MORE INFORMATION CONCERNING ELECTRO-POLISHING MECHANISMS IN HYDROFLUORIC–SULPHURIC ACID MIXTURES

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Abstract

The use of a rotating disc electrode for electrochemical measurements gives precious information concerning mass transport of species. Measurements were performed with a rotating niobium sample in HF-H$_2$SO$_4$ media. Intensity is found as a linear function of the square root of the rotation speed ω which is the signature of an electro-polishing (EP) controlled by the diffusion of the fluorine ion. The value of the related diffusion coefficient D has been estimated from 4 to 14×10^{-8} cm^{2}s^{-1} for different electrolyte compositions. D has also been found lower in aged mixtures. Electrochemical Impedance Spectroscopy measurements were also performed with different EP mixtures with a rotating disc electrode. Both voltamperemetric and EIS measurement prove the central role of fluorine during EP and show that EP mechanisms are modified with the aging of the bath. The observed characteristics can be used to evaluate the quality of acids and to improve the life time of EP mixtures. However, a too high fluorine content in niobium could be the origin of decreased performances noticed on single-cell cavities after EP using modified parameters.

INTRODUCTION

Electro-Polishing (EP) in HF-H$_2$SO$_4$ electrolyte has been efficiently used for the polishing of SRF cavities for decades. Recently, progress has been made in different laboratories to explain mechanisms involved in EP and origins of the aging of the electrolyte [1-3]. Recently, Electrochemical Impedance Spectroscopy (EIS) has been used and the existence of a compact film at the niobium's surface has been put forward [3]. EIS could be also used to evaluate the quality of an electrolyte [4]. In this paper, we will report improved comprehension of the process thanks to the use of a rotating disc electrode. Complementary EIS measurements have been done on different mixtures. They prove that electro-chemical mechanisms are likely to evolve with the aging of the bath. In particular, an increased diffusion of fluorine could make it possible to accelerate the process or to counterbalance the aging of the bath. However, precise borders for the parameters should be fixed because a too high fluorine concentration could be the origin of dramatic performances observed on 1-cell cavities.

VOLTAMPEREMETRIC MEAUREMENTS ON SAMPLES

EP experiments on static niobium samples have been used for a long time to understand and optimize the process. We report here the first use of a rotating disc electrode for electrochemical measurements of niobium in HF-H$_2$SO$_4$ electrolyte [5], which make it possible to get precious information concerning mass transport of species. The samples (10 mm diameter discs) were mechanically polished under the same protocol before electrochemical measurements. We used a system with three electrodes:

- the rotating disc electrode (rotating at speed ω)
- a cathode in aluminium
- an Ag/AgCl reference electrode.

Nota: Information concerning experimental protocol is presented more in detail in [5]. For measurements on samples, potentials are given in respect to the Ag/AgCl reference electrode. For cavity experiments, the voltage corresponds to the potential drop between the cavity and the cathode (no reference electrode is used).
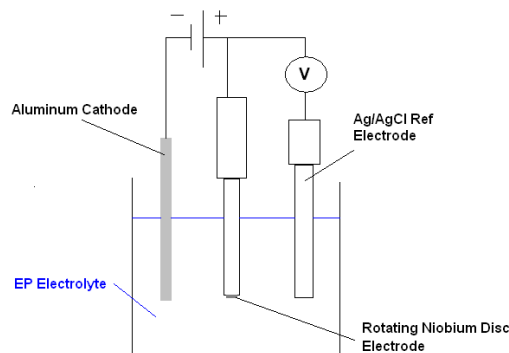
Fig. 1: Set-up with 3 electrodes used (top) and picture of the rotating system for the disc sample (bottom).

The electrolytes were prepared with HF (40% or 48%) and H_2SO_4 (95%) in proportion 1-9, with or without additional Nb_2O_5 dissolved in it. A mixture prepared with HF (48%) will be noted: 1-9(48%). In order to evaluate the evolution of electro-chemical mechanisms during EP, we also used aged mixtures coming from previous experimental campaigns. Characteristics of studied mixtures are given in Table 1. The mixture temperature is controlled $\Delta T=\pm 0.5°C$.

Mixture	A 1-9 (48%)	B 1-9 (40%)	C 1-9(48%) 9g/L Nb	D 1-9(48%) aged
[HF] mol/L	2.78	2.26	2.69	<2.28
[H2O] mol/L	7.93	8.34	8.17	8.18
[HF]/[H2O]	0.35	0.27	0.33	<0.28
Dissolved Nb g/L	0	0	9	>10.28

Table 1: Characteristics of the mixtures studied.

The considered reaction at the anode is the oxidation of niobium into its pentoxide form and its dissolution by hydrofluoric acid. The resulting simplified reaction is:

$$Nb + 5HF \rightarrow NbF_5 + 5H^+ + 5e^- \qquad Eq. 1$$
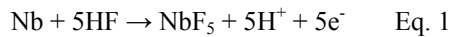
I(V) curves have been plotted at different rotation speeds on Fig. 2. The graph exhibit standard features:
- a first increase in current density with potential,
- an oscillation area,
- a "plateau" for increasing potentials: current does not depend on voltage.

More chaotic oscillations are also expected at higher potentials, but we could not reach this area because of the limitation of the power supply used.
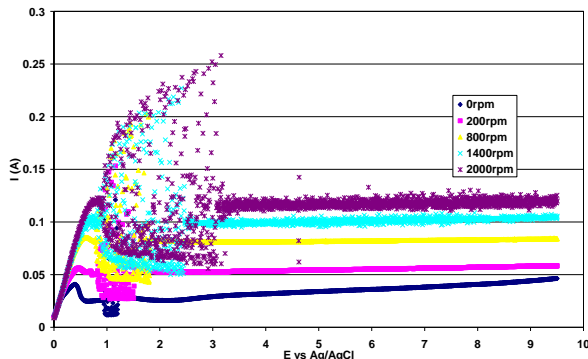

Fig. 2: I(V) curves at different rotation speeds for mixture A.

The rotation speed of the electrode was increased in order to estimate its influence on intensity. We have noticed:

- an increase in the current on the plateau with rotation speed,
- a widening of the oscillating area.

This second aspect is in accordance with an extended competition between removal and forming of the oxide layer. In fact, the kinetic of niobium oxidation increases with potential, whereas, the removal rate of the oxide layer is fastened at higher rotation speeds. The existence of the plateau and the shift towards higher currents at higher rotation speed is liable to a diffusion-limited mechanism. The only specie which might be involved should be fluorine since:
- water addition in EP mixture decreases the removal rate [1],
- addition of niobium in mixture at constant [HF]/[H2O] ratio does not induce a decrease in current [2].

We investigated current evolution for mixtures described in Table 1 as a function of ω. In case of a system limited by diffusion, intensity in steady state i_{ss}, measured with a rotating disc electrode, is given by Eq. 2:

$$i_{ss} = 0.62\,E^{-3} \quad nFSD^{2/3}\nu^{-1/6}\omega^{1/2}C \quad Eq. 2$$

i_{ss} : current in steady state (A)
n : number of electrons in the electrochemical reaction: 1
S : surface of the electrode (cm^2)
D : diffusion coefficient ($cm^2.s^{-1}$)
ν : viscosity (St)
ω : rotation speed of the electrode ($rad.s^{-1}$)
C : concentration of the active specie ($mol.l^{-1}$)

Measurements were made for each mixture at 5 and 9 V, for different rotation speeds. $i_{ss}=f(\omega^{1/2})$ has been plotted for each mixture at 5 V (See Fig. 3). This result does not depend on the potential used for the measures.
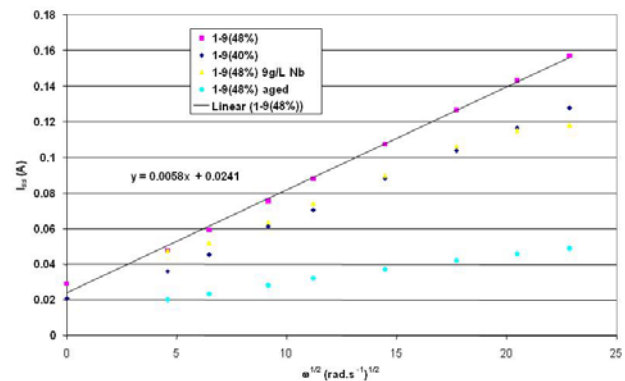

Fig. 3: Proportional relation between I and $\omega^{1/2}$ for A, B, C and D mixtures at 5 V.

We have observed that:
- in each case, the intensity is proportional to $\omega^{1/2}$,
- the coefficient of proportionality is lower for aged mixtures.

We can conclude that EP of niobium in HF-H_2SO_4 electrolytes is limited by diffusion of F^- ion and that the related diffusion coefficient D_{F^-} decreases with the aging of the bath. The corresponding mechanism is the "acceptor" model [6]. The fluorine concentration tends to zero towards the niobium surface and the concentration gradient governs the kinetic of niobium dissolution. It is possible to find an estimation of D_{F^-} thanks to Eq. 2. The only missing parameter is the value of the viscosity of the electrolyte. As an approximation, we have assimilated HF in the EP mixture to H_2O and have chosen the viscosity of the corresponding concentrated H_2SO_4 mixture found in [7]. Values for D_{F^-} are reported in Table 2. Values are in accordance with diffusion coefficient reported for different EP systems in concentrated electrolytes. For example, according to [8], the diffusion coefficient of water for Cu electro-polishing in H_3PO_4, is between 10^{-9} and 10^{-7} cm^2.s^{-1}, depending on the solvatation model considered. Because of viscous electrolytes used, magnitudes are lower compared to those achieved in aqueous solutions (D~10^{-5} cm^2.s^{-1})

Mixture	Potential/ref (V)	D (10^{-8} cm^2.s^{-1})
A 1-9(48%)	5	13.11
A 1-9(48%)	9.5	14.13
B 1-9(40%)	5	13.80
B 1-9(40%)	9.5	14.23
C 1-9(48%) 9g/L Nb	5	8.62
C 1-9(48%) 9g/L Nb	9.5	8.41
D 1-9(48%) aged	5	4.76
D 1-9(48%) aged	9.5	4.46

Table 2: Values calculated for the diffusion coefficient D in A, B, C and D mixtures at 5 V and 9 V.

In all cases, a high rotation speed, responsible for the thinning of the viscous layer, did not alter the surface finishing after EP (see Fig. 4). For example, in the case of the mixture D, the surface of the sample deteriorates in static configuration, whereas it is smoothened at high ω. We might then conclude that it is possible to counterbalance the aging of the bath by increasing the agitation of the electrolyte.

Fig. 4: Bright samples after experiments at high rotation speeds.

EIS EXPERIMENTS WITH DIFFERENT MIXTURES

In addition, complementary EIS measurements have been done on mixtures with different HF concentrations and different amounts of dissolved niobium. The samples used were parallelepipeds, set vertically. Nyquist diagrams were plotted at 4.5V vs. Ref for frequencies between 100 kHz and 0.1 Hz. We notice that the features at high frequencies are similar to previous results obtained by Hui Tian [3]. The characteristics of these features R0 and R1 evolve as a function of the composition of the mixture (see Fig. 5a):

R0: limit of the impedance at high frequency

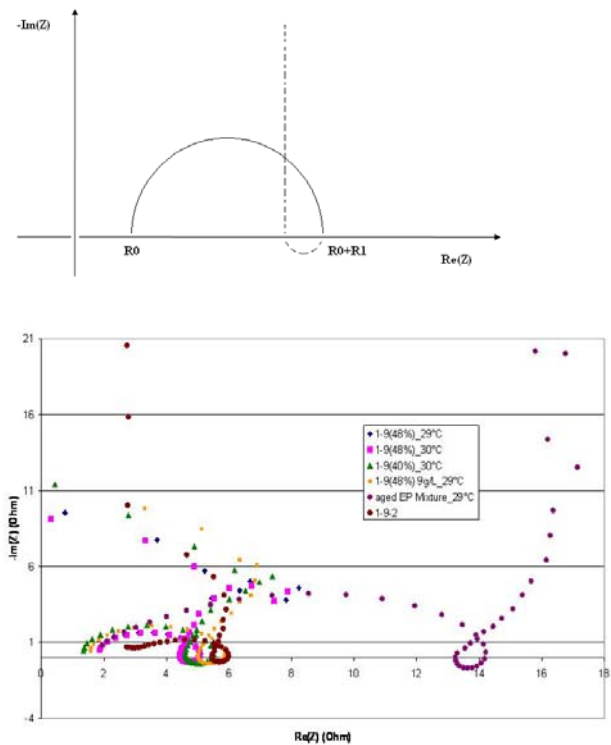R1: diameter of the semi-circle

Fig. 5: a) General shape at high frequency of Nyquist diagrams (top) and b) spectra obtained at 4.5 V vs. Ref. range 100 kHz and 0.1 Hz (bottom).

In particular, we observe that R1 is higher in the aged mixture. A [HF]/[H_2O] has been foreseen to provoke the increase in the polarization resistance R1 [3]. However, this explanation is not sufficient since the addition of water in 1-9-2 mixture (two additional volumes of water) does not increase R1 value: niobium dissolved in solution does also influence the polarization resistance. We can assess that higher water content in EP mixture presents two antagonist effects:

- a light addition (in 1-9 (40%) compared to 1-9 (48%)) provokes a reduction of R0 which should be attributed to a better dissociation of the acids [9].

- a more decreased $[HF]/[H_2O]$ ration in 1-9-2 or aged mixtures provokes a shift of R0 towards higher impedances. This might be due to a modification of the niobium interface.

Therefore we investigated if the compact structure of the interface film highlighted by H. Tian et al. [3] might evolve with bath composition or aging of the electrolyte. In that way, we studied the evolution of R0 in A, B, C and D mixtures as a function of the potential. An increase in R0 with potential would be the signature of a porous structure of the film which thickens with an increasing voltage. As, in [3], R0 is found independent of the voltage in case A. However, for mixtures B, C and D, we notice an increase in the impedance (see Fig. 6). This should be attributed to the thickening of the surface film through a porous structure [10]. The oxide layer would evolve towards a "duplex structure" with the aging of the bath. It is in accordance with other publications [11, 12].
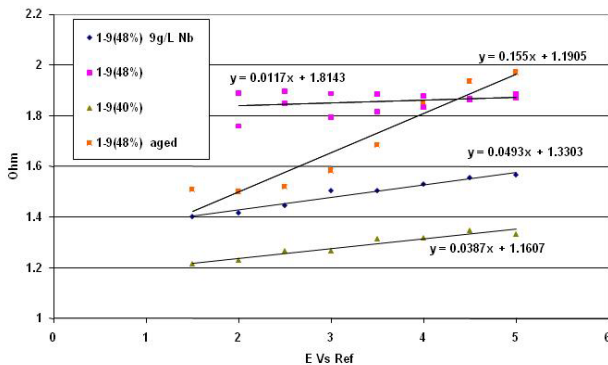

Fig. 6: R0 vs. potential for A, B, C and D mixtures.

We might also add that typical features are observed with microscope at x500 or x1000 magnification (Fig. 7) for samples deteriorating after EP in aged electrolyte. These features might be considered as the signature of the incriminated surface film.
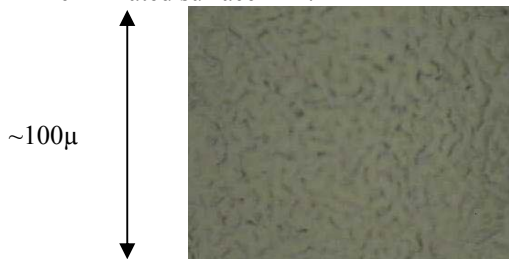

Fig. 7: Typical features observed on samples after EP in aged mixture, with limited fluorine diffusion.

We can draw a sketch for the evolution of electrochemical-mechanisms during EP:
- In a fresh EP mixture, D_{F^-} is high and a compact film is present at the surface of niobium.
- With the aging of the bath, D_{F^-} decreases. The removal rate of the oxide decreases.
- The oxide layer becomes thicker with a "duplex-type" structure: the outer surface is porous.

- This duplex structure generates typical features at the niobium's surface which might cause the deterioration of the surface for aged mixture.

If the flux of F^- ion is increased again with appropriate flow configuration, it is possible to obtain again an improvement of the surface. The mechanisms highlighted from now on give precious information concerning the process. It is necessary to increase the removal rate of niobium during cavity treatment to boost the flux of F- ions towards the niobium interface. It might be achieved by:
- increasing the flowrate of the acid,
- increasing the HF concentration.

Nevertheless, an upper limit for HF concentration has to be determined, because previous experiments show that a too high HF concentration leads to the loss of the diffusion plateau [1].

FLUORINE AND CAVITY PERFORMANCE

Moreover, a high F^- diffusion towards niobium surface could be a possible source of F content in the bulk niobium. In fact, aggressive ions like Br^- are likely to segregate in niobium oxides [13].

Might an increased HF content have an impact on SRF cavities? Some 1-cell cavities were exposed to high fluorine content in different configurations. We experienced effect of concentrated HF exposure on a 1-cell cavity. For this purpose we used C1-03 electro-polished cavity with excellent results. It was filled with HF (48%) during 30' and then rinsed with chloroform. The cavity was tested and its performances were found to have deteriorated dramatically (Fig. 9). This deterioration can not be incriminated to chloroform rinsing since this chemical does not affect cavity performance [14]. Fluorine is a good candidate for this deterioration of the cavity. In fact, it might not be imputable to Q-disease since the cavity was cooled quickly at 4K. Moreover, HF with lower concentration but longer exposure time can be used to rinse cavities [15] or does not generate dramatic H contamination [16]. However, hydrogen contamination can not be totally overshadowed [17]. The cavity was then slightly polished to determinate if the contamination did only occur at low depth. After 20 µm BCP and test at 1.4 K, the performance was still poor. It indicates that the contamination, source of the loss of performance, deeply affects bulk niobium.
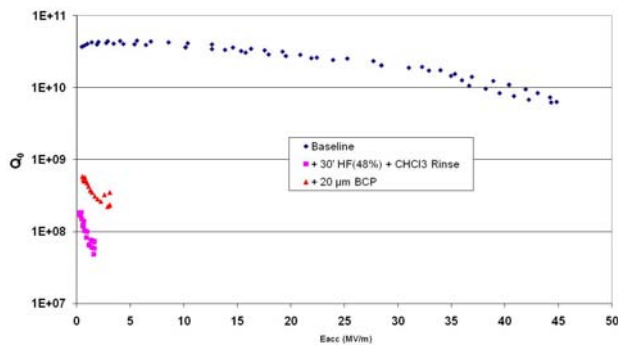
Fig. 9: Dramatic deterioration of Eacc and Q_0 on C1-03 mono-cell cavity after rinsing it with HF(48%).

Moreover, effect of high fluorine concentration was also tested on electro-polishing of 1-cell cavity. New cavity "1AC03" was first electro-polished at 17 V (~ 100 μm) and then electro-polished with a mixture prepared with HF(40%), H_2SO_4(95%), and additional water in proportions $3 - 6.72 - 0.28$. We decided to test this electrolyte on cavity because it was previously used on samples which achieved high brightness. The lifetime of the bath was also achieved [18]. The cavity was electro-polished at a voltage between 3 and 4 V and the removal was approximately 50 μm. The cavity was tested at 1.4 K (Fig. 10). An impressive Q_0 was achieved at low gradient (10^{11}) but a strong Q slope is found with an onset at 5 MV/m.
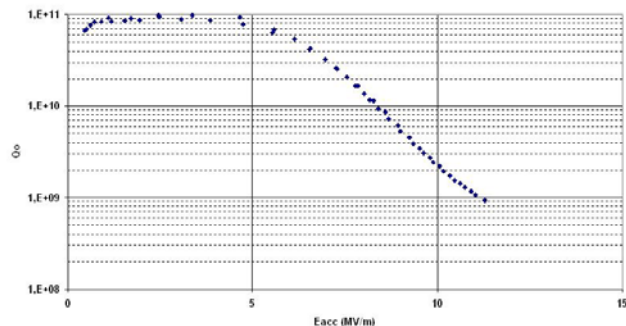

Fig. 10: RF test of the cavity 1AC06 after 100 μm removed with 1-9(40%) and 50 μm removed with 3–6.72–0.28. Q deterioration at low-gradient after EP in highly concentrated HF mixture (50 μm removed).

We have also notice that this early Q-slope is similar compared to the one obtained after horizontal electro-polishing with "BEP electrolyte" with high HF concentration [19]. A last example was also presented at KEK [20], with non removal of Q-Slope by baking after having renewed the surface by EP with highly HF-concentrated mixture. The incriminated mixture used was prepared with 3 volumes of HF for 10 volumes of H_2SO_4. All presented examples suggest possible performance deterioration due to fluorine. More experiments are required to find out a precise correlation.

OUTLOOK AND CONCLUSION

Voltamperemetric and EIS measurements make it possible to better characterize EP process in HF-H_2SO_4 electrolyte. It is limited by the diffusion of F ion towards the niobium surface and the surface film is likely to evolve with the aging of the bath, ending in the deterioration of the surface: the film at the surface has first a compact structure in fresh electrolytes. Its outer structure evolves and becomes porous and thicker with the aging of the electrolyte. Moreover, the EIS measurements suggest that this method could be used to evaluate the quality of an electrolyte. However, additional experiments are required to calibrate this possible method. It is conceivable to increase the removal rate during EP by boosting the acid flow rate or adding HF in the electrolyte. Furthermore, more investigation is required to determine adapted borders. In fact, some results on mono-cell cavities correlated with sample studies suggest that a too high fluorine content in bulk niobium could dramatically deteriorate the cavity performance.

ACKNOWLEDGEMENTS

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