LOW-VOLTAGE ELECTRO-POLISHING OF SRF CAVITIES

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Abstract

First promising results concerning Electro-Polishing at lower voltage of 5 V (abbreviated as LV-EP) has previously been reported [1, 2]. This effort is being pursued and a 1-cell Tesla shape 1.3 GHz cavity has been dedicated to LV-EP and has reached improved gradient exceeding 39 MV/m.

Furthermore, a second cavity has been alternately treated with standard Electro-Polishing (abbreviated as EP) and low-voltage EP. It did not encounter any decrease in performance after LV-EP. This process is then promising for the treatment of large cavities for proton applications. Moreover, long-time EP experiments on niobium samples show that high-voltage EP is more likely to generate impurities in the EP mixture that might contaminate niobium surface. Some results will also be presented concerning efficient field emission removal by chloroform rinsing of 1-cell cavities.

INTRODUCTION

Electro-Polishing is believed to be the most desirable treatment for SRF cavities [3]. EP is an anodic electrochemical treatment carried out in concentrated hydrofluoric - sulphuric ($HF-H_2SO_4$) acids electrolytes in proportions 1-9. The characteristic I(V) curve of the process show a diffusion plateau and in the SRF community, the potential is commonly chosen at the end of the plateau for the polishing of elliptical cavities. 17 V is for example used at DESY for EP of XFEL cavities [4]. We have pursued the investigation work on the influence of EP parameters, initiated in the CARE SRF program and have focused on influence of voltage. We intend to prove that RF results after Low Voltage Electro-Polishing (LV-EP) in horizontal configuration, that is to say, EP in a current oscillation area, at 5 V, are similar compared to standard EP. LV-EP would provide in addition numerous advantages. First analyses indicate that it should generate a decreased particulate contamination. We will also demonstrate that chloroform rinsing of cavities should be considered as an efficient step prior to High Pressure Rinsing.

CHARACTERISTICS OF LV-EP

LV-EP is a constant-voltage Electro-Polishing. The potential is chosen in order to obtain an oscillating current at the beginning of the "plateau" on I(V) curve. Electro-Polishing experiments based on current-oscillation control have been made in different laboratories but at higher potentials, (9-15 V [5, 6]).

For horizontal LV-EP of 1-cell cavities, the typical voltage is 5V, but might evolve slightly as a function of temperature, geometry, and of aging of the electrolyte. For flat samples, oscillations start at a lower voltage (3 V). Previous results on samples have also proved that a decreased voltage increases the life time of the EP mixture. This might be correlated to a decreased HF vaporization [7] or to the modified surface of niobium during LV-EP [8, 9]. In fact, in aged mixtures, surface porous film at the niobium surface should be thinner at lower voltage, and thus favourable to a brighter surface. Contrary to standard EP, oscillations have regular amplitude (Fig. 1). Furthermore, because of this lower voltage, the heat produced by Joule effect during EP is decreased. As a consequence, it is easier to control the temperature of the electrolyte, and if this working temperature is low, it is possible to work without heat exchanger.
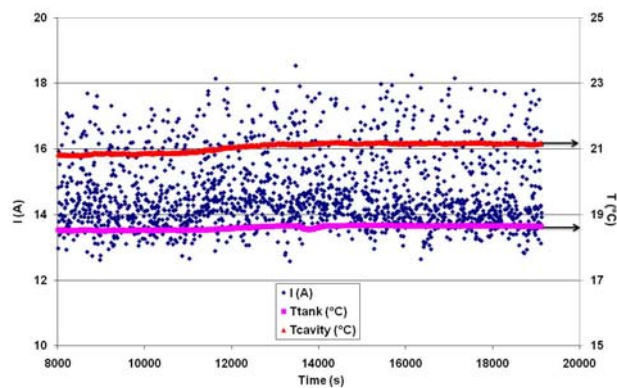

Fig. 1: Intensity and temperature vs. time for C1-21 cavity during LV-EP (5.4V). Characteristic oscillations observed. Electrolyte temperature is very stable.

Precisely, most of the cavity measurements presented in this paper result from LV-EP at low temperature (~20°C) which did not require the use of a cooling system. As a consequence, removal rate was low (around 20 mA/cm^2) compared to standard EP at 30°C and 17 V. As the working point is located at the beginning of the "plateau" on I(V) curves [9], and because of the exponential evolution of intensity with temperature [10], it is logical to expect a decreased removal rate difference for LV-EP at 30°C.

However, it is possible to take advantage of the reduced heat production to anticipate an easy electrochemical polishing of large elliptical cavities. By way of example, surface of 5-cell cavities for high energy proton application in SPL should be twice as high as the surface of a 9-cell Tesla-shape cavity. In such conditions, EP at 17 V would necessitate powerful cooling devices and large amounts of acid to prevent overheating. Moreover different strategies might be considered to compensate the decrease in removal rate and benefit from additional advantages of LV-EP described in coming paragraphs:

- The use of the vertical configuration, characterized by a higher niobium surface in contact with acid, coupled with LV-EP, is an alternative to compensate the decrease of removal rate due to lower voltage.

Because of electrochemical mechanisms involved in EP, it is also possible to investigate different strategies to increase removal rate [9]:

- an increased HF concentration
- an increased electrolyte agitation

Experiments on 1-cell cavities have to be pursued in order to determine acceptable ranges for HF concentration and acid flow rate.

INFLUENCE OF POTENTIAL ON RF PERFORMANCE

A Tesla 1-Cell cavity (manufactured by CERCA Company) has been dedicated to LV-EP experiments. After first sequences, the cavity reached 32MV/m. Additional material was removed to evaluate the performance of the cavity. It still improved and reached 35 MV/m (total ~150 µm removal) and 39 MV/m (total 175 µm removal).
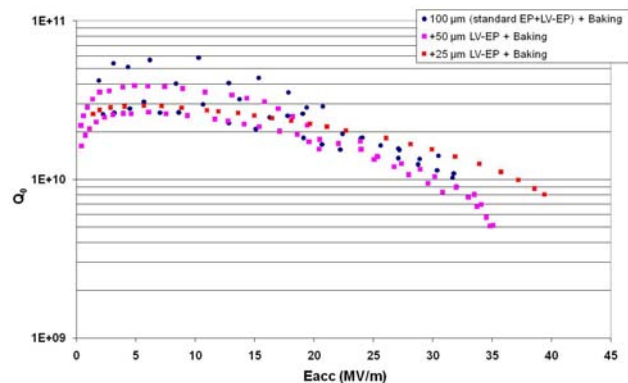

Fig. 2: RF tests at 1.4 K. Improvement of the gradient for C1-21 cavity after successive LV-EP sequences.

The observed inner surface of the cavity is very bright with a different aspect compared to cavities electro-polished at 17 V: surface appears to be rougher. This rougher surface could result from the absence (or the thickening) of the viscous film at the niobium surface during EP. Replicas of the surface have been made in order to compare qualitatively surfaces achieved at 5 and 17 V. If rougher surface is confirmed at 5 V, RF performance should not be correlated to that physical aspect.

In addition to this, 1DE1 1-cell cavity (DESY cavity), has been used for complementary experiments. This cavity was previously electro-polished several times at 17 V [11]. The last test (35 MV/m, limited by quench) has been taken as a reference. Additional 50 µm were then removed by LV-EP. The obtained gradient is comparable to the previous one achieved at 17 V. This result confirms that LV-EP provides gradients similar to those obtained with standard EP. An operating voltage between 5 and 17 V should not be considered to have an impact on cavity performance.
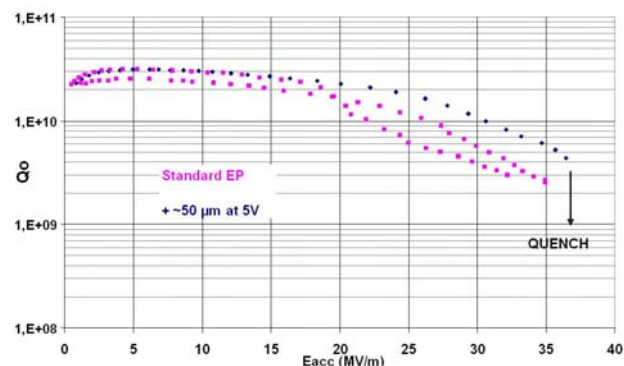

Fig. 3: Successive RF results at 1.4 K on 1-cell 1DE1 cavity after standard EP at 17 V and LV-EP at 5 V. No decrease in performance is observed after LV-EP.

IMPURITIES GENERATED VS VOLTAGE

Electro-polishing of niobium in HF-H_2SO_4 is known to generate some impurities [12]

- sulphur and H_2S generated by cathodic reduction of SO_4^{2-} and chemical reaction between H_2SO_4 and Al [13]
- aluminum salts, due to light oxidation of Al in concentrated HF-H_2SO_4 electrolytes

Previous investigations demonstrated that low [HF]/[H_2SO_4] content and high voltage were favourable to high sulfur generation [14]. In this study, we intend to isolate the parameter voltage in highly concentrated HF – H_2SO_4 electrolyte. In fact, two main electrochemical reductions take place at the aluminum cathode during EP.

- reduction of H^+ into H_2
- reduction of SO_4^{2-} ion into H_2S and S

The main reaction is the reduction of H^+ into H_2. Nevertheless, a cathodic overpotential might modify this balance, as suggested by previous results in [14]. We have to investigate this possibility. With this purpose in mind, we used an electrolyte with reduced HF concentration to generate a significant and measurable impurities forming: long term Electro-Polishing experiments were carried out on flat samples in a mixture prepared with HF (40%), H_2SO_4 (95%) (mass percents), and deionized (DI) water, respectively in proportions 1-9-1. Two baths A and B of 900 ml were prepared for experiments at 20 V and 5 V. Two similar niobium square samples (30x30mm²x3mm) were used for experiments in A and B mixtures. Table 1 summarizes data concerning experiments A and B.

Nota: "A" or "B" will refer to the corresponding electrolyte as well as the sample which is electro-polished inside.

Experiment	A	B
Voltage	20 V	5 V
Duration	4041 min	6907 min
Temperature °C	25 – 35 °C	25 – 30 °C
Mass removed	9.18 g	9.11 g
Spots on surface at the end	**yes**	**no**

Table 1: Parameters for experiments A and B.

After the EP experiments, samples were extracted from EP mixtures and rinsed with DI water.

- In case A, the whole surface of the sample is covered with sticky yellow spots. (See Fig. 4)
- In case B, the surface is bright.

Fig. 4: A (left) and B samples after long EP experiments at 20 and 5V. Sample A is covered with yellow spots.

The yellow stains are removed neither by additional ethanol rinsing, nor chloroform rinsing. They are so sticky that it is necessary to scratch the surface with a sharp metallic implement to remove them. We have thus strong hints of increased contamination at higher voltage. To confirm that point, we went on with the analysis of electrolytes A and B. The described protocol was carried out to extract impurities in both electrolytes:

- one sample of 200 ml is taken from each mixture,
- the 200 ml of electrolyte are mixed with 100 ml of chloroform in a pear shape separating funnel,
- distinct acid and organic phases are separated,
- the acid phase is rinsed a second time with additional 100 ml of chloroform,
- distinct acid and organic phases are separated for the second rinsing step,
- the two organic phases obtained are rinsed several times with DI water in order to remove residual acidity,
- once the pH of the rinsing water is neutral, the two organic phases are evaporated.

As shown, impurities were found in the four solution samples. Mass measured are related in Table 2.

Sample	A (20 V)	B (5 V)
1st Rinse	4.5 mg	2.6-2.7 mg
2d Rinse	1.2-1.3 mg	0.9-1.2 mg

Table 2: Mass of impurities found after chloroform extraction.

The mentioned impurities are yellow colored, probable signature of sulfur contamination, also found in [15]. The impurities will be analyzed as well as the powder extracted from the stains on sample A, to precisely characterize involved molecules.

HYDROGEN CONTAMINATION VS POTENTIAL

Furthermore, it is vital to check that changing the operation potential has no impact on Q-disease. In fact, it is logical to anticipate that fast current oscillations which reflect the removal of the oxide layer on the niobium

surface might enhance hydrogen incorporation in the bulk material. Two samples previously baked (800 °C-24 h) were electro-polished at the same temperature (~ 30 °C) respectively at 20 V and 3 V (to obtain characteristic current oscillations). Experiment details are given in Table 3. Both samples were then sent to DESY for hydrogen analysis. No sustained H contamination is observed after LV-EP.

Experiment	20 V	3 V
Duration	67 min	255 min
Removal	150 µm	150 µm
H content	2 ppm	1 ppm

Table 3: Hydrogen measurement on flat samples after LV-EP at 3V and EP at 20 V.

EVALUATION OF CHLOROFORM RINSING OF SRF CAVITIES

Various rinsing recipes have recently been proposed and tested within ILC S0 program. More precisely, ethanol rinsing prior to HPR, is considered as a reliable recipe for field emission cure and obtaining of high yield. Alternative rinsing recipes (Hydrofluoric acid rinsing, detergent rinsing) have also been investigated in different laboratories [16].

We tested at Saclay the rinsing of 1-cell cavities with chloroform. This is motivated by the high solubility of sulfur in chloroform [12, 13]. As a consequence:
- sulfur removal should be more efficient in chloroform,
- it is possible to re-use the same volume of solvent to rinse different cavities.

For this purpose, we have taken advantage of the C1-03 electro-polished cavity, heavily polluted during the last pumping procedure (oil pumped inside the cavity). As a result, the accelerated gradient was limited by strong field emission. The cavity was disassembled and treated with the protocol: + 30 min chloroform rinsing + HPR + assembly in clean-room. Field emitters were efficiently removed, and the cavity reached an excellent gradient (44.8 MV/m at 1.4 K), without Q_0 deterioration at low field (See Fig. 5).
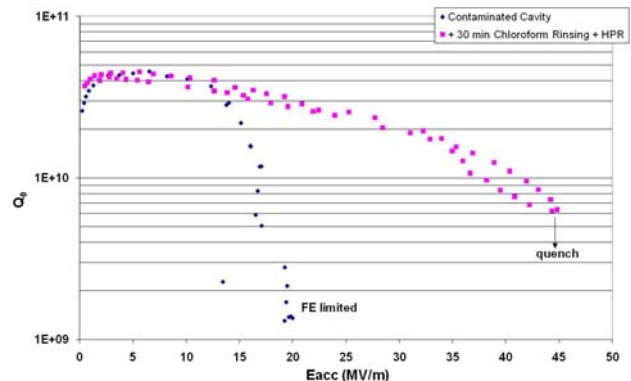
Fig. 5: RF tests at 1.4 K. Removal of field emission in C1-03 after chloroform rinsing.

A second 1-cell single crystal cavity, 1AC06, impacted by field emission after the previous BCP treatment was rinsed with chloroform. Field emission was also cured (Fig. 6).
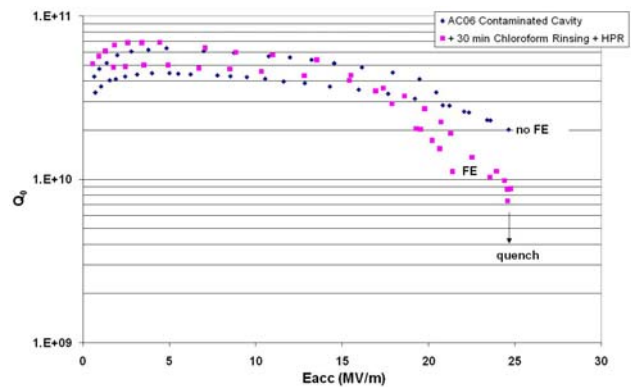
Fig. 6: RF tests at 1.4 K. Removal of field emitters on 1AC06 cavity after chloroform rinsing.

The chloroform that was used was of average quality (stored in metallic can). It gives however satisfactory results. Nevertheless, after extensive use of the solvent, field emission appears after the rinsing of cavities. The concerned volume was evaporated and many impurities were found afterwards (Fig. 7). These impurities will be analyzed to determine if they principally come from the process or result from the solvent itself.

Fig. 7: Impurities are found in the chloroform used for several cavity rinsings.

OUTLOOK AND CONCLUSION

RF tests on single-cell cavities indicate that electro-polishing at low-voltage makes it possible to reach satisfactory gradients. Some resulting advantages should be put forward: higher lifetime of the electrolyte, easy control of the EP, no need for heat exchanger during process. Ongoing results tend to prove that LV-EP is liable to decrease the forming of impurities during the process. Characteristics of LV-EP make this process especially suited to the possible electrochemical treatment of large proton cavities. Replicas of the inner surface have been made after LV-EP for profilometry measurements. If rougher surface after LV-EP is confirmed, voltage and surface finish would not influence superconductive properties of the surface. The only drawback of LV-EP is the decreased removal rate achieved. Studies are on going in order to find a counterbalance (use of vertical EP, of higher stirring and temperature of the electrolyte, of higher HF concentrations). Furthermore, chloroform rinsing has been successfully tested out on 1-cell cavities as a cure to remove field emission.

ACKNOWLEDGEMENTS

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