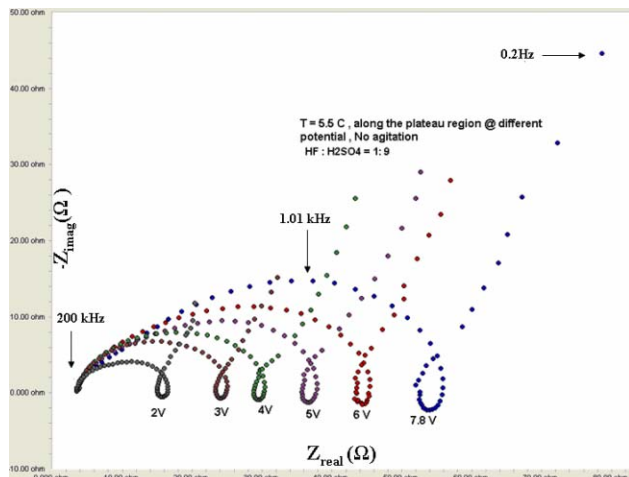


Figure 8: A series of Nyquist plots determined at the different potentials along limiting current region.

### EIS study of different flow condition

EIS experiments also have been conducted under different flow conditions. The flow rate near to the anode surface is estimated to 4 ~ 5 cm/sec, which is of the scale relevant to typical nine-cell cavity horizontal EP processing. With increasing flow rate, as shown in Figure 9, the polarization resistance  $R_p$  decreases. The double layer capacitance,  $C_{dl}$  determined from the angular frequency at the top of the semicircle  $\omega_{max} = 1/R_p C_{dl}$ , decreases with potential and remains constant with agitation, as shown in Figure 10. The anode potential displayed in Figure 9, 10 is ohmic (IR) corrected, the IR drop is determined from impedance measurements.

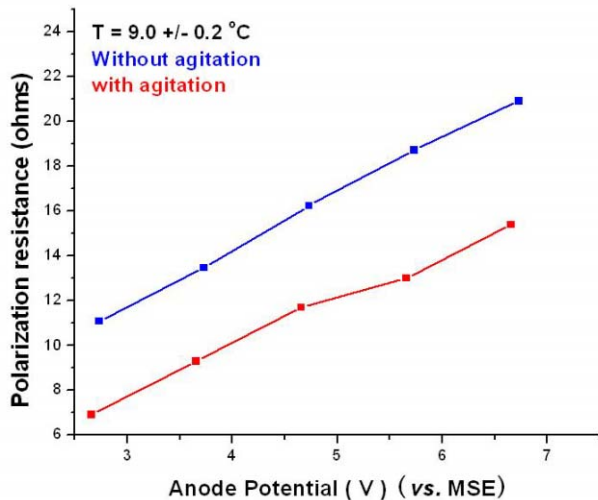


Figure 9: Polarization resistance of the high frequency loops under different potential and flow rates

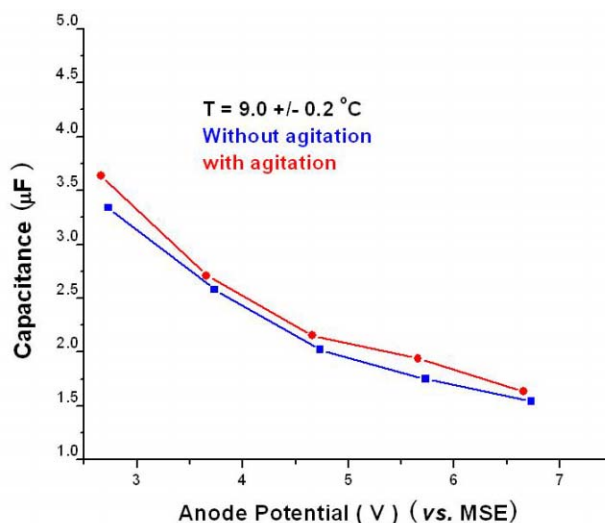


Figure 10: Effective double layer capacitance under different potential and flow rates.

### What we have learned from EIS studies?

By considering table 1, we find that our EI data is consistent with the compact salt film model and neither with the porous salt film nor the adsorbates-acceptor model. To summarize, we find that solution resistance remains constant at different potential and flow rate, which basically rules out application of the porous salt film model. Polarization resistance increases with different potential also excludes the adsorbate-acceptor model, the change of capacitance under various potential and flow condition further suggests that compact salt film model could describe part of the Nb EP process.

### The Implication of EIS

As discussed previously, the surface change during electrochemical process can be directly observed through the change of impedance characteristics.

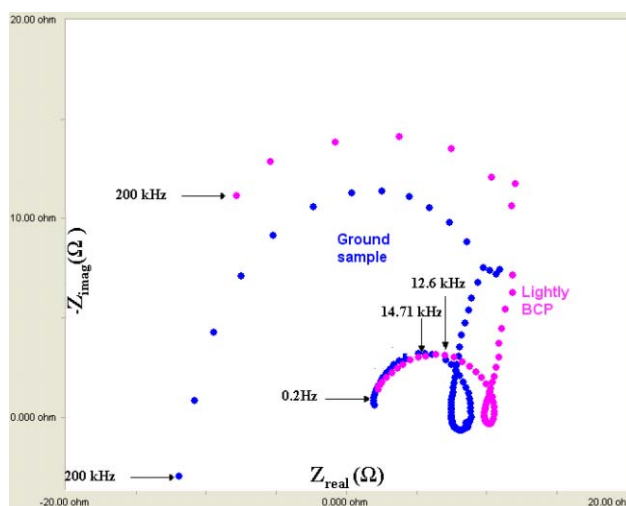


Figure 11: Nyquist plot of EIS spectrum of mechanically ground sample and light BCP sample

In this study, we explored the potential use of EIS for monitoring the Nb surface during the electropolishing. Figure 11 shows the EIS spectrum of a ground sample and a lightly BCP sample with different surface roughness as measured by AFM as indicated from Figures 12, 13. Our result shows that there is signature difference in EIS response. With capability of well controllable characterization of Nb surface roughness [16]; this preliminary study indicates that this technology could be further explored as a promising on-line feedback.

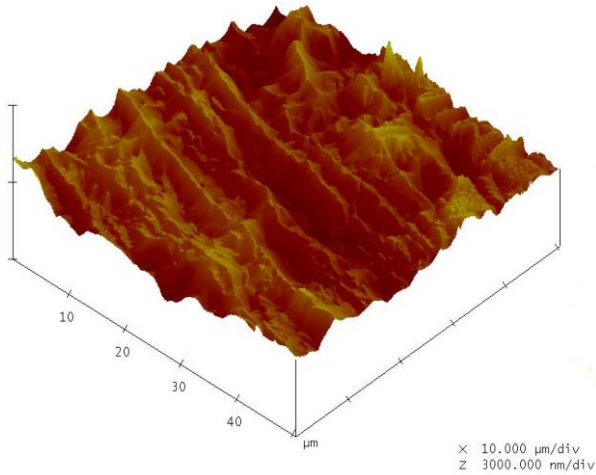


Figure 12: AFM image of mechanically ground sample

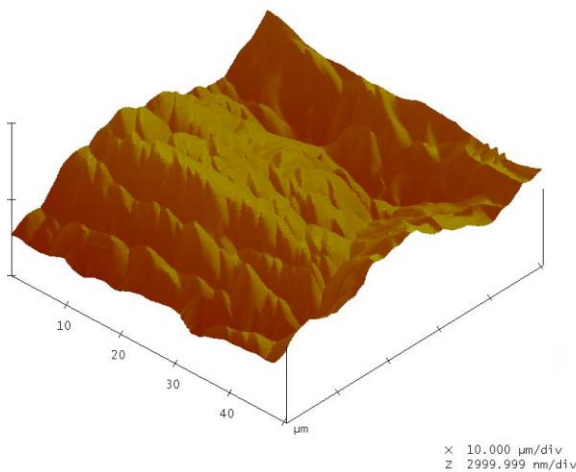


Figure 13: AFM image of light BCP sample

### CONCLUSION

Through using a reference electrode, the potential drops at the anode, electrolyte and cathode are separated, which helps to find out the anode current density is strongly affected by local temperature and HF concentration. These findings trigger further microscopic understanding about the effects of operating parameters involved in Nb EP process mechanism and put the emphasis on understanding the mass transport limiting species. High frequency impedance provides strong evidence of the presence of a compact salt film at the Nb surface under limiting current condition as depicted in Figure 14.

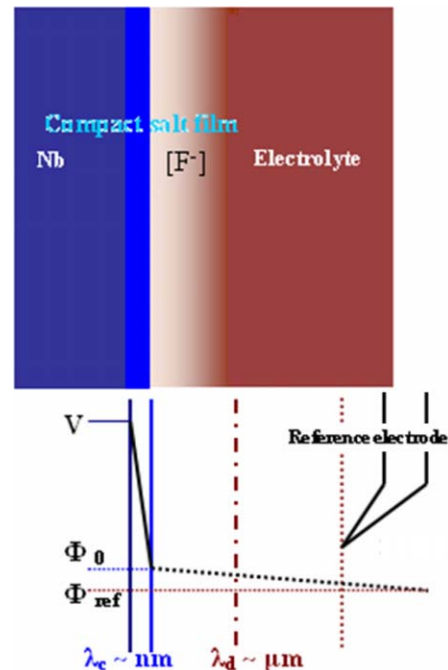


Figure 14: The compact salt film model of Nb EP process.

Under this physical picture of Nb EP, some important concepts could be stated as: sulfuric acid tends to anodize the Nb under polarization potential producing the "compact salt film"- " $\text{Nb}_2\text{O}_5$ " [1, 15]; HF tends to dissolve the Nb oxide under kinetic control with the "at the surface" concentration of F ion; F ion concentration "at the surface" is limited by how fast it diffuses through the electrolyte; the local gradient in  $\text{F}^-$  concentration produces the desired polishing action.

The knowledge of Nb EP mechanism will be very helpful for improving the cavity EP production for achieving a high reproducibility SRF performance. The implication of EIS for monitoring Nb surface during electropolishing shows this technology could be potentially used as a source of on-line feedback. Careful correlation of process condition and obtained smoothies is the subject of future study, and it will provide a solid basis for designing an effective niobium electropolishing operation.

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### REFERENCES

- [1] F. Eozénu, A. Aspart, C. Antoine, B. Maliki, CARE Report 06-10-SRF. EU contract number RII3-CT-2003-506395, (2006).
- [2] H. Diepers et al., Phys. Lett., 37(A), (1971) p. 139-140.
- [3] K. Satio et al., Proc. of 4th SRF workshop, (1989).

- [4] V. Palmieri, Proc. of 11<sup>th</sup> SRF workshop, (2003).  
[4] C. Boffo et al., Proc. of 12th SRF workshop, (2005).  
[5] J. Huo et al., J. Appl. Electrochem. 34, (2004) p. 305-314.  
[6] Solartron Technical Report , No . 004/83  
[7] M. Matlosz et al., J. Electrochem. Soc. 141 (2), (1994) p. 410-418.  
[8] C. E. Reece et al., TUP62, these proceedings.  
[9] D. Landolt, Electrochimica Acta., 32(1), (1987) p. 1-10.  
[10] R. D. Grimm, et al. J. Electrochem. Soc. 139(6), (1992) p. 1622-1629.  
[11] R. D. Grimm, et al. Corr. Sci. 36(11) , (1994) p. 1847-1868.  
[12] O. Piotrowski et al., J. Electrochem. Soc. 145(7), (1998) p. 2362-2368.  
[13] S. Magaion et al., J. Electrochem. Soc., 140 (5), (1993) p. 1365-1373.  
[14] M. Matlosz, Electrochimica Acta. 40(4), (1995) p. 393-401.  
[15] I. Arsova, J. Serb. Chem. Soc. 71(2), (2006) p. 177-187.  
[16] H. Tian et al., WEP 04, these proceedings.