

NIOBIUM ELECTROPOLISHING IN AN AQUEOUS, NON-VISCOUS HF-FREE ELECTROLYTE: A NEW POLISHING MECHANISM*

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Abstract

Faraday is working with Jefferson Lab to develop an improved process for electropolishing niobium RF superconducting cavities in an electrolyte free of hydrofluoric acid, to create microscopically clean and smooth niobium surfaces on the cavity interior. Conventional electropolishing of niobium cavities is based on a viscous electrolyte with an approximately 20 micron thick diffusion layer,[1] containing hydrofluoric acid as a depassivation agent. The FARADAYIC Electropolishing process combines pulse reverse electric fields and aqueous, low acid, non-viscous electrolytes to control current distribution and oxide film formation during metal removal. This eliminates the need for a depassivation agent, such as hydrofluoric acid. This program is aimed at understanding this new electropolishing mechanism, and optimizing it to achieve the desired oxide formation, reduced defect density and high performance. The feasibility of the process has been demonstrated using an aqueous sulfuric acid solution in conjunction with the FARADAYIC Process to electropolish niobium to surface finishes below 1 nm over a 2 x 2 micron area.

INTRODUCTION

State-of-the-art finishing for niobium cavities uses chemical polishing or electropolishing.[2] In chemical polishing, a mixture of concentrated nitric, hydrofluoric and phosphoric acids is used: the nitric acid forms a niobium oxide layer, which is dissolved by the hydrofluoric acid, with the phosphoric acid acting as a buffer to prevent high reaction temperatures.[3] Typical removal rates achieved using this technique are about 1 $\mu\text{m}/\text{min}$. However, the resulting surface roughness is an order of magnitude higher than conventional electropolishing and the grain boundaries are enhanced, which may degrade the quality factor.[4]

In conventional electropolishing, an electrolyte of concentrated sulfuric and hydrofluoric acid is used in combination with a constant voltage. Oscillations in the electropolishing process have been observed, which likely correspond to oxide film growth and dissolution. Voltages may be as high as 25 V with current densities of 10 A/dm^2 . [5,6,7] Conventional electropolishing achieves metal removal rates up to 0.5 $\mu\text{m}/\text{min}$. [8] Higher rates (e.g. 0.65 $\mu\text{m}/\text{min}$) have been obtained with buffered electropolishing,[4] which uses a lactic, sulfuric, and

hydrofluoric acid electrolyte.

Disadvantages of both chemical and conventional electropolishing processes include the use of hydrofluoric acid to achieve breakdown of the passive film on the surface. Ideally, a polishing process for superconducting Nb cavities will have attributes that include the following:

- Electrolyte free of hydrofluoric acid
- Control of surface roughness to a microscale finish, $R_a \leq 0.1 \mu\text{m}$
- Surface free from contamination after polishing
- Current distribution control that enables uniform polishing across the entire cavity surface
- Controlled removal of at least 100 μm

TECHNICAL APPROACH

Faraday has achieved a technical breakthrough with the demonstration of the feasibility of the FARADAYIC Electropolishing process, which employs sophisticated electric fields to control oxide film formation during metal removal, to achieve Nb polishing without hydrofluoric acid. FARADAYIC Electropolishing differs from conventional electropolishing through the use of a user defined, asymmetric waveform (in comparison to a constant voltage/current) permitting benefits that include:

- Control of oxide film formation,
- Improved polishing uniformity by producing a more homogenous current distribution through the control of process parameters,
- Increased metal removal rates, if desired, and
- The use of low-acid or neutral, aqueous electrolytes.

Pulse and pulse reverse electrolysis have been applied to special applications in edge and surface finishing.[9,10] A generalized pulse reverse electrolysis waveform is shown in Figure 1, and consists of an anodic peak current density, i_a , and associated on time, t_a , a cathodic peak current density, i_c , and associated on time, t_c , and an off time, t_0 . (*Please note: voltage control is often preferred for metal removal; however, it is easier to discuss the theory in terms of current control.*) The sum of the on times and off time is the period of the waveform. The anodic, D_a , and cathodic, D_c , duty cycles are the ratios of the respective on times to the period. In contrast to conventional DC processes where the control variable is either constant voltage or current, the FARADAYIC Electropolishing process introduces several key process parameters that are user defined: the peak anodic current density, anodic on time, and duty cycle. The proper selection of these variables is critical for the successful implementation of the process due to the strong

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influences that the variables have on mass transport rates, current distribution and metal removal rates.

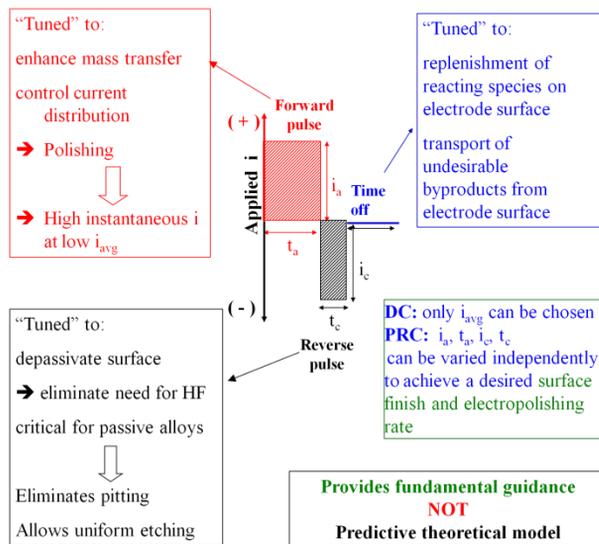


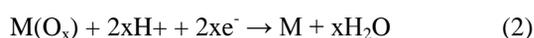
Figure 1: Generic FARADAYIC ElectroPolishing waveform.

Amelioration of Process Instabilities

There are several fundamental improvements that can be applied to conventional electropolishing. The main advantages of electropolishing processes are often offset by poor dimensional control and process stability that results from the complex, stochastic nature of the process. Due to the heat generation, gas evolution at the cathode, and precipitation products, the electrolyte properties, such as thermal conductivity, density, and flow velocity, are changing in the interelectrode gap.[11,12] These electrolyte property changes make it extremely difficult to maintain constant polishing parameters and adversely affect the precision of the process. One of the advantages of the FARADAYIC Electropolishing process is that heat can be removed during the off time.

Oxide Film Generation

Niobium forms an oxide film that is self-healing and reforms in the presence of oxygen or water. Since this passive film has low electrical conductivity and prevents the cavity surface from direct contact with the electrolyte, anodic dissolution cannot proceed without breakdown of the film. For conventional electrochemical polishing, hydrofluoric acid is required to breakdown the passive layer. Partial breakdown of the oxide film can occur causing pitting. The FARADAYIC Electropolishing process addresses this pitting problem by reducing the passive film during the reverse period. By adjusting the process parameters, we can selectively consume the nascent oxygen gas or the oxide film on the surface by the following reactions:

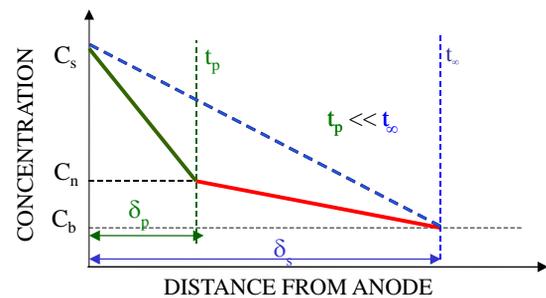


Mass Transport Effects

The theory of mass transport during pulsed electrolysis has been discussed previously.[13,14,15] In steady state electrolysis, the diffusion layer thickness, δ , is a time-invariant quantity for a given geometry and the solution hydrodynamic condition that develops within it. In pulsed electrolysis, δ begins to establish itself as soon as the electric field is applied. The thickness is 0 at the beginning of the pulse and increases to its steady state value, which is what happens during a direct current process. In pulsed electrolysis, however, the current can be interrupted before δ is fully established. By selecting the appropriate off time, this allows the dissolved ions to diffuse away from the electrode surface and the surface concentration to drift back to its original value before the next pulse. The concentration of reacting species in the vicinity of the electrode pulsates with the pulse frequency. The corresponding diffusion limiting current density, a measure of the removal rate, would be equal to an infinite value at time zero and decrease to a steady state value equivalent to the DC limiting current density.

Ibl [16,17,18] discussed a “duplex diffusion layer” consisting of an inner pulsating layer and an outer stationary layer. Landolt also suggested the existence of a pulsating diffusion layer.[19] Since the thickness of the pulsating diffusion layer is determined by the waveform parameters, we call this the “electrodynamic diffusion layer” (Figure 2).[20] Assuming a linear concentration gradient across the pulsating diffusion layer and conducting a mass balance, Ibl derived the pulsating diffusion layer thickness (δ_p) as:[17]

$$\delta_p = (2Dt_{on})^{1/2} \quad (3)$$



δ - hydrodynamic (Nernst) diffusion layer

δ_p - pulsating “electrodynamic” diffusion layer

δ_s - stationary diffusion layer

Figure 2: Representation of the Duplex Diffusion Layer.

where D is the diffusion coefficient and t_{on} is the pulse length. When the pulse on time is equal to the transition time (τ), the concentration of reacting species at the interface drops to zero precisely at the end of the pulse. An expression for τ is provided in the following equation:

$$\tau = ((nF)^2 C_b^2 D) / 2i_p^2 \quad (4)$$

More exact solutions are given by integrating Fick’s diffusion equation:

$$\delta_p = 2((Dt_{on})/\pi)^{1/2} \quad (5)$$

$$\tau = \pi((nF)^2 C_b^2 D)/4i_p^2 \quad (6)$$

Yin,[21] using a similar approach as Ibl, derived the same equation for the pulsating diffusion layer for “pulse-with-reverse” electrochemical processes. The key points used in the development of the FARADAYIC Electropolishing process are: (1) the electrodynamic diffusion layer thickness is proportional to the pulse on time, and (2) the transition time is inversely proportional to the current. The ratio between the limiting current density in the FARADAYIC Electropolishing process, i_p , versus that in steady state, i_{lim} , is:

$$i_p / i_{lim} = [\delta_p/\delta (1 - \gamma_a) + \gamma_a]^{-1} \quad (7)$$

Since δ_p must be smaller than δ , higher instantaneous limiting current densities can be achieved in pulsed processes. A higher limiting current density relates directly to a higher instantaneous metal removal rate. Therefore, the overall removal rate of a pulsed process can rival a DC process, despite a duty cycle < 100%, while enjoying enhanced process performance.

Another key consideration when trying to design a waveform is the current distribution that will develop. There are two important aspects that must be taken into account. First, is the current distribution a function of primary (geometrical), secondary (kinetic) or tertiary (mass transport) considerations? Second, what is the relationship between the pulsating boundary layer thickness and the surface profile height?

The current distribution developed in DC processes is controlled by primary effects. The FARADAYIC Electropolishing process supplements the primary effects with both secondary and tertiary effects, which tends to make the current distribution more uniform, as compared to primary current distribution alone. Therefore, the current distribution in FARADAYIC Electropolishing can be substantially different than that achieved in conventional DC processes. By understanding the influence of the pulse waveform parameters on current distribution, parameters can be selected to enhance either localized or uniform current distribution.

If the pulse on time is much longer than the transition time, tertiary effects dominate the current distribution. For this case, additional criteria that influence current distribution are the concepts of macroprofile and microprofile. In a macroprofile (Figure 3a), the surface roughness is large compared with the diffusion layer thickness, and the diffusion layer tends to follow the surface contour. Under mass transport control, a macroprofile results in a uniform current distribution and conformal dissolution. In a microprofile (Figure 3b), the surface roughness is small compared with the diffusion layer thickness. Under mass transport control, a microprofile results in a localized current distribution and non-uniform dissolution. Note that in the absence of mass transport control, the primary and/or secondary current distribution effects control the process.

Waveform Sequencing

A further extension of this macro/microprofile concept is waveform sequencing. Experience at Faraday has shown the need for waveform sequencing (Figure 5) when polishing surfaces to a very low Ra. Depending on the electrolyte flow past the surface, a macroprofile may exist, and a specific waveform is chosen to polish this surface. As the surface becomes much smoother, the macroprofile may transition to a microprofile. In order for a lower Ra to be achieved, the waveform must be changed (Figure 4). An advantage of the FARADAYIC process is that these distinct waveforms may be preprogrammed into the rectifier, so that process control is simplified. Faraday used this approach to electropolish stainless steel valves to an Ra of 0.12 μm for Swagelok.

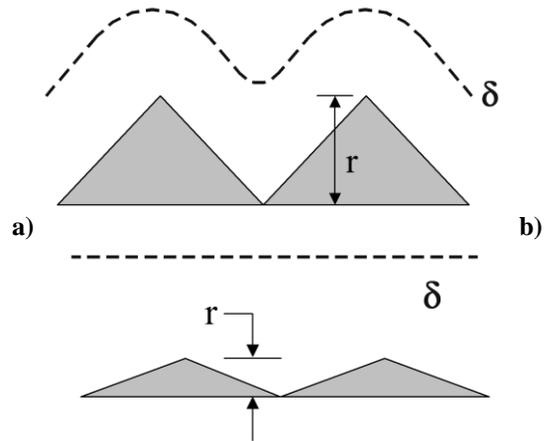


Figure 3: a) macroprofile ($\delta \sim r$); b) microprofile ($\delta > r$).

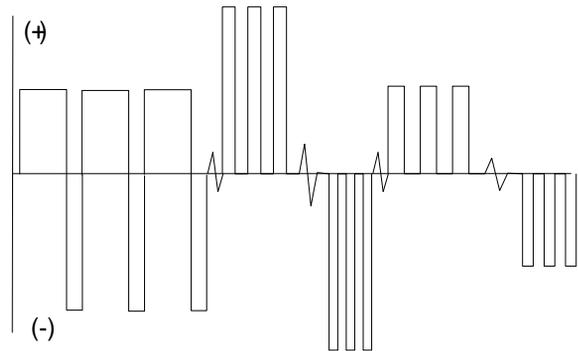


Figure 4: Generic waveform sequencing, used to electropolish materials to a very low Ra.

EXPERIMENTAL

1 inch square Nb coupons were electropolished using the FARADAYIC process in a simple electrolyte of 31 wt% H_2SO_4 + 300 ppm Triton-X, a commonly used surfactant. A chiller was used to maintain an electrolyte temperature of < 16°C throughout the electropolishing process. The coupons were cleaned by rinsing in a DI water stream, and ultrasonication at 70°C in 1-2% Liquinox and DI water, followed by drying using isopropanol. The surface finish of the coupons was assessed at Jefferson Lab, using either scanning electron

microscopy (SEM) or atomic force microscopy (AFM). Polishing rates ranged from 0.8-5 $\mu\text{m}/\text{min}$, and polishing depths ranged from a few microns to over 400 microns.

RESULTS

Figure 5 shows an SEM micrograph and an AFM scan of a Nb coupon surface after FARADAYIC ElectroPolishing. Faraday achieved extremely good surface finishes, with an R_a less than 1 nm over a 2x2 and 10x10 μm scan range (Table 1). The surface was found to be very clean, with a few defects that were likely introduced to the sample in the process of characterization.

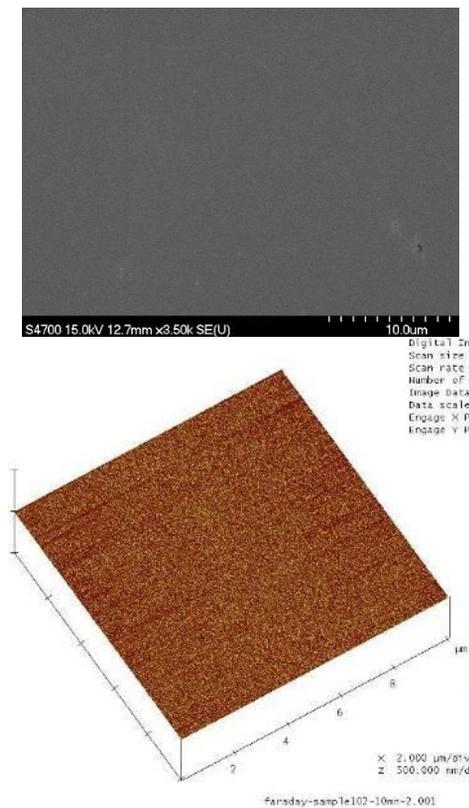


Figure 5: Nb coupons after the FARADAYIC ElectroPolishing process: top) SEM image, bottom) AFM image, 2 μm vertical scale.

Table 1: Electropolished coupon surface finish as assessed by JLab using Atomic Force Microscopy.

Scan Size μm	Scan No.	R_{max} nm	R_a nm	RMS nm
50 x 50	1	35.00	2.71	3.34
	2	37.30	3.54	4.73
	3	69.66	3.74	4.69
10 x 10	1	22.59	2.25	2.87
	2	16.16	0.41	0.54
2 x 2	1	9.42	0.36	0.46

CONCLUSIONS

A novel, eco-friendly electropolishing technology for niobium has been demonstrated at the coupon level. This technology utilizes a pulse reverse electric field to control oxide film formation and current distribution, enabling uniform electropolishing to a very low R_a , in an electrolyte that does not contain hydrofluoric acid.

Faraday filed utility patents (U.S. and International) on the FARADAYIC ElectroPolishing technology: Title: Electrochemical System and Method for Machining Strongly Passivating Metals; U.S. Patent Application No. 10240426; Foreign (PCT) Application No. PCT/US11/39354.

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