EXPLOITING NEW ELECTROCHEMICAL UNDERSTANDING OF NIOBIUM ELECTROPOLISHING FOR IMPROVED PERFORMANCE OF SRF CAVITIES FOR CEBAF*

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Abstract

Recent incorporation of analytic electrochemistry into the development of protocols for electropolishing niobium SRF cavities has yielded new insights for optimizing this process for consistent, high-performance results. Use of reference electrodes in the electrolyte, electrochemical impedance spectroscopy (EIS), rotating disk electrodes (RDE), and controlled sample temperatures has greatly clarified the process dynamics over the empirical understanding developed via years of practice. Minimizing RF losses at high operational gradients is very valuable for CW linacs. Jefferson Lab is applying these new insights to the low-loss 7-cell cavity design developed for the CEBAF 12 GeV Upgrade. Together with controlled cleaning and assembly techniques to guard against field-emission-causing particulates, the resulting process is yielding consistent cavity performance that exceeds project requirements. Cavity tests show BCS-limited Q well above 30 MV/m. Detailed process data, interpretation, and resulting rf performance data will be presented.

INTRODUCTION

A number of accelerator applications require CW accelerating gradients in the 15-25 MV/m range. In addition, the present ILC design requires 35 MV/m. In all cases, maximization of Q in the intended operating range is of great interest for minimizing cryogenic capital and operating costs. Fine grain niobium etched with BCP rather consistently exhibits a degradation of Q roughly in the 18-20 MV/m range. Since the mechanism creating these non-linear losses appears to be associated with peak magnetic fields, it is appropriate to describe the phenomenon as typical with peak flux densities greater than 60-80 mT.

Electropolished fine grain Nb surfaces do not exhibit the same Q drop. While electropolishing protocols—predominately derived from the pioneering work at KEK for TRISTAN [1]—have been developed empirically and often yield excellent results, recent and on-going research is yielding new insights that enable confident process refinements and perhaps significant future evolution for improved cost and reliability.

Excellent progress has been reported internationally in obtaining reproducible high-gradient performance from niobium cavities electropolished with a common protocol

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and subsequently cleaned and assemble under controlled conditions.[2,3]

REVIEW OF RECENT ELECTROCHEMICAL ANALYSES

Electrochemical Cell Analysis

In order to deepen our understanding of the systematics of electropolishing niobium, we engaged the collaboration of electrochemists who guided us into reformulating our basic understanding of the electrochemical cell which is the circuit used for electropolishing niobium cavities. [4] By using a standard reference electrode one learns that under typical electropolishing conditions, the bulk of the potential drop occurs at the surface of the anode (niobium). The next larger fraction of the potential drop occurs at the cathode (aluminum) in an amount that is proportional to the cathode current density. A small fraction of the applied power supply potential is dropped across the electrolyte. An implication of the above is that it is in error that one conceives of the current flow through the electrolyte as one would in an electrostatics problem.

By measuring the frequency response of the impedance of the niobium-(sulfuric/hydrofluoric electrolyte)-aluminum electrochemical cell under controlled conditions, one can gain insight into underlying processes. This technique, called Electrochemical Impedance Spectroscopy, EIS, is stock and trade for the corrosion community. Such measurements revealed definitively that the standard electropolishing of niobium proceeds via anodization of niobium by the sulfuric acid moderated by the dissolution of the anodized layer (Nb_2O_5) by the available fluoride ions and hydrogen gas production at the cathode (hydrolysis of water). The desirable rate-limiting condition is the diffusion-limited arrival of fluorine at the anodized surface. When the process is thus diffusion limited, the cell current is independent of the applied cell voltage – thus the so-called plateau. This may be simply understood as altering the anodization layer thickness while maintaining the same steady-state reaction processes at the active surface.

The basic reason that achieving such a plateau condition is desirable is that the local rate of material removal is then insensitive to variations in the local chemical potential associated with specific crystallographic orientations or local material defects. In addition, the gradient in F- concentration away from the surface linked to the diffusion rate provides preferential removal of topographical features with aspect ratios that "poke through" the diffusion layer.

Clarification of the above description was only possible via experiments which carefully controlled the process temperatures. 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.

An implication of the above description for electropolishing niobium cavities is that if the cell is truly in a temperature-controlled plateau condition, then current density—and thus material removal rate—will be uniform over the entire anode, moderated only by variations in the local F⁻ concentration due to impeded or effectively enhanced diffusion.

The **first lesson learned** was to establish control of cavity process temperatures to promote uniform and reproducible processing.

Diffusion-limited F as the Rate-limiting Element

Another standard electrochemical technique was employed to directly characterize the fluorine diffusion in the electrolyte. The Rotating Disk Electrode (RDE) is a device used to systematically drive convective mixing so as to overcome diffusion. By measuring the plateau current density as a function of the rotation rate of the niobium (anode) disk, one is able to discern the diffusion constant of the active species. Such results have been reported recently and lead to a measurement of the F⁻ Nernst diffusion layer thickness in the standard electrolyte of 15-20 µm. [5,6] The most active leveling, then, is expected below this scale, **a second lesson**.

A second feature discovered via use of RDE techniques with this system is clear evidence for the presence of another, yet unidentified, oxide dissolution process at elevated temperatures. This second 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. The reaction rate of this second process is a rather steep function of temperature. Initial data suggests that this etching process contributes over half of the material removal at temperatures of 30°C and above. If the objective is obtaining maximally smooth surfaces, one is advised to avoid such etching processes. Since this hypothetical dissolution process acts to remove the (presumably amorphous) anodized layer rather than crystalline niobium, however, it may well proceed without contributing crystallographic etching due to variable chemical potentials. With the second process present, however, one would expect less leveling effect per unit thickness removed than from a solely diffusion-limited process.

A **third lesson learned to be** from basic studies is to push the cavity process temperatures down to minimize effects of such parasitic etching. A trade-off for this control, however, is slower reaction rates and thus longer processing times, unless the HF concentration is raised.

For a given process condition at the niobium cavity surface, the overpotential required at the cathode depends on two factors: cathode current density and temperature. The cavity plateau current density—determined by the electrolyte and temperature—and area define the total current. This total current and the cathode surface area then determine the required cathode current density. Customary practice in commercial electropolishing is to maximize the surface area of the cathode to minimize the required overpotential and thus the non-beneficial power requirement. If the cathode area is too small, the needed current density may then require a cathode overpotential that is high enough to drive additional undesirable chemistry, such as the precipitation of sulfur, which in turn generates particulate field emission sources inside the SRF cavity. [7]

The cylindrical geometry of typical accelerator cavities constrains the choice of cathode geometries. Use of creative arrangements which increase the effective surface area of a coaxial cathode or which lower the required overpotential to drive water hydrolysis at the required current density will minimize or avoid the precipitation of sulfur and also provide a more power-efficient implementation of the cavity electropolishing. This is a **fourth lesson to be learned.**

LIGHT EP OF JLAB 7-CELL CAVITIES

The JLab horizontal electropolishing facility has been described elsewhere. In addition to technique improvements involving handling and assembly of hardware for the cavity treatments, [2] some procedure refinements have focused on temperature stabilization and control. One modification consists in the addition of external water spray cooling. This arrangement eliminates the need for the electrolyte to also play the role of process coolant. Thermocouples with wireless readout monitor the niobium wall temperature. In this way we improve temperature uniformity and confirm process conditions corresponding to those of controlled bench studies.

In preparation for the 12 GeV Upgrade project of CEBAF, an effort was mounted that sought to exploit lessons learned from the on-going ILC cavity R&D as well as the basic process R&D and apply these to JLab 7-cell cavities of the design intended for the CEBAF upgrade.[8] In contrast to the ILC S0 program, we were free to alter the common protocol in the interest of both work-flow efficiency and perhaps enhanced control.

Encouraged by the excellent performance improvement obtained via light EP applied to a heavily BCP'd spare cavity—the 17 MV/m to 35 MV/m performance change of the cavity HG006 was reported at PAC09 [9]—we pursued the concept of providing only a light final electropolish to CEBAF cavities, leaving the "bulk" removal of the "surface damage layer" to the more easily applied BCP process, folding in lessons learned from the recent basic electrochemical process analyses.

Thus far in 2010, twelve 7-cell in-house built cavities with the LL cell shape were given light electropolish (~30 µm) after bulk BCP and 10h heat treatment at 600°C. We sought to stabilize the cavity wall temperature

at 20°C during EP, as illustrated in Figure 1, which displays cavity and electrolyte temperatures, cell voltage and current during the electropolishing of R100-1. Three of these cavities were previously operational in CEBAF in the prototype cryomodule *Renascence*. The other nine cavities were of the design to be used in the 12 GeV Upgrade. The "R100" set has been fabricated this year.[10]
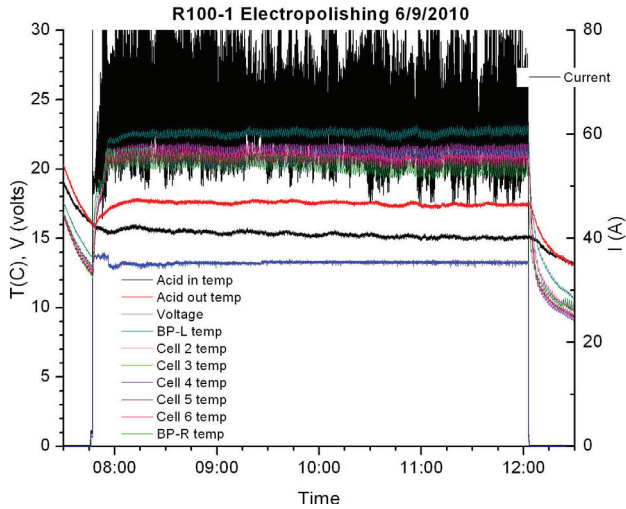

Figure 1: Controlled electropolishing process parameters.

After ultrasonic cleaning, high-pressure ultra-pure water rinse, clean assembly, and 120°C bake for 24 or 48 hrs, the cavities were RF tested at the 12 GeV operational temperature of 2.07K. Performance results for this set of ten cavities are shown in Figure 2. Table 1 summarizes the process parameters used for this set of cavities, as well as the resulting performance. All cavities exceeded the project requirements.

On the basis of this data set, we expect that the 12 GeV Project will adopt this light EP process as an alternate baseline for the 80-cavity set for that project. Further

investigations will continue to optimize cavity processing protocols with respect to cost, reliability, minimum losses, and peak supportable fields.
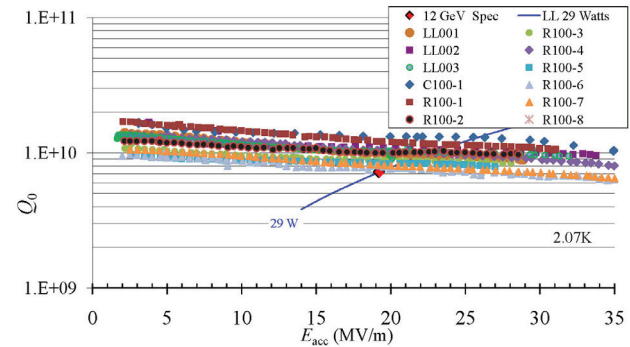

Figure 2: Performance of 7-cell cavities after light EP.

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[10] See F. Marhauser's contribution THP009 to these proceedings.

Table 1: Processing Parameters and Performance Results with Light EP on BCP'ed CEBAF 7-cell Low Loss Cavities

	BCP			EP							
Cavity	$\Delta d_{avg\ eqtr}$ (μm)	EP date	H_2O Spray	T_{eqtr} (°C)	I_{avg} (A)	t_{EP} (min)	Δd_{avg} (μm)	j_{avg} (mA/cm^2)	Q @ 20MV/m 2.07K	$E_{acc-max}$ (MV/m)	Limit
LL001	>240	3/17/2010	x	15.0	50	375	38.7	13	1.0E+10	29.0	quench
LL002	>240	1/7/2010		26.0	127	128	33.7	33	1.0E+10	43.2	Pwr
LL003	>240	12/16/2009		24.5	64	272	36.0	16	1.0E+10	31.0	quench
2nd		1/14/2010		26.0	114	105	24.8	29	1.0E+10	32.0	quench
3rd		4/12/2010	x	19.5	139	45	13.0	36	1.0E+10	34.0	thermal
C100-1	>150	4/7/2010	x	19.5	135	44	12.4	35	-	-	-
2nd		4/8/2010	x	19.5	132	72	19.8	34	1.2E+10	37.0	quench
R100-1	160	6/9/2010	x	21.0	64	250	33.4	17	1.2E+10	32.5	RF pwr
R100-2	110	7/2/2010	x	20.0	67	255	35.6	17	1.0E+10	28.6	RF pwr
R100-3	95	7/15/2010	x	18.5	56	208	24.2	14	9.0E+09	28.0	1 mSv/h
R100-4	100	7/23/2010	x	19.5	59	277	34.1	15	8.5E+09	27.0	1 mSv/h
R100-5	100	7/29/2010	x	20.0	65	190	25.6	17	1.0E+10	37.5	quench
R100-6	110	8/2/2010	x	20.0	73	238	36.0	19	7.3E+09	35.5	1 mSv/h
R100-7	110	8/6/2010	x	20.0	75	189	29.2	19	8.0E+09	36.7	LHe
R100-8	145	8/12/2010	x	20.5	70	237	34.6	18	1.0E+10	24.0	leak