

PARAMETERS INVESTIGATION FOR NIOBIUM ELECTRO-POLISHING

F. Éozéno, M. Bruchon, J. Gantier
CEA-Saclay, DSM/DAPNIA/SACM - 91191 Gif/Yvette – FRANCE

Abstract

Electro-polishing (EP) experiments are carried out on niobium samples at Saclay in order to highlight the influence of parameters such as temperature and acids concentrations (hydrofluoric and sulfuric). First results given at the 12th SRF Workshop have been completed. The importance of the HF/H₂O ratio has been precisely investigated and diluted mixtures have been tested during long time experiments: removal rates, surface states, lifetime of the bath and possible hydrogen contamination will be reported.

In addition, some experiments have been carried out with dissolved niobium in fresh mixtures, giving some ideas about mechanisms involved in EP. Furthermore, dissolved salts as well as different acids have been tried as an alternative for hydrofluoric acid use.

INTRODUCTION

Electro-Polishing (EP) of niobium cavities is the surface treatment that enables to reach the highest gradients [1]. Generally, cavities are treated in horizontal position, half filled with circulating acid. This process is developed at KEK and DESY where practical descriptions and promising results have been achieved [2]. In spite of the discrepancy in achieved gradients for 9-cell cavities after EP [3], this process seems essential on view of the large scale cavity treatments for projects such as ILC.

Experiments to test the gradient reproducibility for different rinsing procedures are lead worldwide. Nevertheless, EP parameters themselves are maintained fixed in the RF community: electrolyte prepared with hydrofluoric HF (40-48w%) and sulfuric H₂SO₄ (95w%) acids in volume proportions of 1 – 9, voltage above 14 volts, comparable acid flows and cavity rotation speed. Nevertheless it is worth investigating new sets of parameters that could induce several advantages: less dangerous process, less impurities formed, less electrical consumption etc. This work is carried out within the Work Package 5.1 of CARE SRF framework: Best EP-Parameters on Single-Cell. A preliminary study on samples is necessary to guide single-cell cavity EP improvements. First results for single-cell cavity treatment will be presented elsewhere [4].

EXPERIMENTAL SET-UP AND NOTATIONS

Experiments are carried out in a Teflon vessel. The

cathode is in aluminum or copper and niobium samples surface is 9 cm² (one side). A separation divides the vessel into two parts and prevents the hydrogen bubbles formed at the cathode to migrate to the niobium sample. Bath is stirred with a magnetic stirrer and temperature is controlled by a coolant system.

Percentages concerning source acid concentrations are given in weight percentage. For example, most of the acid mixtures are prepared with HF at 40 or 48% (weight percents), H₂SO₄ at 95% and possible additional water.

Notation for mixtures' composition: proportions are given in volume, and H₂SO₄ is marked HS. Example for a mixture prepared with 1 volume of HF (40%) for 9 volumes of H₂SO₄ (95%) and 1 volume of additional water: 1vol HF_{40%} – 9vol HS_{95%} – 1vol H₂O.

Furthermore, concentrations in mol/L are quoted in square brackets.

In experiments concerning electrolyte's efficiency to achieve polishing, brightness of the samples will be measured with respect to time.

IMPORTANCE OF HF AND H₂O CONCENTRATIONS

Previous experiments [5] have shown that samples electro-polished with high HF concentrations achieved high brightness, as well as high removal rates for long EP time. On the contrary, light addition of water seems undesirable since experiments carried out with the mixture 1vol HF_{40%} – 9vol HS_{95%} – 1vol H₂O showed a fast deterioration of the surface and low removal rates [6]. The matt surface should be attributed to the presence of a porous oxide layer whose growth is faster than its dissolution. In that view, a high [HF]/[H₂O] ratio seems desirable to achieve efficient EP with a long lifetime of the mixture.

To confirm this assumption, EP experiments were carried out with "1-9" mixtures prepared with two different concentrations for the HF source solution (40% and 48%). We have the following ratios:

- For a 1vol HF_{48%} – 9 vol HS_{95%}:
[HF]/[H₂O] ~0.35
- For a 1vol HF_{40%} – 9 vol HS_{95%}:
[HF]/[H₂O] ~0.27

In both cases, [H₂SO₄] is the same: ~ 16 mol/L

Furthermore, EP was carried out at 3 different voltages: 8 (dark/light blue), 14 (orange-red) and 17 (green) volts in Figure 1. We use circle/triangle dots to respectively represent results for mixtures prepared with 48%/ 40% hydrofluoric acid.

* We acknowledge the support of the European Community-Research Infrastructure Activity under the FP6 "Structuring the European Research Area" program (CARE, contract number RII3-CT-2003-506395) and of the "Région Ile-de-France".

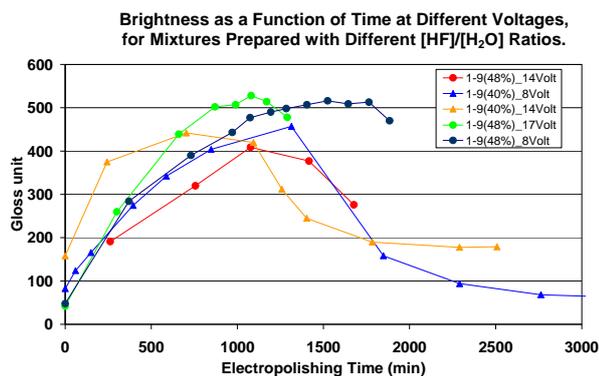


Figure 1: Evolution of gloss during EP at different voltages for ‘standard’ 1-9 mixtures prepared with different HF concentrations. The lifetime of the mixture is longer for higher $[HF]/[H_2O]$ ratios and lower voltages.

For EP at 8 volts, brightness decreases after longer EP time (and larger amount of dissolved niobium) for the curve with circle-dots. That is to say, the lifetime is longer for the bath with the higher $[HF]/[H_2O]$ ratio. This point is confirmed by sequences at 14 volts.

Moreover, experiments give some hints concerning influence of the potential. If we consider mixtures prepared with HF at 48%, the higher the voltage is, the lower is the lifetime of the bath. It is confirmed by experiments with mixtures prepared with HF at 40%. The shorter lifetime of the mixture at high potential could be correlated to a higher continuous local vaporization of the hydrofluoric acid in the mixture (high sample temperatures are measured during experiments).

[HF]/[H₂O] RATIO MORE RELEVANT THAN NIOBIUM DISSOLVED IN SOLUTION TO EXPLAIN AGING?

We explained in the previous part that the water concentration increase provoked a premature deterioration of the samples’ surface. However, amount of dissolved niobium is the retained parameter for changing electrolytes during cavities EP. Niobium concentrations up to 9g/L are used without performance deterioration [7]. In this part, we will strive to distinguish influence of one parameter from the other to explain aging of the bath.

We will compare 3 experiments with niobium samples electro-polished for long periods in 3 different mixtures.

- A 900 mL of a fresh 1vol HF_{40%} - 9vol HS_{95%} mixture
- B 11.59 g of Nb₂O₅ dissolved in 900 mL of a fresh 1vol HF_{40%} - 9vol HS_{95%} mixture
- C 11.59 g of Nb₂O₅ dissolved in 900 mL of a fresh 1vol HF_{48%} - 9vol HS_{95%} mixture

Characteristic concentrations of the 3 mixtures are summed up in the following Table 1.

Mixture	A	B	C
[HF] mol/L	2.26	2.16	2.69
[H ₂ O] mol/L	8.34	8.58	8.17
[HF]/[H ₂ O]	0.27	0.25	0.33
Dissolved Nb g/L	0	9	9

Table 1: Initial amount of dissolved niobium and fluorine content in A, B and C mixtures.

Gloss evolution of a niobium sample during EP in the different mixtures at 8 volts is given in Figure 2. With the ‘standard’ mixture A, brightness increases up to 1300 minutes and then deteriorates. B and C mixtures include similar amounts of dissolved niobium. Mixture B has the lowest $[HF]/[H_2O]$ ratio and does not provide smoothing conditions as in C (with the highest ratio) where the sample is electro-polished during a long period, which is superior or equal to the one obtained for the mixture A.

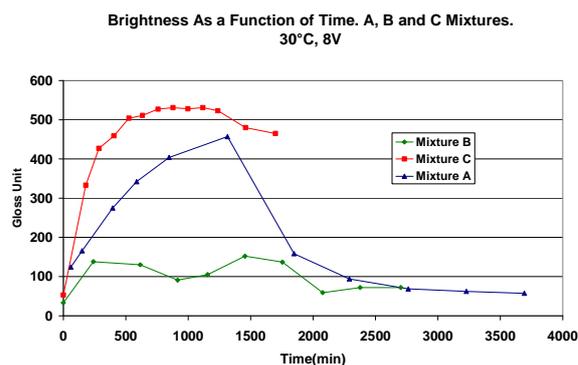


Figure 2: Gloss evolution during EP at 8 volts for A, B and C mixtures. A low $[HF]/[H_2O]$ ratio is believed to be the main cause of the deterioration of the surface.

Regarding these observations, we might foresee that water content is more relevant in the causes of the deterioration of the surface during EP.

Furthermore, experiments carried out with A, B and C mixtures might provide some understanding concerning EP mechanisms: In the niobium case, it should be considered between the acceptor mechanism where the limiting step is the diffusion of reactive species from solution to surface (F^- or FSO_3^- in our case) and a Metallic Ion Diffusion limiting step (in our case, diffusion of Nb^{5+} ions from anode surface to bulk phase would be the slowest mechanism) [8]. Let us consider $I(V)$ curves plotted (between anode and cathode) in Figure 3 for A and C mixtures. The plateau is found at similar current densities although the niobium contents, and consequently Nb^{5+} concentration gradients in the mixture are substantially different. On the contrary, an increase in HF concentration leads to increased current densities [6]. A F^- diffusion limited mechanism should be then considered as the most probable possibility.

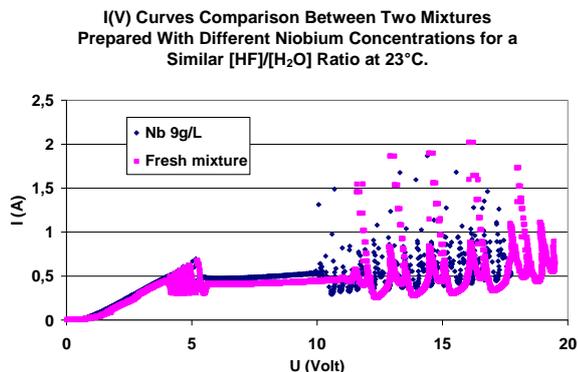


Figure 3: I(V) curves for A and C mixtures.

PRELIMINARY RESULTS WITH EIS

We discussed in the previous paragraph of the importance of $[HF]/[H_2O]$ ratio on aging. If a F^- diffusion must be kept in mind, we shall not forget that a too high fluorine concentration is an origin of the destruction of the viscous layer at the niobium's surface and a too high water concentration provokes a deterioration of the surface, even if the I(V) curve shows a plateau [6].

We will investigate in this paragraph if Electrochemical Impedance Spectroscopy (EIS) is a method that we might apply to niobium EP, and if the $[HF]/[H_2O]$ ratios mentioned above would influence the response.

In EIS, the impedance Z of the electrochemical system is studied as a function of the frequency: A potential $E_0 + \delta E \cdot \sin(\omega t)$ is applied to the electrode at a stationary state. The response $Z = U/I$ might be considered in Nyquist Diagrams. Three mixtures have been tested:

- 1vol HF_{48%} – 9vol HS_{95%}.
- 1vol HF_{40%} – 9vol HS_{95%}
- 1vol HF_{40%} – 9vol HS_{95%} – 1vol H₂O

We worked with an Ag/AgCl reference electrode and niobium samples were mechanically polished with the same protocol, prior to EIS. Potentials were chosen on the "plateau" of the I(V) curve previously plotted with the reference electrode.

We notice in Figure 4 that when $[HF]$ increases, features of Nyquist diagrams are modified. It suggests that electrochemical phenomena vary with bath composition. Furthermore, the limit for upper frequencies in diagrams corresponds to resistivity of the system (electrolyte and of possible porous surface film [9]). We notice that the higher water content, the less resistive bath that must be attributed to the higher conductivity of the electrolyte with higher water concentration.

So the diagrams confirm the importance of the $[HF]$ concentration, but complementary experiments must be carried out to make theoretical models fit the diagrams in each case. These models might be complex and might evolve with the aging of the bath.

EIS Diagrams for Different Mixtures.

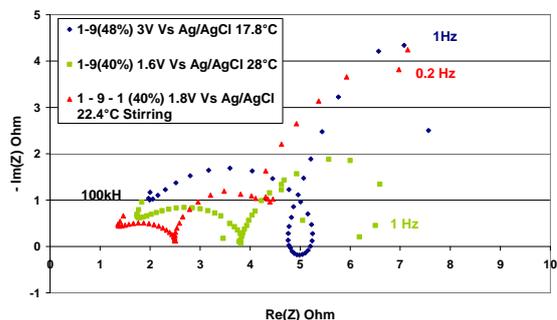


Figure 4: EIS measurement for 3 different mixtures: 1vol HF48% – 9vol HS 95%, 1vol HF40% – 9vol HS 95% and 1vol HF40% – 9vol HS 95% – 1vol H₂O.

Furthermore, we should not forget that EIS measurements can only be made in stationary conditions and that electro-polishing also occur at high potentials, in oscillations area where current is unstable and resulting EP phenomena more complex.

UNFRUITFUL TESTS WITH DISSOCIATED SALTS AND WITH OTHER ACIDS

High hydrofluoric concentrations are favorable for effective EP. Nevertheless, this chemical is undesirable from safety configurations. Could it be replaced by other product? Furthermore, sulfuric acid is the main component in standard EP electrolytes. This acid is constraining considering sulfur impurities formed during the process [10], a possible cause for performance deterioration in cavity performance [3]. We decided to treat niobium samples with dissolved fluoride ammonium NH₄F instead of using HF and we also prepared mixtures with hydrochloric acid HCl and phosphoric acid H₃PO₄ to respectively act as substitute for HF and H₂SO₄.

A sample was treated with an electrolyte prepared from a mixture made of 900 mL of H₂SO₄ (95%), 100 mL H₂O and with 40g of NH₄F (1.1 mol). As some particles are at the surface, we might think that the salt is not totally dissociated. Long time experiments EP at 8 volts were carried out at ~25°C. Both removal rate (less than 0.4 μm/min) and obtained surface states were not satisfactory. Micrographies of the surface at the maximum gloss after 905 min EP are presented in Figure 5.

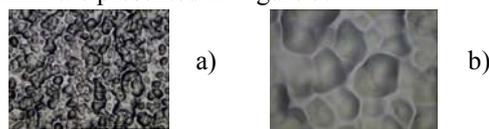


Figure 5: Surface of the niobium after EP in an electrolyte where HF is replaced by 40 g NH₄F. a) x 50 b) x 200. The surface is not smoothed.

Furthermore, HF-H₃PO₄ and HCl-H₃PO₄ mixtures have been investigated in 1-9 volume proportions at room temperature. In both configurations, EP is not possible

because of a very low current intensity (in HCl-H₃PO₄ case, the niobium surface is passivated).

These tests with these new mixtures are unsuccessful. We will contemplate in the next paragraph another possibility to achieve easier and safer EP.

EFFECTIVE EP WITH DILUTED MIXTURES?

We showed previously that light addition of water was undesirable in terms of removal rate and surface state. Nevertheless, former experiments at very high water concentrations induced higher removal rates [11]. At first glance, these two statements seem contradictory. However, effective EP with less concentrated EP would involve cumulative benefits:

- Mixtures would be easily prepared.
- They would be safer.
- Less sulfur production would be expected [10].
- The removal rate could be high.

I(V) curve has been plotted (see Figure 6) with a diluted mixture 1vol HF_{48%} - 2vol HS_{95%} - 7vol H₂O to investigate a possible plateau and find an appropriate voltage to carry out long time EP experiments.

Nota: As aluminum is corroded in such mixtures containing dissociated acids [12], we replaced the aluminum cathode by a copper one.

The I(V) curve highlights a 5 volt large plateau (between 5 V and 10 V) with a high current density: intensity is increased by more than 100% compared to the 'standard' 1-9 mixture. Higher current densities with such an electrolyte should be attributed to a better acid dissociation resulting in an increased ionic conductivity in the electrolyte, as it has been shown with EIS results.

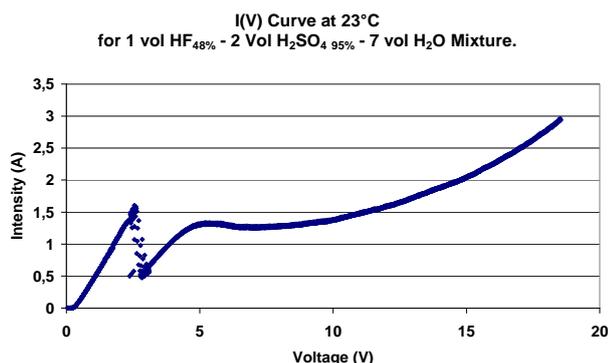


Figure 6: Intensity Vs Voltage curve at 23°C for the mixture 1vol HF_{48%} - 2vol HS_{95%} - 7vol H₂O.

We might find effective EP conditions with such characteristics. In that way, long time EP experiments were carried out at 8 volts. Brightness as a function of time is reported in Figure 7, and compared to the one achieved with the 'standard' 1vol HF_{40%} - 9vol HS_{95%} mixture.

Brightness as a Function of Time for a Diluted Mixture Compared to the 'Standard' one.

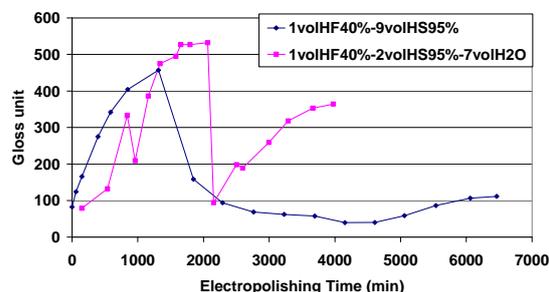


Figure 7: Brightness as a function of time during EP with 1vol HF_{48%} - 2vol HS_{95%} - 7vol H₂O mixture compared to the standard 1-9.

In addition, Figure 7 shows that the lifetime of the mixture 1vol HF_{48%} - 2vol HS_{95%} - 7vol H₂O is consequent since the sample had to be changed to extend the experiment after sequence #10 (2000 min). After 4000 min EP (sequence #17), Nb concentration in the electrolyte is over 30g/L and it is still efficient. Nevertheless, it is necessary with this mixture to remove a deep layer of niobium to reach the maximum brightness compared to the 'standard' mixture (maximum is reached for an amount which is doubled compared to the 1-9 mixture).

Unfortunately, EP with diluted mixture implies a major drawback: Hydrogen measurements on samples carried out at DESY proved that EP with such mixtures provokes huge H contamination that should lead to Q disease (a hydrogen concentration up to 15 µg/g was measured). As a consequence, diluted mixture can not be used for a final EP. However, as the lifetime and achieved removal rates seem promising, an interest as EP for heavy removal material before annealing could be contemplated. Some details concerning single cell EP with a mixture 1vol HF_{48%} - 2vol HS_{95%} - 7vol H₂O will be presented in [4].

OTHER PERSPECTIVES

The 'standard' mixture has proved to be very efficient in term of maximal gradient. Electrolyte with higher HF concentrations could provide some benefits: higher removal rates, longer lifetime of the bath and less impurities in the bath are expected [10]. Nevertheless, higher HF concentrations are not innocuous in terms of safety and conforming to strict regulations.

Different mixtures are used to electro-polish metals similar to niobium. Methanol is used to electro-polish tantalum [13]. With regard to dangerousness, methanol is not desirable... Some patents [14] involve use of organic environment to achieve EP. Unfortunately, removal rates in such a case are lower. Addition of lactic acid in 'standard' mixture has also been successfully tested on samples [15] and alternative electrolytes as ionic liquids [16] could present a promising alternative.

Another aspect to take into consideration is the diversity of mixtures used in different laboratories all

over the world. At the present time, the 'standard' 1-9 is accepted as the most desirable mixture for the ILC cavities treatment. Nevertheless, electrolytes are prepared with different source mixtures. (HF 40w% or, 48w%). As we have put forward the influence of [HF]/[H₂O] on the EP efficiency, it is urgent to fix precise specifications in acid contents in order to compare without ambiguity results achieved on cavities in the SRF community.

CONCLUSION

Mixtures prepared with HF, H₂SO₄, and H₂O with wide concentration range have been investigated. From this study, we intend to test two configurations on cavity for RF test:

- Mixtures with high HF concentration (3vol HF_{40%} - 6.72vol HS_{95%} - 0.28vol H₂O), expecting longer lifetime of the bath and less sulfur produced after EP.
- Mixture with high water content (1vol HF_{48%} - 2vol HS_{95%} - 7vol H₂O) that could be effective for heavy material removal (long lifetime of the bath).

Other configurations are investigated worldwide in different laboratories. Some of them are promising, and correlated aspects such as removal rates, lifetime of the bath, possible hydrogen contamination, and impurities generation should be taken into account in an early stage.

ACKNOWLEDGEMENTS

We thank our colleagues from DESY, especially X. Singer, for hydrogen measurements on niobium sample.

We deeply acknowledge C. Ferry, N. Gruet, Y.Charles, and A Poulesquen from L3MR at CEA Saclay for their support concerning EIS experiments.

REFERENCES

- [1] K. Saito et al. "Superiority of Electropolishing over Chemical Polishing on High Gradients", Particle Accelerators, Vol. 60, 193-217 1998.
- [2] L. Lilje et al., "Achievement of 35MV/min the superconducting nine-cell cavities for TESLA", Nucl. Instr. & Meth. in Physics Research, Section A, 2004.
- [3] N. Steinhau-Kühl et al. "Update on the Experiences of Electro Polishing of Multi-Cell Resonators at DESY". Proceedings of the 12th International Workshop on RF Superconductivity (SRF2005), Ithaca, NY. Pp 464-466.
- [4] F.Eozenou et al. "Single-Cell Electro-Polishing at CEA Saclay: First Results". This conference.
- [5] F. Eozenou et al. "Efficiency of Electropolishing Versus Bath Composition And Aging: First Results". Proceedings of the 12th International Workshop on RF Superconductivity (SRF 2005), Ithaca, New York, USA, July 10-15, 2005.
- [6] F.Eozenou, A. Aspart, C.Antoine and B. Malki "Niobium Electro-Polishing : Best EP Parameters". CARE-Report-06-010-SRF
- [7] T. Saeki KEK. Presentation "Quality Control Study With Single-Cell Cavities" at TTC meeting in KEK. 26 sept 2006.
- [8] D. Landolt, "review article : fundamental aspects of electropolishing". Electrochimica Acta, 1987. 32(1): p. 1-11
- [9] R.D Grimm et al. "AC Impedance Study of Anodically Formed Salt Films on Iron in Chloride Solution". Journal of the Electrochemical Society. Vol.139. No6. June 1992.
- [10] Aspart et al. "Aluminum and sulfur impurities in electropolishing baths". Physica. C. Superconductivity (Phys., C Supercond.) ISSN 0921-4534. 2006, vol. 441, no 1-2 (13 ref.), pp. 249-253.
- [11] Shou Huajun. Internal training period report at CEA Saclay (from 05/01/2003 to 08/31/2003).
- [12] C. Vargel, ed. "Corrosion de l'Aluminium". Technique et Ingénierie Série Matériaux. 1999, Dunod: Paris.
- [13] O. Piotrowski, C. Madore, D. Landolt. "Electropolishing of tantalum in sulfuric acid – methanol electrolytes". Electrochimica acta, Vol 44, Number 19, 15 May 1999, pp. 3389-3399.
- [14] Piesslinger-Schweiger et al. United States Patent 20070029209. www.freepatentonline.com/20070029209.html
- [15] A. Wu et al. "Smooth Nb surfaces fabricated by buffered electropolishing". Applied Surface Science, v. 253, iss. 6, p. 3041-3052.
- [16] Palmieri et al. Alternative Electropolishing Of Niobium. International Workshop on "Thin Film Applied To Superconductive RF And New Ideas For Pushing The Limits Of RF Superconductivity". Legnaro (Italy). 2006. October 9-12th