

# THE TRANSFER OF IMPROVED CAVITY PROCESSING PROTOCOLS TO INDUSTRY FOR LCLS-II: N-DOPING AND ELECTROPOLISHING\*

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## Abstract

Based on the R&D efforts of colleagues at FNAL, Cornell, and JLab, the LCLS-II project adopted a modification to the rather standard niobium SRF cavity surface processing protocol that incorporates a high temperature diffusion doping with nitrogen gas. This change was motivated by the resulting higher  $Q_0$  and the prospect of significantly lower cryogenic heat load for LCLS-II. JLab is responsible for managing the cavity procurement for the LCLS-II project. The first phase of the procurement action is to transfer the nitrogen-doping protocol to the industrial vendors. We also seek to exploit improvements in understanding of the niobium electropolishing process as part of the production processing of the TESLA-style LCLS-II cavities. We report on the technology transfer activities and progress toward the envisaged performance demonstration of vendor-processed cavities.

## N-DOPING REQUIREMENTS

Based on the multi-lab R&D effort that validated the discovery from FNAL of the beneficial effects of nitrogen doping of niobium cavities and explored its sensitivity to process variations, the LCLS-II project selected a particular protocol for cavity preparation that has consistently yielded higher  $Q_0$ , and thus lower cryogenic losses, than has previously been accessible. This R&D effort has been documented [1-5], and the subsequent preparation of cavities for the two LCLS-II prototype cryomodules are reported at this conference.[6-11]

By conference time the cavity vendors for the LCLS-II project have been selected. Both vendors visited JLab and FNAL to consult regarding modifications to the cavity treatment protocols compared with prior experience. Furnace gas flow control requirements were discussed. Procedures for controlled cavity electropolishing were discussed. Vendors observed application of both processes to cavities at JLab. Vendors are now in the process of adapting their own facilities to accomplish the modified processes. First commissioning runs are anticipated soon after the conference. Per the terms of the contract, JLab staff will advise and assist. Vendors are required to pass a qualification test by successfully processing two cavities supplied by the project, success being demonstrated by documented process control and acceptable high- $Q$  performance of cavities delivered to JLab under vacuum for cryogenic test.

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The cavity preparation protocol is a relatively minor, but controlled variation on the now rather standard niobium cavity surface preparation methods developed by the community over the past decades. It involves low-pressure nitrogen gas exposure at the end of a 800 °C vacuum bake, followed by a light electropolish (EP) removing a few microns from the cavity surface. The control parameters associated with the heat treat cycle issued to the vendors are listed in Tables 1 and 2.

Table 1: Vacuum Heat Treatment and Nitrogen Doping

Step	Temperature (°C)	Duration (min)	$P_N$ (mTorr)
Hydrogen degassing	800 ± 10	180 ± 5	0
Nitrogen doping	800 ± 10	2 ± 0.1	26 ± 15%
Vacuum annealing	800 ± 10	6 ± 0.1	0

Table 2: Range of Doping Parameters

$P_N$	22-30 mTorr (2.9 – 4.0 Pa) $P_{avg} = 26$ mTorr (3.5 Pa)
$T_N$ (doping)	2 min ± 6 sec
$T_A$ (annealing)	6 min ± 6 sec

This doping by thermal diffusion is followed by controlled electropolishing of the cavity interior surface, to remove 5 μm on average with nominally uniform removal, or 5 μm from the cell equator region.

The vendors have flexibility regarding the particular implementations used to meet these requirements. The lab R&D effort adequately demonstrated that cavity loss characteristics are not highly sensitive to protocol details, so that successful realization of project requirements appears confident. Nevertheless, as reported elsewhere in this conference, research continues into the basic material dynamics of the beneficial effects of nitrogen doping, and there are prospects that further refinements may yet be accessible.

In order to build assurance with vendor N-doping facilities and processes, metallographically smooth niobium samples are being provided for doping simultaneously with initial cavities. These will be returned to JLab for controlled bench EP and dose analysis via SIMS and compared with similar samples treated in the lab facilities.[12]

After successful doping has been demonstrated, the vendors will proceed with fabrication of new cavities and then finish them with the monitored doping and subsequent light EP, delivering completed production

cavities under vacuum ready for cryogenic RF acceptance testing for the LCLS-II cryomodules.

## HISTORY OF NIOBIUM EP

In addition to the nitrogen doping technology, we seek to transfer to vendors the progress in understanding and control of the cavity electropolishing process that have evolved over the last few years. Here we summarize the theoretical understanding of the present standard niobium electropolishing process using the HF:H<sub>2</sub>SO<sub>4</sub> in 1:9 reagent ratio concentration electrolyte. As they have opportunity, the vendors may seek to incorporate improvements into their electropolishing processes.

Initial development of the Nb cavity EP process was done in an empirical manner without benefit of scientific characterization of the underlying process dynamics and understanding of the interplay of many variables which affect the actual removal of Nb material in specific locations. Research undertaken at JLab and Saclay in 2005-2011[13-20] made fundamental contributions to elucidating the Nb electropolishing process based on HF:H<sub>2</sub>SO<sub>4</sub>. The KEK and DESY-led EP development [21-25] preceded this work such that the methodologies employed for Tristan, TTF, and XFEL cavity work were not able to benefit from the improved process insights that came later. The CEBAF Upgrade project, with methods that were frozen some time later was able to benefit from some of the insights. Even that, however, was forced to freeze a set of process parameters that was adequate for the project requirements, leaving little free energy for actual scientific process optimization.[26, 27] Beneficial use of the new insights was made in the new cavities for ATLAS and ILC cavity work at ANL.[28-30] Historically, in response to the observation of significantly more removal from small ID surfaces compared with cavity equator surfaces during EP operations without cavity temperature monitoring, various strategies of “masking” the axial Al cathode in these regions have been attempted with mixed success.

With JLab now responsible for specifying and managing the cavity procurement for LCLS-II, there is potential to allow that project to benefit from the improved technical insights. In addition, one also seeks to generalize the Nb cavity EP process, so that it becomes increasingly geometry independent, accommodating 3D structures with large aspect ratios and non-cylindrical symmetry.

## REVIEW OF KEY FEATURES OF THE STANDARD NB HF:H<sub>2</sub>SO<sub>4</sub> EP PROCESS

Lessons learned so far regarding analysis and exploitation of Nb EP may be distilled into the following:

- Electropolishing, in contrast with etching or electro-etching, is accomplished by effecting material removal in a way that is blind to crystal structure and preferentially removes asperities over grooves.
- The electropolishing process is an active balance of two competing processes at each location on the

niobium surface: growth of Nb<sub>2</sub>O<sub>5</sub> via anodization by sulfate ions and dissolution of the niobium oxide by fluorine ions.

- Current and a minimum local potential at the anode (cavity) surface is required to grow the oxide.
- The process requires five free electrons for each Nb atom removed.
- The process operates locally under “diffusion control” meaning that the accessibility of the fluorine to the surface limits the reaction rate and thus the local steady-state current density.
- All other factors being constant, the reaction rate is directly proportional to the HF concentration.
- The diffusion rate is temperature dependent, so the local reaction rate is dependent on the local temperature.
- The corresponding diffusion length is of order 20 μm. On this scale, the concentration of F<sup>-</sup> ions goes from zero at the surface to essentially bulk value. The concentration gradient contributes to surface profile leveling on this scale.
- Variation of temperature over the surface of a Nb cavity during EP results in variation of removal rates.
- A marker for such “diffusion control” is the occurrence of a “plateau” on the I-V curve of the electrolytic cell.
- In the plateau region, an increase of the applied potential results in no increase in steady-state current flow.
- The “power supply” voltage applied between the anode (cavity) and cathode gets divided into three elements: (a) anode surface potential, (b) ohmic drop through the electrolyte, and (c) cathode surface potential.
- The “plateau” is due exclusively to (a). Increased applied voltage produces only an increased thickness to the oxide layer in steady-state sufficient to drop the increased potential across the increased thickness, with no additional current flow.
- The potential drop (b) is very much dependent on cavity/cathode geometry and conductivity of the electrolyte.
- The cathode potential (c) is required to drive hydrolysis evolving hydrogen gas sufficient so that the total integrated current passing through the active cathode surface area matches the total current growing the oxide on the niobium surface.
- In typical commercial applications, one wants to maximize the cathode surface area, so that the required current flow is attained with minimum polarization of the cathode.
- Higher polarization potential on the cathode wastes energy and also increases the reaction rates of other (parasitic) electrochemical processes. One such process in the present circumstance is the precipitation of solid sulfur.
- The reaction rates of such parasitic chemical processes increase with local temperature, although

the cathode temperature is typically well controlled in current cavity EP implementations, since it is also the supply line of fresh, cooled electrolyte.

- For a given cathode and anode geometry, electrolyte concentration, and cavity surface temperature, the “plateau” in the I-V curve begins when all of the Nb surface is anodized.
  - The reaction rate is then uniform over the surface even though the oxide thickness will likely not be uniform.
  - The anodization thickness will be maximum on surfaces closer to the cathode (where there is less potential drop through the electrolyte), and thinnest in locations farther from the cathode.
  - Small sample measurements have demonstrated that if temperature is controlled, the plateau condition extends beyond a polarization potential of 25 V.
- A consequence of the uniform reaction rate across the cavity under the “plateau” condition is uniform local current density.
- This uniform current density, however, is flowing through the locally maintained oxide thickness which presents a resistive impedance.
- The local dissipative power,  $I^2R$ , will then vary over the cavity surface because of the variation in  $R$ , not the variation in  $I$ .
- Without careful temperature control, the variation of local dissipative power, even within the plateau region, will result in variation of surface temperature and thus reaction rate, which in turn increases the local  $I$ , compounding the non-uniformity of local material removal.
- Use of the electrolyte secondarily as process coolant is problematic because of the complex 3D geometry, with locally varying flow conditions.
  - This problem is aggravated if the applied voltage is significantly higher than the low end of the plateau. The non-beneficial extra heat inherently increases the temperature differentials.
- For the standard electrolyte, there is evidence of an additional parallel electrochemical etching process which is proceeding simultaneous to the diffusion-limited electropolishing.
  - This process is rather steeply temperature dependent and becomes dominant above  $\sim 35^\circ\text{C}$ .
  - For occasions when optimum surface smoothness is required, one should avoid such temperatures.

To summarize the implications for controlled, uniform polishing with minimum generation of sulfur:

- Provide conditions which tend to assure temperature uniformity and control over the cavity surface being polished.
- Maximize exposed cathode surface area
- Minimize the generation of unnecessary and counter-productive heat by operating near the low end of the plateau in the I-V curve.

## EP DEVELOPMENT RUN WITH 7-CELL CAVITY J100-2

In order to gain clear data to test the implications of the above understanding, a set of controlled EP runs were staged and executed on the 7-cell cavity J100-2, a cavity with CEBAF C100 design, fabricated from ingot niobium and previously tested in 2010-2011. The study was undertaken to illustrate the effect of changing the applied anode-cathode voltage on the cavity temperature distribution and thus local removal rate distribution. This was done for two cases, (a) with the Al cathode surface area partially restricted via wrapping of the beamtube regions and a narrow range near the irises with Teflon tape, and an attached Teflon mesh screen sometimes intended to aid break-up of evolved hydrogen bubbles (the configuration used for the C100 cavities for the CEBAF 12 GeV upgrade), and (b) with the same Al cathode installed in a completely stripped bare state (un-masked).

The cavity was outfitted with seven thermocouples on the cavity surface, three on equators, two on irises (the cavity has no stiffening rings, allowing good access to the irises), and two on the beampipes. As is customary with JLab cavity EP runs, the readings from these thermocouples were recorded continuously through the process.

The JLab horizontal cavity EP system includes external water spray on the cavity from below in order to help control the cavity temperature. The present system uses local city water which (being principally derived from local surface waters) has significant seasonal variation in temperature and may be cooled by heat exchange with a  $5^\circ\text{C}$  glycol supply but has no provision for the addition of heat. Variation of this supply temperature also occurs on the time scale of tens of minutes, requiring manual operator compensation control via adjustments to the glycol flow to the heat exchanger. While this spray has been commonly referred to as “cooling water”, it has also been observed on occasion to function as a heat source offsetting the cold temperature of the circulating acid electrolyte.

Figure 1 shows the cavity temperature monitors and current as the applied voltage between anode (cavity) and cathode (Al rod) was varied for the two cathode configurations.

Individual thermocouples reported the typical cyclic response corresponding to the 1 rpm rotation of the cavity during processing. In order to discern systematic responses to mean temperature and voltage, smoothed versions of the same data are displayed in Fig. 2. Among other features, one may observe that as the applied voltage is reduced, the equator temperatures (EQ) transition from being cooler than the irises to being slightly warmer than the irises. One expects this to similarly track with local removal rate variances for reasons cited above.

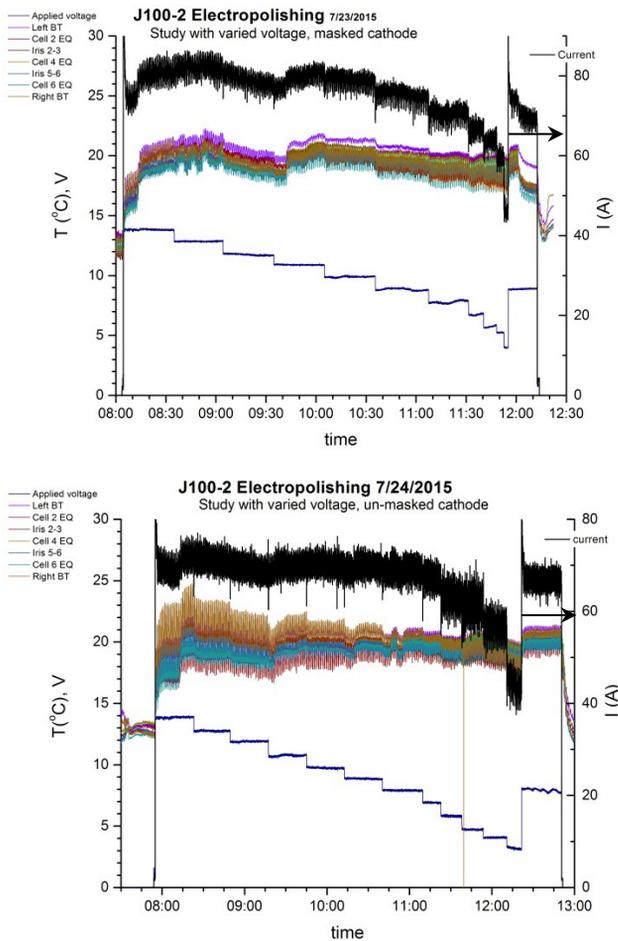


Figure 1: Temperature and current response to varied applied voltage during EP of J100-2.

Analysis of the data reveals a 2.0 A/°C overall temperature sensitivity with constant voltage operations and ~1.3 A/hr current decrease during each run due to consumption of HF from the electrolyte. Applying these correction factors to the process current allows us to directly observe the I-V response curves with all other process variables constant. These data are plotted in Fig. 3. Consistent with the process description above, the desired plateau condition extends down to ~7.0 V in the un-masked cathode condition, but the plateau in the masked cathode case only begins at ~12.5 V because of the significant polarization potential required at the cathode to drive the higher required current density.

These results suggest that, at least for the JLab horizontal EP configuration, use of an un-masked cathode together with an applied potential of 8 volts is a very attractive operating condition. This will reduce the applied power by almost 50%, while easing the temperature, and thus removal, uniformity challenge, and also further reducing the risk of sulfur production at the cathode.

The cavity vendors for LCLS-II are currently considering for themselves how to incorporate these lessons learned for niobium EP into their processes.

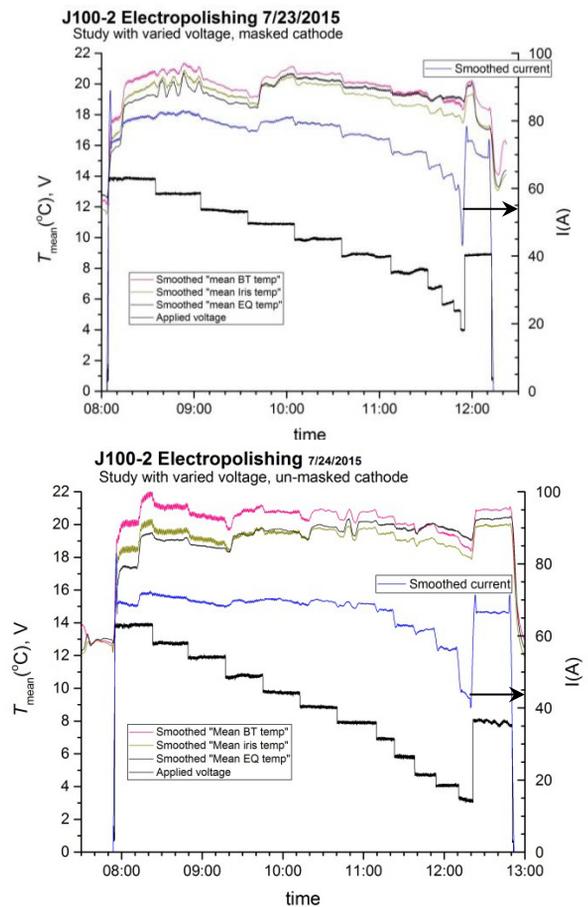


Figure 2: Smoothed versions of the data in Fig. 1.

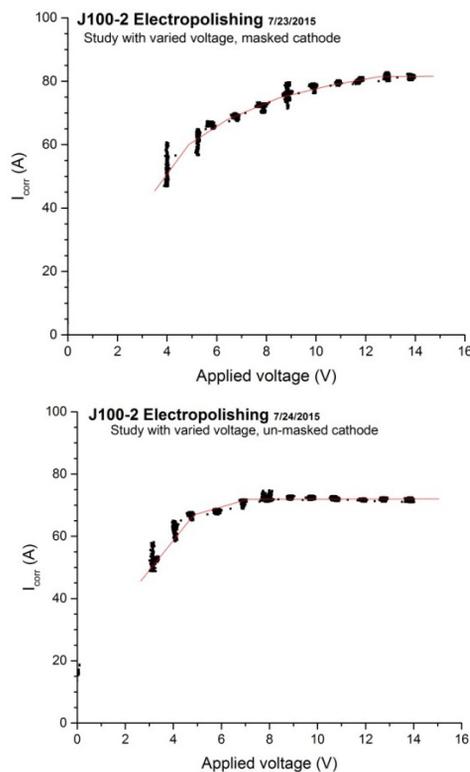


Figure 3: Corrected I-V curves for the masked and un-masked cathode conditions. (Lines are eye-guides.)

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## REFERENCES

- [1] A. Grassellino, et al., *Superconductor Science and Technology* 26, 102001 (2013).
- [2] M. Liepe, et al., in *International Particle Accelerator Conference 2014* (Dresden, Germany, 2014), p. 2627.
- [3] A. D. Palczewski, et al., in *International Particle Accelerator Conference 2015* (Richmond, Virginia, 2015), p. 3528.
- [4] A. D. Palczewski, et al., in *27th Linear Accelerator Conference* (Geneva, Switzerland, 2014).
- [5] D. Gonnella, et al., *Journal of Applied Physics* 117, 023908 (2015).
- [6] M. C. Ross, in *SRF2015* (Whistler, BC, Canada, 2015), p. MOBA01.
- [7] A. Grassellino, in *SRF2015* (Whistler, BC, Canada, 2015), p. MOBA06.
- [8] M. Liepe, et al., in *SRF2015* (Whistler, BC, Canada, 2015), p. MOBA08.
- [9] A. D. Palczewski, et al., in *SRF2015* (Whistler, BC, Canada, 2015), p. MOBA07.
- [10] M. Liepe, et al., in *SRF2015* (Whistler, BC, Canada, 2015), p. MOPBA033.
- [11] A. D. Palczewski, et al., in *SRF2015* (Whistler, BC, Canada, 2015), p. MOPB040.
- [12] H. Tian, et al., in *SRF2015* (Whistler, BC, Canada, 2015), p. MOPB107.
- [13] H. Tian, et al., *Journal of The Electrochemical Society* 155, D563 (2008).
- [14] A. Aspart, et al., in *12th International Workshop on RF Superconductivity* (2005).
- [15] F. Eozéno, et al., in *12th International Workshop on RF Superconductivity* (Ithaca, New York, 2005).
- [16] F. Eozéno, et al., *Phys. Rev. ST Accel. Beams* 17, 083501 (2014).
- [17] F. Eozéno, et al., *Phys. Rev. ST Accel. Beams* 13, 083501 (2010).
- [18] H. Tian and C. E. Reece, *Phys. Rev. ST Accel. Beams* 13, 083502 (2010).
- [19] L. Zhao, et al., in *15th International Conference on RF Superconductivity* (Chicago, IL USA, 2011), p. 129.
- [20] C. E. Reece, et al., in *23rd Particle Accelerator Conference* (Vancouver, BC, 2009), p. 2126.
- [21] K. Saito, et al., in *4th International Workshop on RF Superconductivity* (KEK, Tsukuba, Japan, 1989), p. 635.
- [22] K. Saito, et al., in *8th International Workshop on RF Superconductivity*, edited by V. Palmieri (Abano Terme, Italy, 1997), p. 795.
- [23] F. Furuta, et al., in *2006 Linear Accel. Conf.* (Knoxville, Tennessee USA, 2006), p. 299.
- [24] L. Lilje, et al., *Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment* 516, 213 (2004).
- [25] L. Lilje, et al., *Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment* 524, 1 (2004).
- [26] C. E. Reece and H. Tian, in *Proceedings of Linear Accelerator Conference LINAC2010* (Tsukuba, Japan, 2010).
- [27] A. Reilly, et al., in *15th International Conference on RF Superconductivity* (Chicago, IL USA, 2011), p. 542.
- [28] M. P. Kelly, et al., in *15th International Conference on RF Superconductivity* (Chicago, IL USA, 2011), p. 680.
- [29] S. M. Gerbick, et al., in *15th International Conference on RF Superconductivity* (Chicago, IL USA, 2011), p. 576.
- [30] T. Reid, et al., in *15th International Conference on RF Superconductivity* (Chicago, IL USA, 2011), p. 576.