

# BIPOLAR EP: ELECTROPOLISHING WITHOUT FLUORINE IN A WATER BASED ELECTROLYTE\*

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## Abstract

For more than thirty years, preparing superconducting RF cavities for high performance has required the use of dangerous and ecologically damaging chemicals. Reducing the personnel and environmental risks associated with using these chemicals is a priority at Fermilab. Therefore, Fermilab pursued a project to adapt a non-hazardous and relatively benign bipolar electropolishing technique to SRF cavities that Faraday Technology, Inc. developed. Faraday initially developed this electropolishing technique to polish metal alloys used in automotive and semiconductor components as well as medical devices and implants. By modifying the cathodic/anodic interaction via a pulse forward/pulse reverse technique, Fermilab and Faraday Technology demonstrate the capability to polish 1.3 GHz single-cell cavities utilizing an aqueous 10% sulfuric acid electrolyte. We present the development of bipolar EP for single-cell 1.3 GHz cavities and show the results from vertical tests achieving gradients greater than 40 MV/m.

## INTRODUCTION

Electropolishing remains the fundamental surface preparation process to achieve high gradients and quality factors for all current and proposed SRF-based accelerators utilizing elliptical cell RF cavities [1-3]. The benefits of electropolishing niobium, utilizing variants of the Siemens recipe from 1971 are well published and well known throughout the SRF community [4]. In recent years, EP has even improved the performance of low-beta structures despite complex mechanical and fluid dynamic complications posed by the resonator geometry [5]. Though promising, alternative material removal techniques like centrifugal barrel polishing (CBP) [6,7] are unlikely to displace EP as a baseline processing step due to its reliability, effectiveness, and widespread use. Unfortunately, significant negative aspects remain with EP even though it is a mature technology for elliptical cavity processing.

Electropolishing niobium with a mixture of concentrated sulfuric and hydrofluoric acids carries significant personnel safety concerns as well as negative environmental impact [8]. EP is an unavoidable evil for the niobium RF cavity performance preparation process. Each facility that utilizes the EP process must abide by a litany of safety and environmental standards controlled by a variety of groups. In the United States Department of Energy (DOE) system, cavity processors must abide by

the ubiquitous Occupational Safety and Health Administration (OSHA) and Environmental Protection Agency (EPA) requirements as well as local EPA and facility specific environmental safety and health groups and their layers of rules and standards. For these reasons, it is in the best interest of all cavity processing groups to minimize the use of hazardous and environmentally problematic chemicals.

Several groups have pursued niobium chemistry on a less hazardous and more environmentally benign path with some success [9,10]. As with the intent of this previous work, this program's motivation was to seek an alternative to the baseline EP process provided the process did not substantially degrade RF performance.

Occasionally, funding becomes available to pursue a research opportunity that is a bit far afield from SRF but has a potentially large impact on the standard way of doing business. With research funds from the American Recovery and Reinvestment Act (ARRA), Fermilab engaged in one such opportunity with Faraday Technology, Inc. to develop an ecologically 'friendly' alternative to standard EP. Pulse forward/pulse reverse EP (referred to as bipolar EP from here forward) of niobium in a water-based electrolyte without the need of fluorine looked like a promising but uncertain technique [11]. The primary potential benefit of bipolar EP was the potential to replace the baseline EP process and thereby dramatically reduce safety and environmental impacts of the current EP technique. In addition, bipolar EP may offer "industrial process benefits" in terms of vertical cavity processing without the need for rotation.

This paper describes the process by which Fermilab and Faraday Technology, Inc. developed single-cell bipolar EP for single-cell 1.3 GHz cavities. This paper also explains the project development history beginning with niobium coupon studies and culminating in multiple 1.3 GHz single-cell cavity tests, some of which resulted in accelerating gradients above 30 MV/m and quality factors above  $1\text{E}+10$  at a 2 K test temperature.

## BIPOLAR EP PROCESS BACKGROUND

The electrochemistry behind the bipolar EP technique is described in detail in a paper published at this conference and elsewhere [12,13]. In brief, bipolar EP, or pulse-forward, reverse-pulse technique uses an anodic forward pulse to grow an oxide layer on the reacting surface. The anodic pulse is followed by a delay, or voltage off-time, that dissipates the heat, removes reaction by-products, and replenishes active agents needed for the reaction. A cathodic pulse then reverses the voltage and reduces the passive oxide layer on the reacting surface. Figure 1

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shows a general representation applied anodic/cathodic waveform.

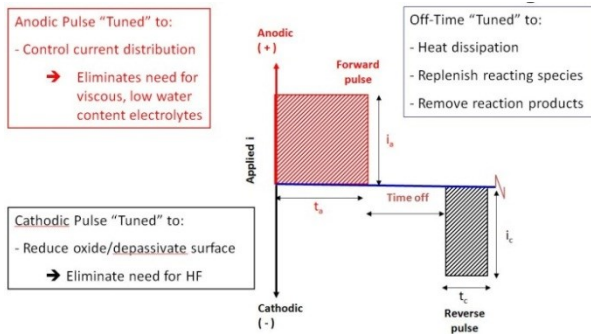


Figure 1: General bipolar EP representation.

The advantage of utilizing this electropolishing technique over the Siemens technique is that one controls the anodic and cathodic pulse characteristics which allow reaction tuning. Forcing positive and negative voltages at particular rates as well as on and off times allows control of reaction rates, heat generation, and polishing characteristics. In addition, and most importantly for the goals of this study, the electrochemistry also does not require the presence of fluorine to depassivate the oxide layer. In contrast, the Siemens EP process is not particularly 'tunable' and functions most effectively at a constant DC voltage, a controlled temperature, and with sufficient fluorine available to reduce the niobium oxide layer.

Bipolar EP and its wide range of operating variables present some difficulty determining the right operating parameters for the desired polishing regime. Reaction rates, surface finish characteristics, and oxide thicknesses change with the chosen waveform. This paper does not claim the discovery of an optimal waveform for niobium cavity polishing, in fact minimal goal oriented waveform parameter optimization was conducted. Rather, it presents the development of a functional waveform and process that produces high quality surfaces compatible with high gradient and quality factors in SRF cavities.

## BIPOLAR EP PROJECT

### Project Goals

This project had several specific goals [14]. The primary objectives were to prove that bipolar EP process polished niobium with an HF-free electrolyte, to produce a high-quality RF surface compatible with the traditional EP technique, and to operate on existing horizontal electropolishing tools. This last objective was intended to provide a 'drop-in' electropolishing technique usable in the horizontal EP tools located at Fermilab, Argonne, and elsewhere.

Fermilab narrowed the project scope such that the only desired modifications to an existing process and EP tool were the HF-free electrolyte (5-10%  $H_2SO_4$  in an aqueous solution), bipolar power-supply, cathode, and electrical connections. This scope definition made the most compelling case to pursue further work and expand to

multi-cell 1.3 GHz cavities with the achievement of successful RF performance tests. Due to funding limitations, the scope of the bipolar polishing effort was limited to single-cell cavities.

As part of the cavity polishing program, Faraday Technology, Inc. constructed a small electropolishing facility that functioned similarly to the facilities located at Fermilab and Argonne. Faraday Technology, Inc., fabricated a horizontal EP tool based on the EP tool built for the Cavity Processing Laboratory at Fermilab which was in turn based heavily on the EP tool designed and built at the Joint ANL/FNAL Superconducting Surface Processing Facility at Argonne [15]. Figure 2 shows the EP tool constructed at Faraday, Technology, Inc.



Figure 2: Horizontal EP tool installed at Faraday Technology, Inc.

### Initial Polishing Results

Fermilab provided four 1.3 GHz single-cell cavities for the bipolar EP project. The first cavity (TE1NR001) was a sacrificial test cavity used to develop the polishing waveform. Since the coupon polishing effort yielded a set of parameters that produced a  $0.2 \mu m$  Ra surface finish, the project transitioned to cavity polishing. The Faraday Technology, Inc. scientists used TE1NR001 to perform fifteen test polishing cycles. They attempted to overcome technical problems due to the horizontal orientation, cathode masking ratios, electrical connection heating issues and suspected conduction limitations due to hydrogen gas bubbles on the cathode with a low flow ( $< 1$  gpm) electrolyte.



The horizontal orientation was proving not to work well with the low viscosity aqueous electrolyte. Due to these problems, the cavity was oriented vertically (Fig. 3) and the electrolyte flow rate increased to 3 gpm.



Figure 3: Vertical bipolar EP configuration.

Since the electrolyte did not entrain hydrogen bubbles and readily carried them out in solution, the typical vertical EP limitation with highly viscous nine part 95%  $\text{H}_2\text{SO}_4$  and one part 48% HF electrolyte did not exist. These process modifications resulted in a stable process temperature and a desirable waveform as shown in Figure 4 and described in detail elsewhere [11,12].

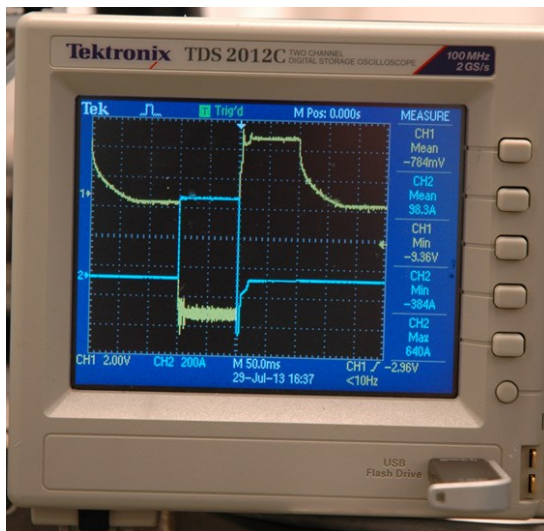


Figure 4: Final pulse forward, pulse reverse waveform used to polish single-cell 1.3 GHz cavities.

At this stage of development, the waveform and process parameters still resulted in low removal rates of approximately  $1.5 \mu\text{m}/\text{hour}$ . Due to the use of high viscosity electrolytes under mass transport control, Faraday's experience in developing bipolar EP in low viscosity electrolytes for other applications is that the process is faster. We believe that bipolar EP waveform parameters could similarly be developed for electropolishing of SRF cavities. However, for niobium electropolishing a current transient in the anodic current response was observed and attributed to a transition from oxide film formation/growth to oxygen evolution [11,12]. It was suggested that the bipolar EP mechanism occurred by removal of the niobium oxide during the cathodic pulse and was termed "cathodic electropolishing" [11,12]. In any event, the presence of the anodic current transition is believed to be important to effectively electropolish niobium. Consequently, to adapt bipolar EP from coupons to single-cell cavities, the timing of the waveforms was lengthened to provide sufficient time for the anodic current transition [12]. However, surface finish and appearance were acceptable and the process achieved a typical 2:1 removal ratio of between the beam tube and equator. Figure 5 shows an optical inspection image of TE1NR001 after the bipolar EP waveform development.

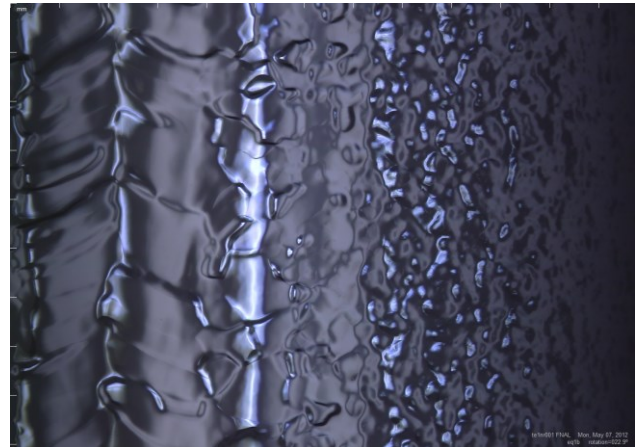


Figure 5: Optical inspection image of TE1NR001 after bipolar EP waveform development studies.

Unfortunately, further waveform optimizations, including duty factor improvement, voltage optimization, and shortening of off-time duration to improve removal rates were not possible due to lack of remaining funds and project timeline. The process required evaluation for RF compatibility, thus the cavity polishing and performance sequence began. All subsequent cavity polishing was performed using the 5-10 wt%  $\text{H}_2\text{SO}_4$  waveforms described at this conference [12].

In all cases, Faraday Technology, Inc. performed all bipolar electropolishing processes, ultrasonically cleaned the cavities, and shipped them to Fermilab for final processing. The final processing and test sequences that Fermilab performed varied based on particular investigations. We describe the details of each process and test sequence as well as cavity test results below.

## 09 Cavity preparation and production

### G. Basic R&D bulk Nb - Surface wet processing

### Performance Experiment #1

Goal: Verify vertical test performance of bipolar EP on a single-cell 1.3 GHz cavity (TE1DESYB5).

Process Sequence:

- Vertical test #1 for baseline performance of BCP treated cavity.
- Light Vertical Bipolar EP - > 10 $\mu$ m removal at equator.
- High pressure rinse and vertical test preparation
- Vertical test #2.

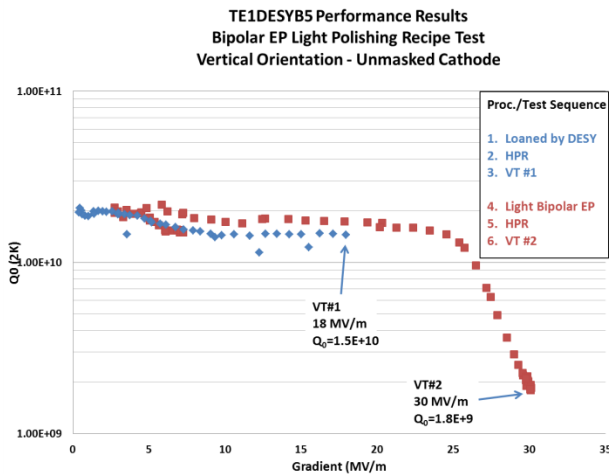


Figure 6: Baseline and post-bipolar EP test results of TE1DESYB5 trial cavity #1.

The results of this test (Fig. 6) showed an increase in gradient and quality factor from the baseline test. Strong high field Q slope exists above 25 MV/m. This test proved that bipolar EP, at a minimum, yielded an RF surface equivalent to standard buffered chemical polishing treatment and similar to EP without 120C bake. No further tests were performed on this cavity.

### Performance Experiment #2

Goal: Perform bulk electropolish on a poor performing cavity (TE1AES007) using Bipolar EP to determine process compatibility.

Process Sequence:

- Vertical test #1
- Bulk Vertical Bipolar EP - > 50 $\mu$ m removal at equator.
- High pressure rinse and vertical test preparation
- Vertical test #2.

### TE1AES007 Performance Results Bipolar EP Bulk Polishing - Vertical Orientation

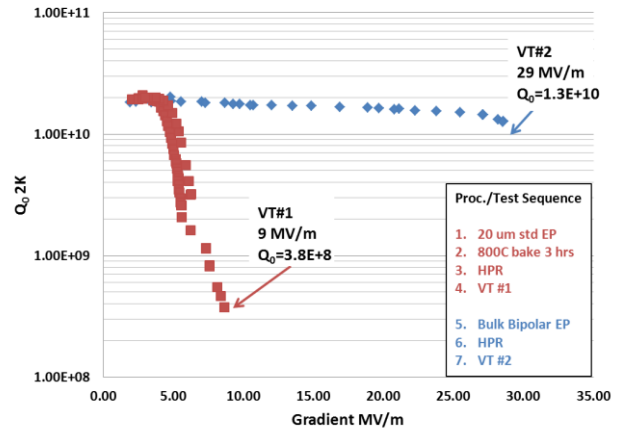


Figure 7: Bulk bipolar EP test on poor performing TE1AES007.

The test result (Fig. 7) shows a performance typical of traditional electropolishing yielding a gradient limited by quench at 29 MV/m at a  $Q_0$  of 1.3E+10. Based on this result, it was important to understand whether bulk and light bipolar EP cause Q-disease.

### Performance Experiment #3

Goal: Evaluate Q-disease behavior due to bulk and light bipolar EP.

Process Sequence:

- 100 K hold
- Vertical test #3
- 800C bake 3 hrs with end caps (no-foils)
- High pressure rinse and vertical test prep
- Vertical test #4
- Light Bipolar EP – 20  $\mu$ m at equator
- High pressure rinse and vertical test prep
- 100 K hold
- Vertical test #5

### TE1AES007 Performance Results Bipolar EP Q-disease Studies

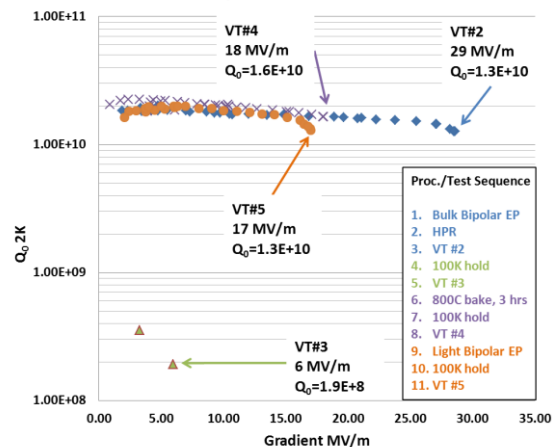


Figure 8: Q-disease studies of bipolar EP on cavity TE1AES007.

The performance curve in vertical test #3, as shown in Figure 8, clearly shows Q-disease. This behavior is typical of a traditionally bulk electropolished cavity. TE1AES007 was then baked at 800 C for three hours with niobium caps to help eliminate furnace-born contamination. The Q-disease was eliminated as shown by the vertical test #4 curve. The quench field was limited to 18 MV/m due to an unknown defect.

The final Q-disease test included an additional light bipolar EP of approximately 20  $\mu\text{m}$  at the equator and a 100K hold during cool-down. No Q-disease exists and the quench field matches closely the previous test.

Since tests showed that light bipolar EP is unlikely to cause Q-disease, we tested a cavity with known high performance in both gradient and  $Q_0$  to verify full performance compatibility with traditional EP. Cavity TE1AES012 was used because of its previous very high performance showing a quench gradient of 44 MV/m and a  $Q_0$  at 35 MV/m of  $1.7\text{E}+10$ .

### Performance Experiment #4

Goal: Evaluate whether light bipolar EP is capable of producing gradients  $> 35$  MV/m at a  $Q_0$  of  $1\text{E}+10$ .

Process Sequence:

- Baseline EP vertical test #1
- Baseline light EP vertical test #2 (light surface damage repair + Q disease test)
- Bipolar light EP
- High pressure rinse and vertical test prep
- 120 C bake
- Vertical test #3 (standard probe)
- High pressure rinse and vertical test prep
- Vertical test #4 (shortened probe)

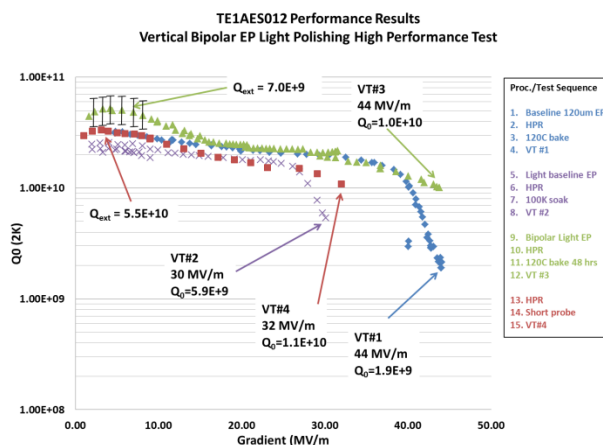


Figure 9: High performance evaluation of light bipolar EP on TE1AES012.

The curves from the first and second vertical tests were performed separately from this program. The first curve shows the result after traditional EP. The second curve is a result following a light EP performed to repair possible surface damage due to an RF feedthrough failure.

The cavity received a light bipolar EP prior to the third test. The curve for vertical test #3 (Fig. 9) shows a return

to the 44 MV/m quench field shown in test #1 with an almost identical  $Q_0$  of  $1.8\text{E}+10$  at 35 MV/m. An abnormal cool down took place that may have affected the low-field  $Q_0$ . A very interesting effect of Q enhancement was found at low field, where a Q of  $\sim 5\text{E}10 \pm 1.75\text{E}+10$  (measured with  $Q_{\text{ext}} \sim 2\text{E}+09$ ) was measured. From a Q vs. T measurement it appeared to be attributable to an almost zero low field residual resistance. It is worth mentioning that an abnormal cool down had taken place that may have affected the low-field  $Q_0$ , perhaps because of smaller (compared to standard) thermogradients generated across the cavity during the unusual cool down. The cavity was accidentally left for a couple of hours at 100 K and to avoid risk of Q-disease it was warmed up to 220 K and then quickly cooled back down to 2 K. This is different from the typical cool down which goes rapidly from 300 K to 2 K, with large thermogradients across the dewar.

The final vertical test shows a  $Q_0 \sim 3.2\text{E}+10$  at 5 MV/m which is in line with previous tests. No additional processing was performed other than an HPR and vertical test preparation. A shortened coupler probe with  $Q_{\text{ext}} \sim 5\text{E}+10$  was installed to validate the low field  $Q_0$  measured in test #3. The Q-slope that appears is likely due to residual hydrogen since this cavity had not been degassed throughout its processing history. The residual hydrogen may have yielded low-level Q-disease in this subsequent cavity test even without additional processing [16]. Multipacting or possibly a field emitter induced the quench at 32 MV/m as radiation appeared above 30 MV/m.

### Conclusion

Bipolar EP, or pulse forward-pulse reverse EP, using a dilute  $\text{H}_2\text{SO}_4$  electrolyte produces a high performance RF surface in 1.3 GHz single-cell cavities. The RF performance characteristics of bipolar EP as compared to traditional EP are very similar in that bulk material removal using either technique generally results in Q-disease but light EP does not. The process achieved accelerating gradients above 40 MV/m and  $Q_0$  above  $1\text{E}+10$  at 35 MV/m.

The bipolar EP process requires an electrolyte no more hazardous or ecologically unfriendly than a household cleaner. If implemented as a standard or replacement process to polish niobium cavities, safety and environmental overheads would be reduced to a bare minimum.

In its current state, the bipolar waveform developed during this project results in a slower removal rate than traditional EP. However, bipolar EP is inherently controllable with several adjustable variables including anodic/cathodic voltages, on/off dwell times, and pulse rates. Developing faster material removal rates are possible with further investigation.

Finally, this project discovered a secondary benefit to the bipolar EP process. The best cavity polishing occurs when operated in the vertical orientation without cavity rotation. If vertical bipolar EP is also effective processing



multi-cell cavities, the scalability and reduced costs of the process over horizontal EP are potentially significant.

## ACKNOWLEDGMENT

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