

# QUANTITATIVE EP STUDIES AND RESULTS FOR SRF PRODUCTION\*

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## Abstract

Cavities and their performance quality are major cost drivers in SRF-based projects. EP is a superior chemical treatment, and now is replacing BCP for producing high gradient SRF cavities. To achieve high performance and reliability, which is essential for Nb SRF cavities production, it is important for us to understand Nb EP in detail so that we can tailor it to the best effect. The analytical tools of electrochemistry and surface topography are the means of developing such understanding. The recent incorporation of analytic electrochemical techniques into the development of well controlled protocols for Nb electropolishing will be reported, such as using three electrode method for polarization curve measurements, electrochemical impedance spectroscopy (EIS) to understand the mechanism of EP, and rotating disk electrode (RDE) to study the diffusion coefficient of active species of F ions, and the related diffusion layers etc. Implications of present basic understanding of Nb electropolishing will be introduced. In parallel, investigations for monitoring scale-dependent Nb surface morphology evolution under cavity production condition will be demonstrated, which is expected to lead to design best EP parameters. Directions for the future are aimed at well control, high reproducibility, efficient, EP process for coming SRF-based projects.

## INTRODUCTION

The unique characteristics of Nb SRF cavities have allowed them becoming the building blocks for e charged particle accelerators. A smooth and clean interior surface finishing is paramount to the proper function of SRF accelerator cavities, given that only topmost 40~50 nm layer is directly involved with the rf field [1]. Active acid etching and polishing is required, as is cleaning. EP is an anodic dissolution process. It is characterized by the elimination of micro-roughness (leveling) and the absence of crystallographic and grain boundary attack (brightening) and results in the production of smooth, bright surfaces [2-3], and now is replacing BCP for producing high gradient SRF cavities.

The EP process typically applied to Nb cavities was inherited from Siemens in the 1970's [4], and it has been developed through decade's cavity production practices empirically. Typically, a mixture of hydrofluoric acid (48~49%) and sulfuric acid (96~98 %) by volume ratio of 1:9 or 1:10 which depends on the weight concentration of

hydrofluoric acid and sulfuric acid, is used as the electrolyte.

Typically, EP process used to be conducted at 30°C, and sometimes even at higher temperature during the process practice because the solution itself behaving as a coolant and only the supply and exit flow temperature were monitored not cavity's wall temperature. Recent studies suggest the polishing at lower temperature may present a better surface finishing [5, 6]. For Nb cavity production, applied voltage across the cavity and cathode is 14~15V controlled by power supply and the optimal EP has been done in the continuous current oscillation mode, but the mechanism of current oscillation is still not clearly identified [7]. For a typical shape of SRF cavity, such as ILC and CEBAF, the internal surface area ratio of the niobium cavity (anode) to the high purity aluminum tube (cathode) is about 10: 1.

To achieve high performance and reliability, which is essential for Nb SRF cavities production, especially for the International Linear Collider (ILC) which requires 16,000 nine cell cavities intended to perform at 31.5 MV/m historic high accelerating gradient. Therefore, it is important for us to understand the kinetics of surface smoothing of Nb EP in detail so that we can tailor it to the best effect. The analytical tools of electrochemistry and surface topography are the means of developing such understanding. Recent and ongoing research is yielding new insights that enable a process refinement, and perhaps significant future evolution for improved cost and reliability.

## BASIC UNDERSTANDING ABOUT NB ELECTROPOLISHING

### *Understanding Potentials in Nb Electro-polishing*

During Nb cavity EP process, the applied voltage is the function of anode (Nb) and cathode (Al) potentials, the voltage drops in the electrolyte and voltage drops in the connects and conductors[8]. The cavity process practice uses the power supply only to provide the applied potential, which corresponds to the potential drop between the Nb cavity and the coaxial Al rod cathode. By using a standard reference electrode, such as a saturated Hg/Hg<sub>2</sub>SO<sub>4</sub> or Ag/AgCl, the individual potentials could be measured with respect to the reference electrode. We learned that under typical Nb electropolishing conditions, the majority of the applied voltage drops at the surface of the anode (niobium). The cathode exhibits well-behaved polarization behavior, and it accounts for a significant fraction of the applied potential mainly due to the hydrolysis reaction. The potential drop across the electrolyte is purely resistive. These values are strongly

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dependent upon the electrolyte composition, temperature, relative surface areas of cathode and anode as well as the applied potential. For a typical cavity polishing condition with 15 V applied voltage, the anode polarization potential corresponds to approximately 9 V, the cathode  $\sim 4$  V, and the potential drop in the electrolyte  $\sim 2$  V. The three electrodes set up identifies the effective electrolyte resistivity to be  $\sim 8 \Omega\text{-cm}^2/\text{cm}$  with  $T_{\text{electrolyte}} = 32 \text{ }^\circ\text{C}$  and  $\sim 13 \Omega\text{-cm}^2/\text{cm}$  with  $T_{\text{electrolyte}} = 20 \text{ }^\circ\text{C}$ . For present SRF cavity production practice (elliptical shaped Nb cavity and the coaxial Al rod cathode), the resistive drop through the electrolyte is negligible, but it would affect the establishment of current limited plateau with different anode/cathode geometry. And the potential drop at the cathode surface increases with the decreased surface area of cathode as shown in Figure 1, and the linear relationship between the voltage drop and current density at the cathode shows that electrochemical reaction, which mainly is hydrolysis, belong to typical Faraday reaction. The cathode potential shown in the figure has been corrected with IR drops in the electrolyte between reference electrode and cathode.

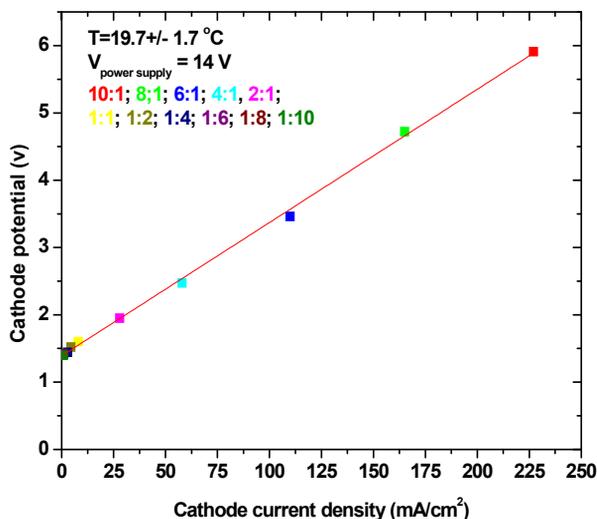


Figure 1: Potential drop on the cathode and cathode current density with the different surface area ratio between of anode (Nb) and cathode (Al) under 14 volts applied voltage at 20°C.

### *Electrochemical Impedance Spectroscopy (EIS) Studies Discloses the Mechanism of Niobium Electropolishing*

By applying an AC potential modulation to an electrochemical cell electrochemical impedance of a system could be measured over a range of frequencies. This technique, called Electrochemical Impedance Spectroscopy (EIS), recently has been used to reveal the mechanism of Nb electropolishing in different laboratories [9, 10], and to gain insight into underlying EP process. The electrochemical impedance of the Nb EP process has been measured as a function of different

potentials and flow rates. These measurements revealed definitively that the standard electropolishing of niobium proceeds via anodization of niobium by the sulphuric acid moderated by the dissolution of the anodized layer ( $\text{Nb}_2\text{O}_5$ ) via the available fluoride ions [9]. The desirable mass transfer controlled rate-limiting condition is the diffusion-limited arrival of fluorine at the anodized surface. When the process is only diffusion limited, on a small scale where diffusion of fluorine ion is essentially isotropic and independent of the crystallographic orientation and grain structure of the niobium surface [11], therefore surface brightening is produced. This process is different from the geometrical levelling, which is caused by the preferential dissolution of the protrusions on the order of the diffusion layer. Once the anodized layer ( $\text{Nb}_2\text{O}_5$ ) has established, the cell current is independent of the applied cell voltage because it is limited only by the dissolution of the anodized layer ( $\text{Nb}_2\text{O}_5$ ) by the available fluoride ions – thus the so-called current limited plateau. The increased applied voltage only alters the thickness of the anodized layer thickness while maintaining the same steady-state reaction processes at the active surface.

It is helpful to note that while there is no current increase with potential increase in the plateau region, there is increased heat deposition via ohmic losses in the anodized layer and all reaction rates increase with temperature, creating unstable conditions unless positive external temperature control is provided [5~7, 12]. Recent EIS studies about different electrolyte mixtures suggest that EP mechanism may evolve with the aging bath. The uncontrolled losses of HF due to vaporization and chemical consumption may contribute to the growth of a porous oxide layer [10].

### *Rotating Disking Electrode Measurements Identifies the Diffusion Coefficient of F Ions*

The Rotating Disk Electrode (RDE) is another standard electrochemical technique was used to improve understanding the Nb electropolishing process recently. Typically a 5 mm diameter well polished Nb disc is rotated rapidly about an axis perpendicular to the surface of the disc electrode, this movement of rotation creates a well defined solution flow pattern in which the mass transport of F ions is deliberately dominated by convection only. This property allows the RDE to be used to calculate F ions diffusion coefficient through the Levich equation. By measuring the plateau current density as a function of the rotation rate of the niobium (anode) disk at the current limited plateau region, one is able to discern the diffusion constant of the active species. The analysis yields an effective diffusion coefficient for fluoride ion on the order of  $10^{-12} \sim 10^{-11} \text{ m}^2\text{s}^{-1}$  under the temperatures studied, yielding a Nernst diffusion layer thickness of 10~20  $\mu\text{m}$ [12]. Therefore, for a static EP process, the active geometrical levelling is expected above this scale, but under this scale surface will be under a crystallographic blind dissolution and is expected to produce a brightening surface finishing.

Besides, the RDE measurements revealed that there is another oxide dissolution process at elevated temperatures. This process is not diffusion limited, nor does its reaction rate vary with applied potential, so it may be described more as etching rather than polishing [12].

### IMPLICATIONS FOR NB CAVITY PRODUCTION

The implications of the above basic understanding for electropolishing niobium cavities are listed as following:

- 1) For a typical cavity process condition, the increase of the effective cathode surface area helps to lower the over-potential on the cathode as shown in Figure 1. Use of creative arrangements which increase the effective surface area of an axial cathode will not only minimize the precipitation of sulphur [10] at the cathode and steady condition near Nb, but also provide a more power-efficient implementation of the cavity electropolishing.
- 2) As discussed previously, at the plateau region, electropolishing of niobium is moderated by the dissolution of the anodized layer via the available fluoride ions. But there is another oxide dissolution process at elevated temperatures. Initial data suggests that this etching process contributes over half of the material removal at temperatures of 30°C and above [5~6, 12]. Therefore the separation of temperature dependent chemical etching, such as push the cavity process temperature down, will enable the diffusion limited mass transfer only, thus allowing for a uniform micro-polishing (brightening), which we assume will enable optimum niobium cavity performance.
- 3) If the maximization of surface smoothness is the objective for certain SRF applications, controlling the uniform starting surface under scale of diffusion layer, which is about 10~20 μm will help to produce a best micropolishing. Previous studies demonstrated that CBP provides a highly reproducible starting surface, which has and could be transformed to a nano-smooth surface finishing by only a 30μm removal by EP [13]. Recent progress on 9 cell cavities in FNAL and other lab demonstrates that CBP is very promising to produce high gradient SRF cavity, but an optimization is needed [14~17].
- 4) In order to have a reproducible surface finishing, it is important to parameterize the Nb EP process and be well-controllable. For example, the hydrogen gas bubbles produced at the cathode must be managed to preclude their affecting electrolyte flow dynamics in the diffusion layer near the Nb surface, and minimize dissolution of hydrogen into the niobium bulk, which can induce serious performance effects. Recently, we introduce the hydrophobic PTFE membrane to shield the

hydrogen bubble but still maintaining ion transportation of electropolishing process, the preliminary results are promising. The detailed information will be reported later.

- 5) To obtain uniform polishing over the surface of a complex 3-D structure, one must ensure that the reaction is diffusion limit at every point. This implies that the surface is covered by an anodization layer, the thickness of which varies so that the sum of the resistive drop through the electrolyte to that point and the resistive drop through oxide layer is constant, since the metallic anode is itself an equal-potential. This condition provides a constraint on viable cathode/anode geometries.

Recent the excellent performance improvement has been obtained via light EP at 20 °C applied to a heavily BCP treated cavities. Now CEBAF 12 GeV Upgrade Project at the Jefferson Lab adopts it as an alternated baseline for the 80 cavities, the on-going production progresses steadily [18]. We sought to stabilize the cavity wall temperature at 20°C during EP by applying external spray cooling for 250 minutes with 38μm removal for C100-RI-006 cavity, one 7-cell cavity for the CEBAF 12 GeV Upgrade Project, as illustrated in Figure 2.

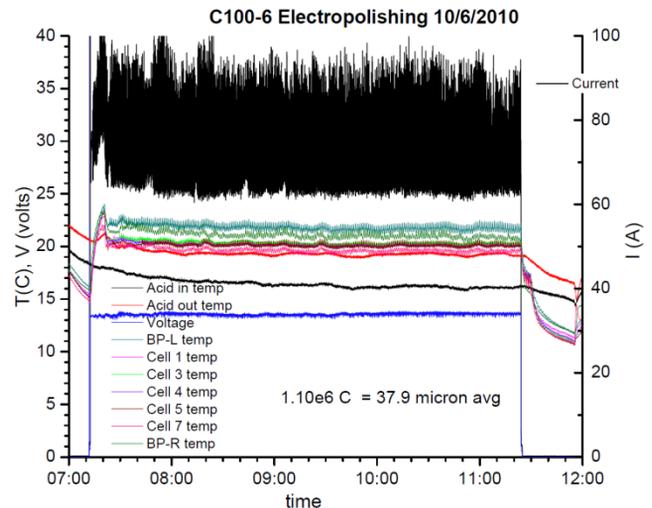


Figure 2: Controlled electropolishing process parameters for C100-RI-006.

Figure 3 shows the performance of C100-RI-006 cavity. In the past, this cavity had undergone heavily BCP treatment and 10 hours heat treatment at 600°C. After ultrasonic cleaning, high-pressure ultra-pure water rinse, clean assembly, and 120°C bake for 24 hrs, the cavity was rf tested at 2.0K. Performance improvement of this cavity after EP is significant and reaches to 41.6 MV/m.

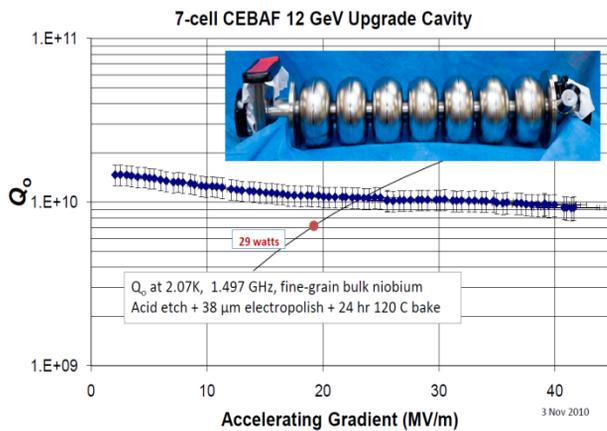


Figure 3: Performance of 7 cell C100-RI-006 cavity after light EP.

### MORPHOLOGY EVOLUTION OF BCP'D NB SURFACE WITH LIGHT EP

HG008 is one of the in housed built 7 cell high gradient cavities with heavily BCP treated and 10 hours heat treatment at 600°C done in the past, the performance has been measured as shown in Figure 4. The performance improvement of Q-drop after low temperature baking at 120°C is typical. After a short duration EP with 30 µm removal, the performance improve from 22 MV/m to 32 MV/m. This result gives strong evidence that the change of the surface morphology after a light EP improves SRF performance, and the results are highly reproducible [5~6, 18]. In order to investigate the nature of performance improvement, this cavity has undergone an extra 30 µm BCP etch. The rf tested is underway and will be reported later.

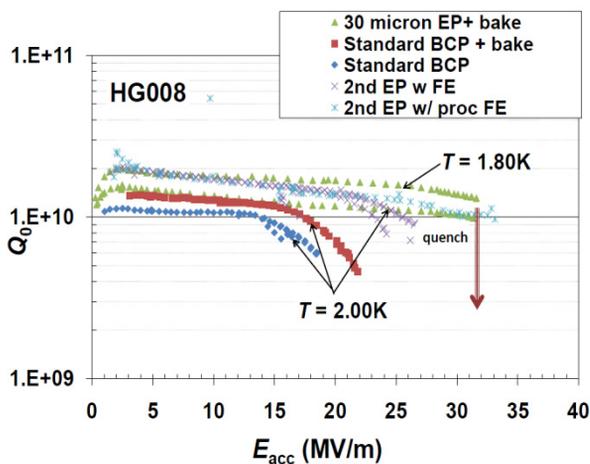


Figure 4: Performance of 7 cell HG008 cavity after BCP, low temperature bake, and light EP.

In parallel, we tried to investigate Nb surface morphology evolution under cavity process conditions as shown above in detail, and expect this study to shed a light for our understanding how the change of the surface

morphology after light EP helps cavity performance improvement, and to enlighten us to design best EP parameters in the future.

Figure 5 lists Nb surface morphology evolution with different duration EP at 20 °C. The measurements were done by using Atomic Force Microscopy (AFM) in 50 µm × 50 µm surface areas. The vertical scale for all of images is 5µm/div. For electroplishing, the applied voltage is 14 V, the reactive surface area ratio of Nb and Al is controlled as 10:1. The distance between Nb and Al is about 98 mm, which is about the distance between cavity equator and the coaxial Al rod during present EP production. The current density is 20 mA/cm<sup>2</sup>, the calculated removal rate is 0.15 µm/min based on the Faraday equation. The total EP polishing time duration is 180 minutes. The each time duration of electropolishing is 30 minutes, with ~5µm removal for each of duration respectively. Then sample was subjected another BCP treatment at 15 °C, with ~30 µm removal.

From above AFM measurements, we could see the short duration EP with 30 µm removal helps smooth all the sharp features due to the preferential grain or grain boundary etching of the BCP'ed surface, but small scale surface features are observable, which could be Nb<sub>2</sub>O<sub>5</sub> clusters reported [19]. The detailed information is deserved a further investigation. After an extra BCP treatment with 30µm removal, BCP wipes out all the improvement of surface smoothness by EP, but seemingly produces a clean surface which is free of observable microscopic Nb<sub>2</sub>O<sub>5</sub> clusters.

Recent studies of power spectral density (PSD) of surface morphology description suggested that there are characteristic patterns associated with frequently occurring topographies [20]. BCP'ed Nb surface is more power law structure dominated, but EP'ed surface may have two other shell superstructure, which are superimposed on small scale fractal structure [21]. We noticed that only 30 minutes EP (~5 µm), at middle frequency range with wavelength from 1 µm to 10 µm, there is noticeable change from power law dominated PSD to other shell superstructure, which could be described as ABC model [22~23], a model is considered as super flat surface with height obeying Lorentzian distribution. Further EP will not alter the PSD patterns but vary the amplitude of PSD slightly. The detailed analysis will be reported later.

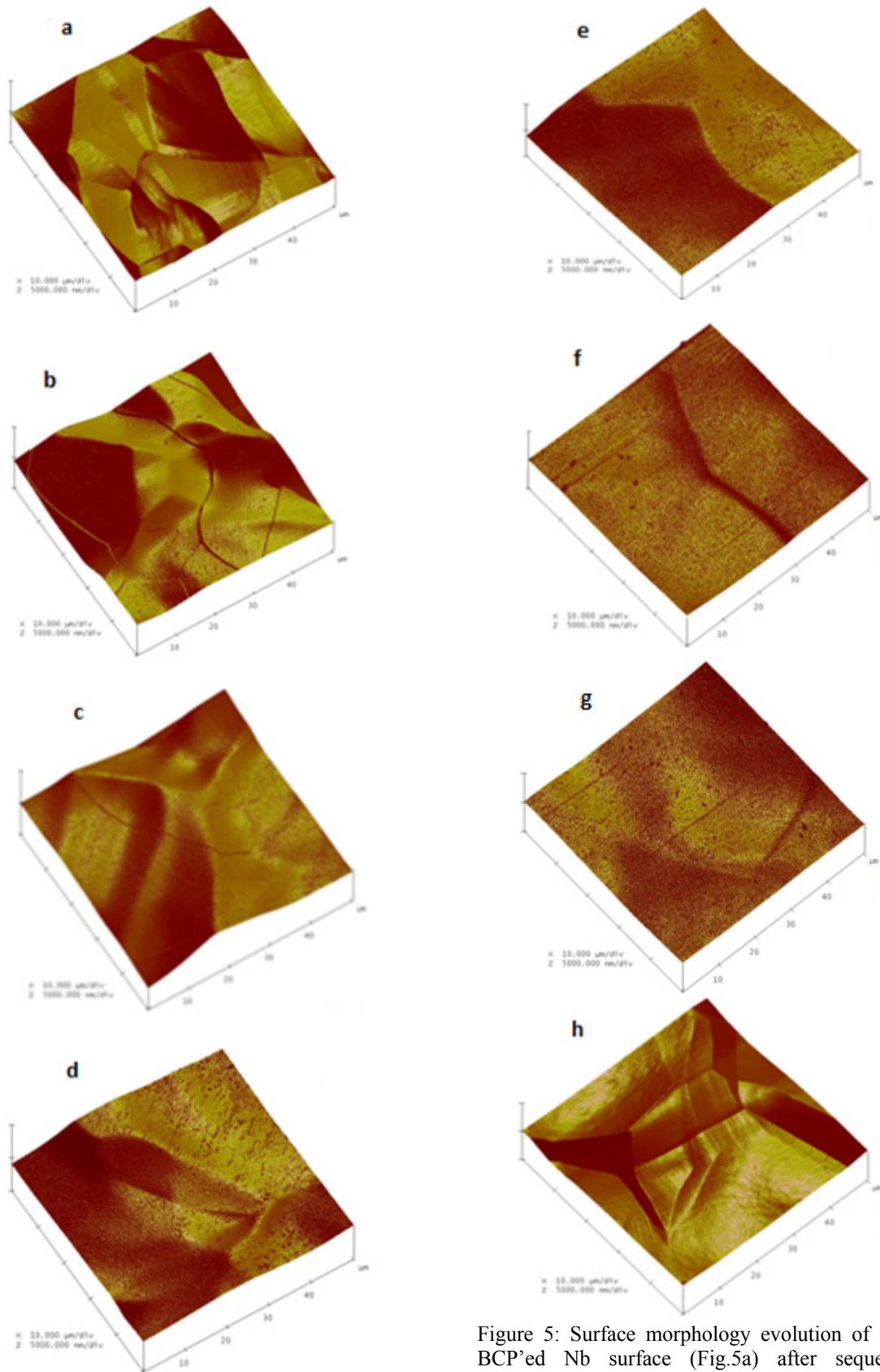


Figure 5: Surface morphology evolution of the heavily BCP'ed Nb surface (Fig.5a) after sequentially 30 minute's duration of EP at 20°C (Fig. 5b, c, d, e, f, g). Fig. 5h is the EP'ed surface with another 30 μm removal by BCP at 15 °C. The vertical scale for all of images is 5 μm/div.

## CONCLUSIONS

The recent incorporation of analytic electrochemical techniques, such as EIS and RDE, into the development of well controlled protocols for Nb electroplishing discloses the mechanism involved in EP, and yields a Nernst diffusion layer thickness of 10~20  $\mu\text{m}$  but a non-diffusion limited dissolution process may active at the elevated temperature. The implications of basic understanding largely improve the cavity production practices. In parallel with it, the detailed studies about scale dependent surface roughness evolution under cavity process helps to investigate the nature of SRF performance improvement, which is expected to lead to design best EP parameters.

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