

## 2.60 “R&D for Electropolishing of Nb for ILC Accelerator Cavities” DoE # 101005

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**Project Overview** The ILC vision comprises 16,000 solid Nb cavities performing at historically high levels, requiring true mass manufacturing. Significant risk still attaches the post fabrication etching and further treatment, despite decades of study. Major gaps remain: 1.) SRF performance has never been determined on the same piece of material as the surface analysis to show the connections clearly. 2.) While SRF cavities have been sectioned to identify field emitters, evidently none has ever been systematically sectioned and the pieces submitted to surface analysis to show the variation in a real system. 3.) A set of analyses to guide process development and for production quality control has never been defined and validated. 4.) A process that can be deployed into manufacturing cannot really be said to exist.

ILC requires a substantially improved technical basis for reliable process engineering of Nb cavity treatments. Our two-year program intending to accomplish it began in September, 2006. We propose to measure in detail the effect of electropolishing (EP), over the parameter range reasonable for cavity processing, on Nb surface chemistry and topography for standard and single crystal materials. We will determine the SRF performance of these material “states” using well-characterized discs in JLab’s Surface Impedance Characterization (SIC) TE<sub>011</sub> cavity. Together we will 1.) process and disassemble complete single cavities to determine the surface variation with location and process parameters and 2.) demonstrate a process to yield the maximum amount of “good” surface in a single cell cavity and determine their SRF performance. We will investigate the effect of post-baking. Such a program is possible only because a very similar program for buffered chemical processing is well along in our group. The resulting technology package will be the foundation for the eventual manufacturing organization to deliver high yield, at target cost cavities that meet ILC’s gradient and quality factor requirements. An adequate level of separate funding for JLab is assumed.

### **Progress from 9/06 to Present.**

Our effort in these seven months emphasized 1.) Fundamental EP Studies. Our VT and W&M doctoral students have constructed instrumented lab EP units and collected new, fundamental data under conditions related to real cavity processing. JLab workers set up EP units for single cell and for full ILC cavities. The involvement of an electrochemist (Prof. Sean Corcoran at VT) has proven crucial. 2.) Performance Enhancement by Low Temperature Baking. We are about to complete a study of the effect of such treatment on surface chemistry and correlate that with performance measurement in equivalently-treated single cell cavities. 3.) System for SRF Performance Measurements on Flat Discs. A painful aspect of materials surface studies related to SRF is that we never do performance measurement and characterization on the same sample. JLab workers and a separately-funded doctoral student built a novel TE<sub>011</sub> mode 7.5 GHz cavity Surface Impedance Characterization (“SIC”). It is being commissioned now and will accommodate 50 mm diameter discs, as do our characterization facilities. We expect to present all the above work at the Beijing SRF meeting this fall. What we have learned has been fed back into cavity processing at JLab.

**1. EP Studies.** We initially emphasized conditions related to ILC cavity processing: cavity horizontal, slowly (~ 1 RPM) rotating, about 60% filled, electrolyte feed entering one end of the (non-rotating) Al cathode and dispensed through downward-facing ports at each equator, anode/cathode area ratio ~ 10:1.

Our laboratory studies benefit greatly from potential measurements using reference electrodes instead of just the power supply. Together with the working and counter electrodes, they provide separate measurement of the potential drops at the cathode, the anode and across the

electrolyte. The effect of temperature on polishing is an important issue. The results in Fig. 1 are from single crystal materials sliced as sheets from an original large ingot. The slices received light ( $< 10 \mu\text{m}$ ) BCP before samples were cut and then another BCP (about  $20 \mu\text{m}$ ) after degreasing the samples. These data are under static flow conditions, primarily with the standard 90:10 sulfuric:hydrofluoric acid mixture.

Several features are noteworthy: The aluminum cathode exhibits a well-behaved polarization resistance that is temperature-sensitive and, despite the large area ratio (10:1), is always able to provide sufficient current. We believe that the polarization potential developed across the cathode resistance and the associated power deposition have not been previously identified in the niobium electropolishing configuration.. The temperature difference between a thermocouple in the bulk solution and one within 5 mm of the cathode was not observed to exceed  $1^\circ \text{C}$ . The potential drop across the electrolyte itself is purely resistive, and influenced by both temperature and HF concentration. For typical cavity polishing conditions of 30 – 35 C and 9:1 solution and 14 V cell (power supply) voltage, the potential drop in the solution is 1 -2 volts.

The anode shows a polarization resistance until the open-circuit potential is overcome, then a transition is observed to a temperature-dependent constant-current plateau. Measuring only the power supply voltages would have combined the anode and cathode drops, causing an apparent increasing slope to the plateau. The temperature dependences of the cathode current at constant voltage and of the anode plateau current each fit a single (but different) exponential function (not shown). Viewed as apparent activation energies, this indicates that a single (but different) process is controlling current at each. 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 fluid temperature increased from 21.3 C to 54.6 C. At the two highest temperatures, the plateau current rises at higher voltages, which we attribute to heating. Wall temperatures of about 40 C at the equator and 50 C at the iris are observed in processing nine-cell cavities, while the temperature of the out-flowing electrolyte is approximately 30 C. Improved process temperature control is necessary to obtain reliable and uniform polishing.

For typical polishing operations, the anode drop is about 9 V and the cathode about 4 V, the rest being in the solution. Though the total electrode currents are equal, the 10:1 area ratio makes the cathode current density (and thus the power density) much higher. Its temperature rises, however, are both small and comparable. More understanding of the electrode reactions and their heat balance is needed. Further, what happens when the interior cavity surface rotates out of the bath, making heat transfer into the electrolyte unavailable, also may be important..

The effect of increasing HF above the widely used 90:10 composition has already been reported by others. We explored decreasing HF concentration, since HF loss is expected during operation of a processing facility. At 21 C with the same 10:1 area ratio, the anode plateau current fell approximately linearly with decreasing HF content, while the cathode current slope was substantially unaffected. This suggests that polishing rate is acceptor-diffusion controlled by HF or a species arising from it. Further our initial evidence suggests that surface oxide film thickness may be greater for lower HF content.

**2. Performance Enhancement by Low-Temperature Baking.** It is widely reported that a final (post-chemistry) treatment consisting of baking at 120 C for 12 to 48 hours and up to 145 C for 3 hours in UHV or air improves cavity performance, most notably high-field Q drop. Baking at about 160 C or higher is adverse. The benefit survives exposure to air. A consensus understanding of its mechanism has yet to emerge. Attaining it will strengthen our scientific understanding of RF superconductivity and may show the way to even greater performance enhancement. Our approach is to apply a wide range of surface characterization tools and to correlate with single-cell cavities.

Our most fruitful approach has been variable photon energy XPS at NSLS soft x-ray undulator beamline X1B, where we are PRT members. The in-situ treatment facility affords opportunity to prepare states of different treatment temperature, time and atmosphere with or without ambient air exposure before spectroscopy. High photon intensity from 300 eV to 850 eV yields electron emission from the Nb 3d levels (200 – 210 eV binding energy) having kinetic energy from about 100 eV to about 650 eV, corresponding to sampling depths (three attenuation lengths) from about 1.76 nm to about 7.01 nm. We previously reported [HT et al.] the advantages of obtaining depth profiles by varying photon energy at fixed take-off angle versus varying take-off angle at fixed photon energy, as is typically done with laboratory XPS machines. Further, data at a series of photon energies showed only Nb +5 at the outer surface and finally Nb 0 as well at the highest photon energies. Careful curve fitting required the inclusion of Nb suboxides for spectra where Nb 0 was visible, indicating their association with the metal/oxide interface.

Fig 2. displays the Nb 3d region acquired at  $h\nu = 750$  eV plotted at constant Nb0 (202.2 eV) for samples baked 12 hours at 120 C or 165 C and not air-exposed vs unbaked. Baked plus air-exposed would be indistinguishable from unbaked. The dominant feature is the loss of Nb +5; spectra after 6 or 3 hour baking at 120 C show successively less Nb 5+ loss. Careful curve fitting presently underway may show some increase of suboxides, but not in any amount comparable to the Nb +5 loss. Spectra (not shown) acquired at  $h\nu = 300$  eV (most surface sensitive) show only Nb +5, though curve-fitting may reveal a trace of sub-oxides. Our observations appear as thinning of the oxide film to a degree controlled by the severity (time, temperature) of the bake. The fate of the oxygen is unclear; is it injected into the lattice? An oxide layer having the same thickness and composition as the original forms upon air exposure. Spectra from air-baked materials (not shown) indicate oxide film thickening and their spectra do not change upon subsequent air exposure, as might be expected. Recall that air-baked materials also show the improved performance.

It is unclear how to combine these observations into an understanding of low temperature baking, other than that when the original Nb<sub>2</sub>O<sub>5</sub> film is fully converted (165 C bake), enhanced performance is not obtained. Observations by our JLab collaborators on single-cell cavities may shed some light. Thermometry during RF testing indicates that some hot spots seen in unbaked cavities substantially disappear after baking and new ones do not appear until higher gradients. So then performance enhancement by low temperature baking is associated with eliminating a small population of strong absorbers, while performance loss by “overbaking” arises from disruption of the original film structure.

**3. SIC System** After establishing well-characterized electropolishing conditions and the resulting effects on topography, we propose to systematically correlate these results with maximum supportable surface magnetic fields on electropolished niobium samples. Our intended tool for doing this is the JLab SIC system. Its commissioning (not funded by this project) continues in parallel with the EP process characterization.

During the past 6 months, rf modal characterization at room temperature and initial cryogenic rf testing was completed. These confirmed the electromagnetic mode identifications and allowed initial characterization of the calorimeter instrumentation. At present, a flange is undergoing a vacuum leak repair and preparations are being made for a first high-field test. We anticipate this system to be commissioned and available for testing electropolished samples during the second program year of this project. While SIC System development is not funded by this project, its progress is important to our success and we therefore report it briefly.

**Future Work** Our work for the remaining five months of the current year and the twelve months of the next year, detailed below, builds on the findings above. The capabilities of our W&M – Jlab – Virginia Tech team are strengthened by the addition of major characterization instruments, all to be in operation by the end of June: 1.) FEI “Titan” 80-300 kV TEM. 2.) FEI

“Helios NanoLab” dual beam FIB/SEM with EBSD; 3.) CAMECA 7f GEO SIMS. 4.) ULVAC/PHI “Quantera” XPS. JLab has received authorization to reprogram other ILC funds to purchase instrumentation for electrical impedance spectroscopy.

**1. Electropolishing.** Our goals are to a.) extend our laboratory replication of the nine-cell process and b.) deepen our fundamental understanding of what is taking place. **Replication.** (to 7/07) The first step will be to incorporate fluid flow adjacent to the anode by making a rotating anode assembly, similar to the device we describe for BCP studies. However, it will now need to be conductive. Initial tests in which the earlier PTFE is replaced by aluminum are promising. (6/07-9/07) The second step is to include exit from and re-entry to the fluid, either by raising and lowering the electrolyte-containing vessel or by tilting the rotation axis of the anode assembly. For example, we do not now know the duration of the transient on immersion – are we mostly polishing in the transient regime? (to 2/08) The third step will be to add Nb to the bath, up to the levels typical of spent electrolytes. (on-going) We will examine the topography of materials polished under the above range of conditions, including leveling of deliberately-introduced features. (on-going) We will work with our JLab collaborators to apply what we learn to single-cell cavities. **Understanding.** Direct correlation of polishing with SRF performance is one of the exciting opportunities here. A first step (7/07-10/07) will be to construct larger scale lab EP equipment that can accommodate the 50 mm wafers used by the SIC equipment. We will then (8/07-11/07) need to do XPS and AFM to establish uniformity. A second element (to 6/08) will be to introduce a further electrochemical probe of the anode surface chemistry: AC impedance spectroscopy, a well-established technique used to characterize the mechanisms controlling behavior of the anode. It is anticipated that, e.g., the so-called “double-layer” capacitance at the anode surface, discernable with this technique, will serve as a direct indicator of the surface micro-roughness, and thus is a potentially valuable process feedback parameter. JLab will obtain separate funding for equipment acquisition. Correlation of polishing behavior with electrochemical mechanism (10/07-9/08) will provide important process development guidance.

**2. Low Temperature Baking.** The acquisition of the PHI Quantera XPS with its capability to examine large batches of specimens unattended makes possible the examination of the entire interior surface of a single cell cavity after cutting into sections (6/07-9/07). Thermometry can locate hot spots that can be examined and compared to the rest of the surface (8/07-5/08). The heating in the XPS machine can bake material associated with or not associated with hot spots, followed by another round of spectra (2/08-9/08). The goal is to identify, then synthesize candidate hot-spot materials to be studied by characterization and by the SIC.(3/08-9/08).

**3. SIC System Items.** The direct correlation of surface modification by electropolishing has yet to be fully characterized. Having systematically characterized the leveling effects of specific processing conditions above, we will (11/07-6/08) use the SIC system to correlate specific topological conditions with associated geometrically-induced peak rf magnetic field limitations. The SIC system is designed to measure the effective  $B_{c1}(T)$  as a function of surface topology. This will yield a performance basis for specifying required surface smoothness for ILC, and, via the other project activities, an electropolishing process that is understood to predictably produce such surfaces. In addition, features identified to be associated with high-field Q drop will be localized and the rf dissipation and material characterized before and after low temperature baking.(4/08-9/08).

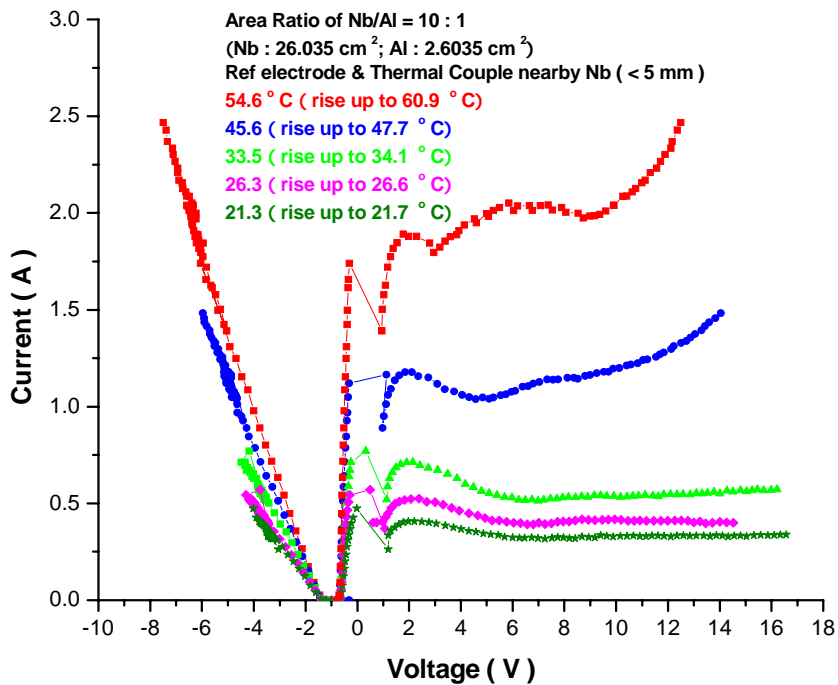


Fig. 1: Electropolishing in static, fresh 90:10 H<sub>2</sub>SO<sub>4</sub> - HF mixture

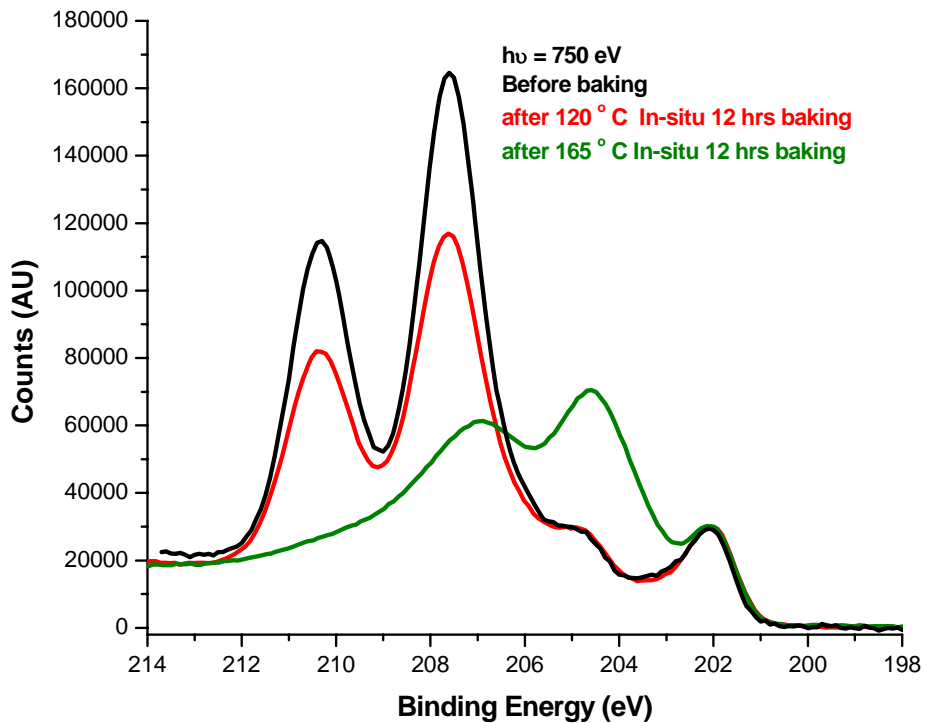


Fig. 2: Comparison XPS of three treatments on single crystal niobium