

# R&D OF ELECTRO-POLISHING (EP) PROCESS WITH HF-FREE NEUTRAL ELECTROLYTE BY BIPOLAR-PULSE (BP) METHOD

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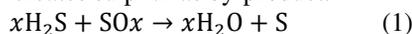
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## Abstract

Currently the Electro-Polishing (EP) process of Superconducting Radio-Frequency (SRF) accelerating niobium (Nb) cavity is performed with the electrolyte that is the mixture of hydrofluoric and sulfuric acids. However, the electrolyte is very dangerous and the environmental load in the disposal process of electrolyte is very heavy. This is the reason why the high cost is necessary in the safe design of facility and the safe operation of process in the conventional EP method. In such a situation, considering the reduction of cost and environmental load in the EP process, we performed the R&D of novel EP process with HF-free neutral electrolyte by Bipolar-Pulse (BP) method. In this presentation, we will report the removal rate, surface roughness and the results of surface analysis for the Nb-coupon samples that were processed by the BP-EP with HF-free neutral electrolyte.

## INTRODUCTION

Final surface preparations of Superconducting Radio-Frequency (SRF) niobium (Nb) cavities play a critical role in order to achieve high performance of SRF accelerator. Electro-Polishing (EP) process with electrolyte that is the mixture of sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) and fluoric acid (HF) is thought to be the best final surface preparation method to achieve higher gradient of SRF cavity and it has already been conventional technology around the world as the standard [1]. Development of Electro-Polishing (EP) method that does not use fluoric acid is desired in the mass-production of SRF cavities in the future project like ILC, because the electrolytic solution used in this method is very dangerous for the operator due to toxic gases (ex. HF, H<sub>2</sub>S, SO<sub>x</sub>) generated in the process and then the complex instrumentation and operation are required for the safety which increase the cost. In addition, it is reported that sulfur is produced as byproduct in the process and this causes degradation of cavity performance [2]. Equation (1) shows the chemical reaction which creates sulphur as by-product.



Then the development of Electro-Polishing (EP) method without sulfur is also desired. In such a situation, Faraday Inc. and FNAL have studied the Electro-Polishing (EP) by Bipolar-Pulse (BP) method with diluted H<sub>2</sub>SO<sub>4</sub> electrolyte for the SRF cavity [3]. In the BP-EP

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method, the sign of applied voltage is periodically switched to positive and negative (Bipolar-Pulse) in the EP process. Typical Bipolar-Pulse (BP) current in BP-EP process is shown in Fig. 1. In the plating process, this method has been widely used and applied in industries in order to obtain uniform thickness of plating. We already performed series of experiments for the BP-EP process of Nb coupon samples with alkaline electrolyte, i.e. diluted NaOH solution, and achieved smooth surface of Nb-coupon sample [4-6]. Therefore, the diluted H<sub>2</sub>SO<sub>4</sub> and/or NaOH electrolytes are already used in the HF-free BP-EP process of Nb surface. However, if we could perform the BP-EP with neutral electrolyte, we can achieve extremely safe BP-EP process and also extreme cost-reduction.

In this paper, we report the BP-EP method with neutral electrolyte. The advantages of neutral electrolyte are listed as followings. 1) Neutral solution is safer than acid and/or alkaline solutions. The BP-EP facility becomes much simpler and the cost of facility might be reduced more drastically. 2) The safety issues in the operation of BP-EP process become much simpler and the operation cost might be reduced more too. It means that the mass-production of SRF Nb cavities might become easier and the cost of cavity might become cheaper. 4) In general, the electrolytic removal processes typified by the micro electro-discharge machining process are based on the neutral electrolyte. Such technologies might give the hint to apply the neutral electrolyte to the BP-EP of Nb surface.

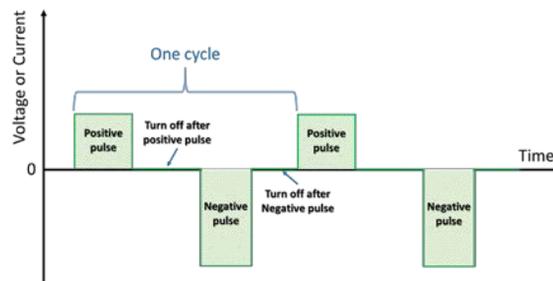


Figure 1: Typical wave form of periodic Bipolar-Pulse (BP) current.

We studied the BP-EP process with neutral electrolyte in the following three steps:

- We selected the best anion in the neutral electrolyte by using several acid solutions in the BP-EP process with Nb-coupon samples.

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- We studied the best concentration of selected anion in neutral electrolyte for the BP-EP process to achieve smooth surface of Nb-coupon samples.
- We studied the condition of pulse-shape in the BP-EP process with selected neutral electrolyte to achieve smooth surface of Nb-coupon samples.

## EXPERIMENTAL DETAIL

### Experimental Setup

The experimental setup of the BP-EP process with Nb-coupon sample is shown in Fig. 2. Nb-coupon is anode and Pt-mesh is cathode. The power source used to generate the Bipolar-Pulse (BP) current was SanRexKPF2F7-10-30PRRS485. The observation and roughness measurement of Nb-coupon surface before and after BP-EP processes were performed by the laser microscope: LEXT OLS3000 OLYMPAS.

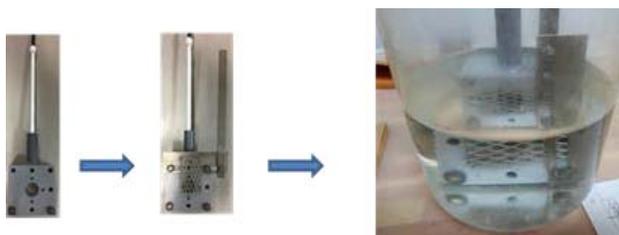


Figure 2: Schematic of the experimental apparatus.

### Preparation of Nb-Coupon Samples

The Nb-coupon sample ( $\phi 20 \times 2$  mm) was masked with vinyl chloride in order to obtain controlled exposure of surface as shown in Fig. 2. The Nb-coupon sample is contacted with Fe-cube (40 mm x 40 mm x 15 mm) and both the Nb-coupon sample and the Fe-cube are moulded in vinyl chloride. A screw hole was made on the side of Fe-cube to connect the steel (S45C) rod which is covered by the tape of fluorine resin. Nb-coupon surface was polished with #320 sandpaper in order to prepare flat and uniform surface. Abrasive particles on the surface due to the polishing were removed by electrolytic degreasing with the solution of NaOH and  $\text{Na}_2\text{CO}_3$ .

## EXPERIMENTAL RESULTS AND DISCUSSIONS

### Experiments with Various Acid Solutions to Select the Best Anion.

We performed experiments with various acid solutions: HCl,  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  in 10 v/v%. Nb-coupon samples processed by BP-EP method with these electrolytes for 10 minutes each at room temperature with the pulse-shape of  $T_{\text{anode}} = 3$  ms,  $V_{\text{anode}} = +3$  V,  $T_{\text{cathode}} = 3$  ms, and  $I_{\text{cathode}} = -9$  V.

The pictures of Nb-coupon samples before and after the BP-EP process with all solutions are shown in Fig. 3. Black particles were generated from the Nb surface with

gas for all Nb-coupon samples. Also metallic glossy surfaces were observed for all Nb-coupon samples after the BP-EP processes.

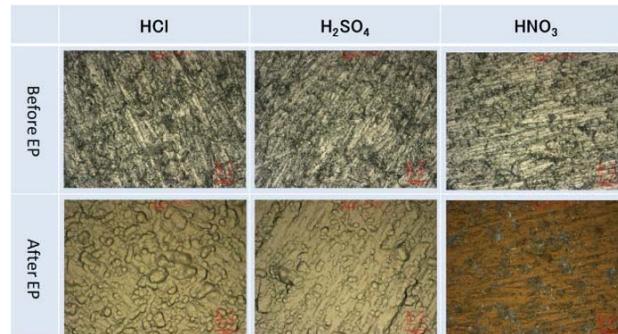


Figure 3: Observation of surfaces before and after BP-EP processes for HCl,  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  solutions.

Removal rates of BP-EP processes with all acid electrolytes are shown in Table 1. The roughness measurements of Nb-coupon samples before and after BP-EP processes with all acid electrolytes are shown in Table 2. Comparing numbers in table 1 and 2, it was found that the Cl-anion gives the highest removal rate and the smoothest surface. We considered that these results might be related to the fact that only the Cl-anion is the reductic acid in these three acids. All solutions after BP-EP processes were analyzed by the ICP method and Nb component was detected in all solutions.

Table1. Comparison of Removal Rate

	HCl	$\text{H}_2\text{SO}_4$	$\text{HNO}_3$
Dissolution amount	4.8 mg	0.9 mg	0.2 mg
Removal rate	0.178 $\mu\text{m}/\text{min}$	0.105 $\mu\text{m}/\text{min}$	0.007 $\mu\text{m}/\text{min}$

Table2. Comparison of Surface Roughness (Ra)

	HCl	$\text{H}_2\text{SO}_4$	$\text{HNO}_3$
Before EP	0.552	0.541	0.546
After EP	0.329	0.533	0.609

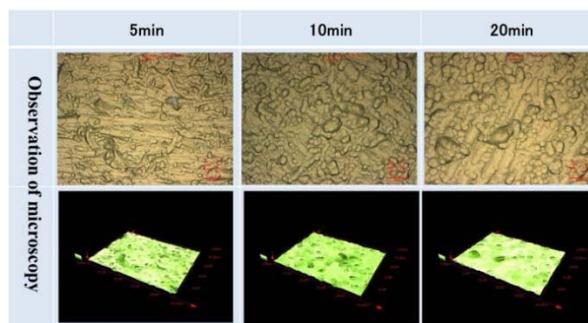


Figure 4: Comparison of surfaces after BP-EP processes for 5, 10 and 20 minutes with HCl electrolyte.

In addition, we performed BP-EP process of Nb-coupon sample with the HCl solution for 20 minutes. During the experiment, we observed and compared the surface of Nb-coupon sample after 5, 10 and 20 minutes,

Table3. Comparison of Removal Rate

	5g/L	20g/L	50g/L	100g/L	200g/L
Dissolution amount (mg)	0	0.9	4.8	4.2	0.9
Removal rate (μm/min)	0	0.033	0.178	0.156	0.033

Table4. Comparison of Surface Roughness (Ra)

	5g/L	20g/L	50g/L	100g/L	200g/L
Before Polishing	0.5422	0.7445	0.5528	0.6360	0.7430
After Polishing	0.5181	0.8817	0.3291	0.4677	1.1688

respectively. The results of the observation and comparison are shown in Fig. 4. The surface became smoother if processing period became longer. Being based on all these experimental results, we selected the Cl-anion for the neutral electrolyte of the BP-EP process of Nb surface.

### Experiments with NaCl Electrolyte.

We performed BP-EP process of Nb-coupon samples for 10 minutes each with changing the concentration of NaCl electrolyte at 5, 20, 50, 100, and 200 g/L,

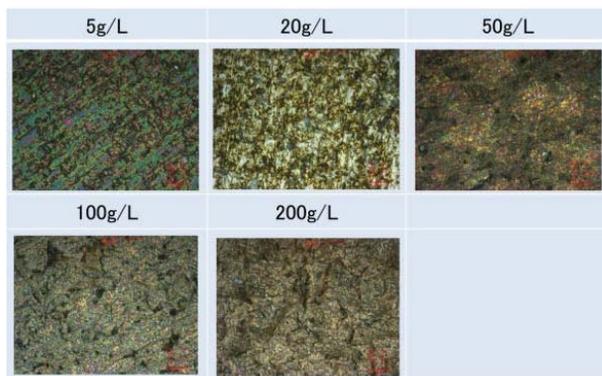


Figure5: Comparison of surfaces after BP-EP process with NaCl electrolyte at the concentrations of 5, 20, 50, 100, and 200 g/L.

respectively. The pulse-shape was fixed to the condition of  $T_{anode} = 3$  ms,  $V_{anode} = +3V$ ,  $T_{cathode} = 3$  ms,  $I_{cathode} = -9$  V. We could not observe any removal by BP-EP process at the concentration of 5 g/L. We confirmed that BP-EP process is possible if the concentration is greater than 20 g/L. White particles were produced in electrolytes during the processes except at the concentration of 5 g/L. The pictures of surfaces for all Nb-coupon samples after BP-EP process are shown in Fig. 5. The pictures show that all surfaces are not shiny and the oxidation film was not removed perfectly for all concentrations.

Removal rates of BP-EP processes for all concentrations of NaCl electrolytes are shown in Table 3. The roughness measurements of Nb-coupon samples before and after BP-EP processes with all concentrations of NaCl electrolytes are shown in Table 4.

In order to evaluate how effectively BP-EP process produces smooth surface, we defined the value:  $100 \times [(\text{roughness before EP}) - (\text{roughness after EP})] / (\text{roughness before EP})$ . If this value is large, then the BP-EP process produces smooth surface effectively. Figure 6 shows these values for all concentrations of NaCl electrolyte. If we see Fig. 6, we find that the range of concentration between 50 and 100 g/L produced rather smoother surface.

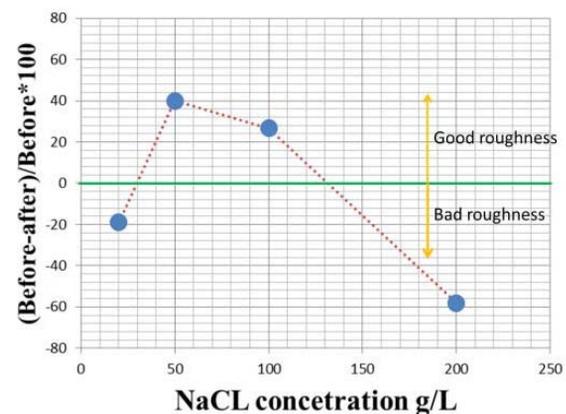


Figure 6: Comparison of the surface roughness of Nb-coupon samples by BP-EP processes with various concentrations of NaCl electrolyte.

### Study on Pulse-Shape in BP-EP process with the NaCl electrolyte.

We studied on the condition of pulse-shape in the BP-EP process with NaCl electrolyte at the concentration of 50 g/L. Figure 7 shows the surfaces after BP-EP process for 10 minutes each with changing the condition of pulse-shape. In the applied conditions, we could not see very clear difference on the surface of Nb-coupon samples.

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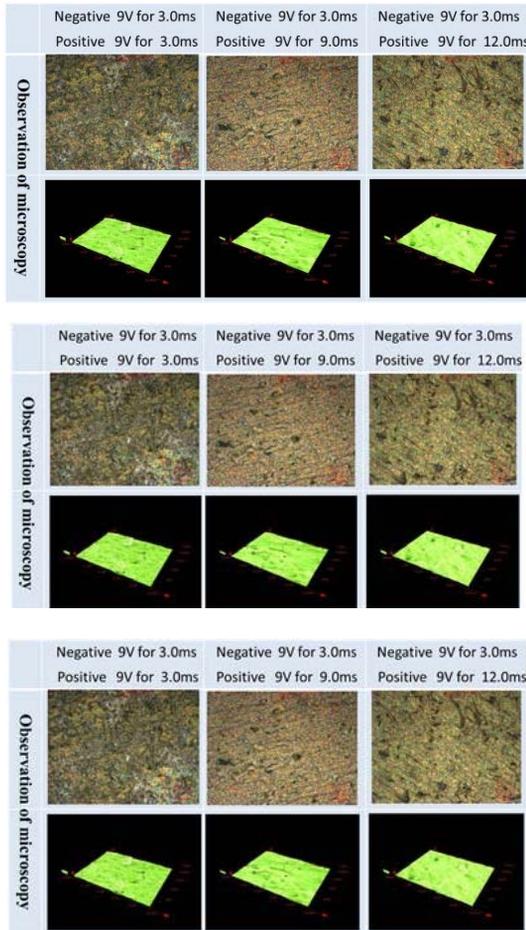


Figure7: Surfaces after BP-EP process for 10 minutes each with changing the condition of pulse-shape.

Table5: Dissolved Amount of Nb and Removal Rate by BP-EP Process in Various Conditions of Pulse-shape

Negative Positive	9V3ms 9V3ms	9V3ms 9V9ms	9V3ms 9V12ms	3V3ms 3V3ms	3V3ms 6V3ms	3V3ms 9V3ms	3V3ms 9V9ms	3V3ms 9V12ms
Dissolved amount (mg)	4.6	4.5	4.4	3.7	4.5	4.5	4.2	4.7
Removal speed (μm/分)	0.171	0.167	0.164	0.137	0.167	0.167	0.156	0.175

Table 5 shows the results of dissolution amount and removal rate of Nb-coupons samples by BP-EP process with NaCl electrolyte at the concentration of 50 g/L in various conditions of pulse-shape. No significant difference was observed for the applied conditions of pulse-shape.

Table 6 shows comparison of surface roughness before and after BP-EP process with NaCl electrolyte at the concentration of 50 g/L in various conditions of pulse-shape. We again evaluated the effectiveness to produce smooth surface by the value: 100 times [ (roughness before EP) – (roughness after EP) ] / (roughness before EP). In table 6, this value is denoted by R. If comparing R in table 6 in various conditions of pulse-shape, it was found that the best condition of pulse-shape was given as

3 V / 3 ms for negative pulse and 6 V / 3 ms for positive pulse. Being based on the series of experimental results, we found that the best condition of BP-EP process for Nb-coupon sample with neutral electrolyte is given when we use the NaCl electrolyte at the concentration of 50 g/L in the condition of pulse-shape: 3 V / 3 ms for negative pulse and 6 V / 3 ms for positive pulse.

Table6. Comparison of Surface Roughness (Ra) before and after BP-EP Process with NaCl Electrolyte at the Concentration of 50 g/L in Various Conditions of Pulse-shape

Negative Positive	9V3ms 9V3ms	9V3ms 9V9ms	9V3ms 9V12ms	3V3ms 3V3ms	3V3ms 6V3ms	3V3ms 9V3ms	3V3ms 9V9ms	3V3ms 9V12ms
Before	0.524	0.455	0.598	0.677	0.684	0.602	0.658	0.515
After	0.456	0.424	0.521	0.470	0.385	0.636	0.446	0.388
R <sup>#1</sup>	13.06	6.86	12.87	30.62	43.68	-5.68	32.24	24.66

\*1  $R = \frac{(\text{Before roughness} - \text{After roughness})}{\text{Before roughness} \times 100}$   
 This was the best condition.

## FUTURE PLAN

The electrolytic removal processes typified by the micro electro-discharge machining process are based on the neutral electrolyte. A group of the University of Tokyo is studying on the electrolyte jet machining based on neutral electrolyte as an advanced electrolytic removal process. We started a collaboration among KEK, Nomura Plating Co. Ltd and the University of Tokyo to utilize the technology of the electrolyte jet machining in the electro-polishing of SRF Nb cavity.

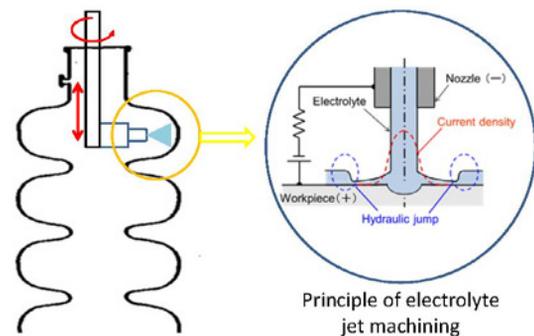


Figure 8: Application of electrolyte jet machining to SRF Nb cavity.

## SUMMARY

We studied Electro-Polishing (EP) process by Bipolar-Pulse (BP) method with neutral electrolyte for Nb-coupon samples.

- We selected the chloride anion (Cl<sup>-</sup>) for the neutral electrolyte based on the experimental results of BP-EP process with various acid electrolytes for Nb-coupon samples.

- We selected NaCl neutral electrolyte for the BP-EP process of Nb-coupon samples. The best concentration of

NaCl electrolyte to give smooth surface was found between 50 – 100 g/L.

·The best pulse-shape condition to give smooth surface was found to be 3 V / 3 ms for negative pulse and 6 V / 3 ms for positive pulse with the NaCl electrolyte at the concentration of 5 g/L.

·We started studies on the technology of electrolyte jet machining in collaboration among Nomura Plating Co. Ltd., the University of Tokyo, and KEK. We will apply the technology of electrolyte jet machining to SRF Nb cavity in the near future.

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