

ELECTRO-CHEMICAL COMPARISONS BETWEEN BEP AND STANDARD EP OF NIOBIUM

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Abstract

Buffered Electrochemical Polishing (abbreviated as BEP) is a process developed at JLAB. It was shown that BEP can produce the smoothest niobium surface ever reported [1,2] with a very fast removal rate. Some encouraging results after BEP on single-cell cavities treated by a vertical set-up have also been reported [3]. Complementary experiments on flat Nb samples have been carried out at CEA Saclay with a rotating disc electrode. Electro-chemical Impedance Spectroscopy measurements were also performed. Experimental results obtained on BEP were compared with those achieved with the standard Electro-Polishing (EP) [4]. Differences in terms of fluorine diffusion and of surface film resistance between BEP and EP have been put forward. Studies are on going to understand if some poor RF test results obtained after BEP with an horizontal set-up as well as with a vertical one [3] are due to the modified electro-chemical mechanisms or the decreased quality of commercial electrolyte used.

INTRODUCTION

BEP is a polishing process developed at JLAB, which gives excellent results in term on roughness on flat samples. An organic acid (lactic acid $C_3H_6O_3$) is used in BEP: the electrolyte is prepared mixing 4 volumes of HF 40%, 5 volumes of H_2SO_4 95%, and 11 volumes of $C_3H_6O_3$ 95% (mass percents). This process is also applied to polish single-cell cavities for tests in different laboratories [2,3]. At CEA-Saclay, some electro-chemical studies have been carried out on samples in order to determine electro-chemical mechanisms involved in BEP compared to standard Electro-Polishing of niobium ($HF-H_2SO_4$ mixtures).

VOLTAMPEREMETRIC MEAUREMENTS ON SAMPLES

Recent results prove that standard Electro-Polishing of niobium in $HF - H_2SO_4$ mixtures is likely to be governed by the diffusion of fluorine ion to the niobium surface [4,5]. Proofs are given using a rotating disc niobium sample. When a process is limited by the diffusion of a molecule or ion, it is possible to increase the current by making faster its mass transport to the surface. More

precisely, the current is then proportional to the square root of the rotation speed of the electrode ω . Such experiments have been made for BEP.

The mixture used was home made. The proportions are 4-5-11 in $HF-H_2SO_4-C_3H_6O_3$. 900 mL of electrolyte was used for the experiments. Three electrodes were plunging in it during measurements: (See Fig.1)

- the niobium sample (anode)
- an aluminium counter electrode (cathode)
- an Ag/AgCl reference electrode

The niobium discs used were 10 mm diameter. They were mechanically polished prior to electro-chemical measurements. The temperature of the electrolyte was controlled ($T=30\text{ }^\circ\text{C} \pm 1\text{ }^\circ\text{C}$)

Nota: For measurements on samples, potentials are given in respect to the reference electrode. For cavity experiments, the potential corresponds to the voltage drop between the cavity and the cathode (no reference electrode is used).

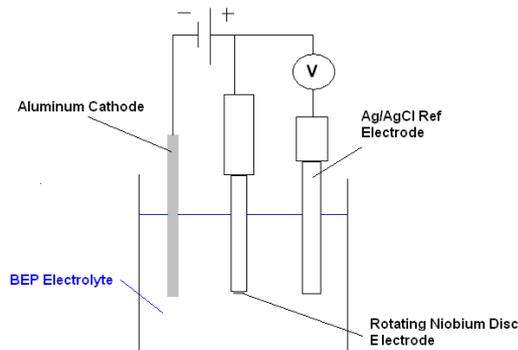


Fig.1: Set-up used for voltamperometric measurements with rotating working electrode (niobium anode).

In a first step, $I(V)$ curves were plotted at different rotation speeds (See Fig.2). For BEP in absence of rotation, the $I(V)$ curve is similar to those obtained with standard EP. A first increase in current is noticed, followed by an oscillation area for potentials between 1.5 and 2.6 V. A short current plateau is visible. A clear increase in intensity is noticed for rising potentials above 3.5 V. This increase might be attributed to oxygen forming due to water dissociation in this area.

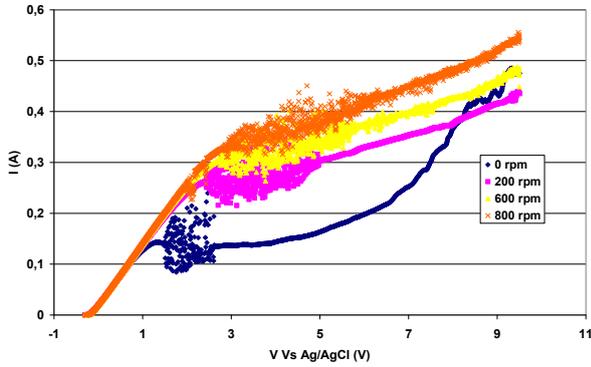


Fig.2: I(V) curves for BEP mixture plotted with a niobium rotating disc electrode at different rotation speeds. T=30 °C.

For higher rotation speeds, the I(V) curves are modified. No plateau is visible and the oscillation area is broadened. The current increases linearly with potential. It might not then be attributed to oxygen forming. The coefficient does not depend on the rotation speed. It is contained between 318 and 382 mA.cm⁻².V⁻¹. Furthermore, current increases with the rotation speed. It is worth noticing if current is proportional to the square root of the rotation speed. With that purpose in mind, current was monitored at 5V for different rotation speeds (Fig 3a). Current is not stable (due to the instability noticed in I(V) curves). However it increases with the rotation speed. For each incrementation, an average current has been calculated and plotted as a function of the square root of ω . The relation is not found proportional, since the current is less sensitive to ω at high rotation speeds (Fig.3b). After measurements, surface was very shiny compared to the surface obtained after measurements with standard EP.

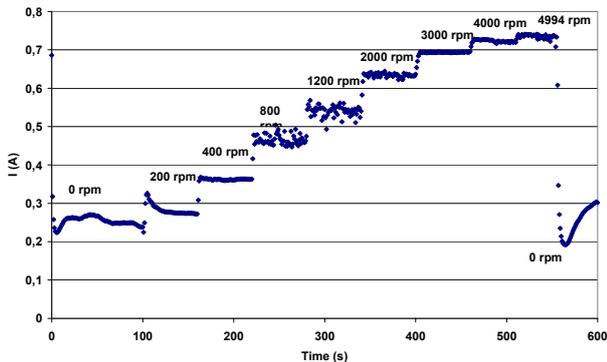


Fig.3a: I(t) obtained at 5V Vs Ag/AgCl with BEP for different rotation speeds. T=30 °C. Intensity increases with electrolyte's agitation.

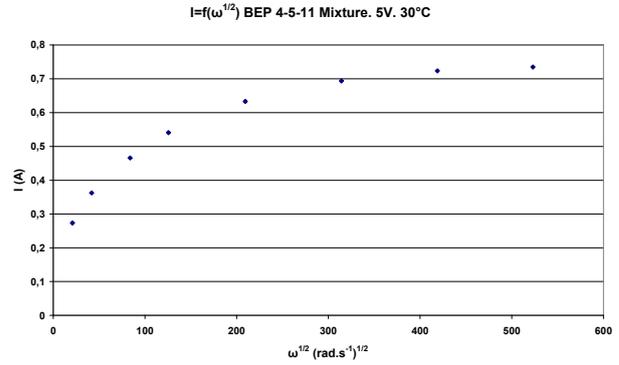


Fig.3b: Intensity as a function of $\omega^{1/2}$ for BEP mixture. T=30 °C. No proportionality is found. The electrochemical system is not governed by diffusion of fluorine.

For BEP, convection, diffusion and electro-migration influence the current density j . No term is negligible in the expression of the mass transport N_i (mol.m⁻².s⁻¹) for each ion i :

$$N_i = -D_i \nabla c_i - z_i w_i F c_i \nabla \Phi + u c_i \quad \text{Eq.1}$$

D_i : diffusion coefficient for specie i : m².s⁻¹

c_i : concentration for the specie i : mol.m⁻³

F : Faraday constant: 96485 C.mol⁻¹

u : fluid velocity in m.s⁻¹

Φ : potential in V

z_i : charge for the ion i

w_i : constant depending on ion i

As a consequence, the quality of the surface finishing will be more sensitive to the uniformity of the electrical field comparatively with standard EP. For this reason, a "ball-shape" cathode has been designed at JLab, which improved brightness achieved on single-cell cavity [6].

EIS MEASUREMENTS ON SAMPLES

Electro-chemical Impedance Spectroscopy (EIS) measurements were also carried out on flat samples with home made BEP electrolyte. The samples used had parallelepiped shape, and were set vertically. For standard EP, it has been shown that spectra strongly depend on HF-H₂SO₄ ratios in the electrolyte. For example, limit at high frequencies and the diameter of the capacitive semi-circle are different [4,5,7]. Similar measurements have been made with BEP mixture (See Fig.4).

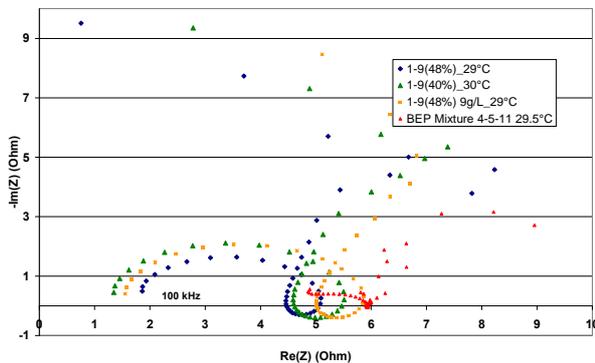


Fig.4: EIS Nyquist spectra obtained for different EP and BEP electrolytes at 4.5V Vs Ag/AgCl. Range 100 kHz - 0.1 Hz. BEP differs significantly from EP.

Spectra differ significantly in BEP case:

- The spectra observed were less stable, especially at low frequencies.
- The feature at high frequencies is modified: the semi-circle observed for standard EP is deformed.
- The diameter of this “semi-circle” is decreased.
- The origin of this feature is shifted towards higher impedances.

It was not possible to obtain stable signals at frequencies under 1 Hz. The real part of the limit at high frequencies will be noted R0 and the diameter of the “deformed semi-circle”, R1, as in [8]. R0 corresponds to the impedance of the electrolyte and of a possible surface film. We did not measure conductivity of BEP electrolyte. However, because of higher water content (10 mol/L vs 8 mol/L for standard EP electrolyte) responsible for a better acid dissociation, conductivity of BEP electrolyte should be higher. The high impedance should be attributed to a resistive surface film at the niobium surface, which could be correlated to “milky” films sometimes observed at the surface of the samples after BEP experiments [9]. The limit R0 at high frequency for BEP has been studied at 4.5 and 5 V (Fig. 5). The spectra obtained for potentials higher than 5 V were not stable.

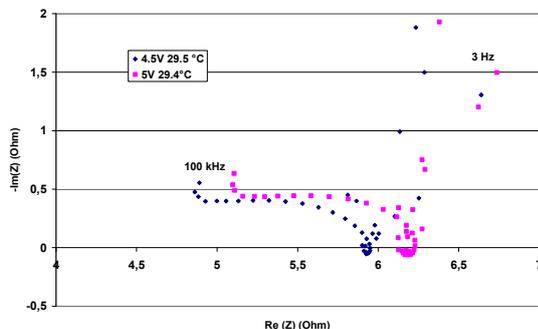


Fig.5: EIS Nyquist Spectra for BEP at 4.5 and 5 V Vs Ag/AgCl. Limit R0 at high frequencies increases with potential.

The obtained impedance at 100 kHz is higher in the 5 V case. It seems that the resistivity R0 of this film depends on the applied potential which would be responsible of its thickening. Furthermore, an additional graph was plotted, translating the curve at 4.5 V in order to obtain a common origin. We observe that both curves are almost superimposable (Fig.6). We might conclude that:

- R0 increases with potential.
- R1 does not depend on potential.

We might also notice that R1 is significantly decreased compared to the standard EP case. Results are in accordance with the “salt film model” [8] and confirm the existence of a porous and resistive film at the surface of the sample during BEP.

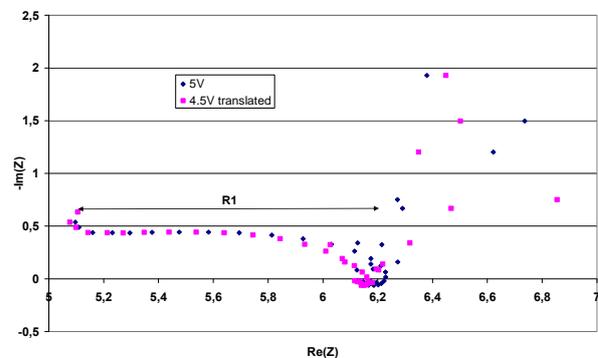


Fig.6: Features obtained at 4.5 and 5 V are superimposable. (Range 100 kHz - 3 Hz).

EIS spectra obtained in BEP case are less stable and do not fit perfectly with standard features obtained for Electro-Polishing mechanisms. However, they confirm that the characteristics of the process differ significantly by comparison with the standard EP case. Main difference should be attributed to the existence of a porous film whose resistance increases with potential.

HORIZONTAL BEP OF SINGLE-CELL CAVITIES

Single-cell cavities have been polished through BEP at Saclay using a horizontal set-up. Commercial electrolyte has been used because it is too constraining to prepare in our laboratory 40 L of acid by mixing large amounts of HF, H₂SO₄ and C₃H₆O₃. However, commercial acid used obviously differs from home-made electrolyte prepared with a precise mixing order [6, 9]. In fact, the acid is dark brown, compared to the colourless home-made electrolyte. The dark colour should be attributed to the presence of carbide particles resulting from chemical reactions with lactic acid during the mixing of the acids [10]. During BEP with commercial electrolyte, foam appears at the surface of the liquid. I(V) curves were plotted to determine an adequate potential for single-cell cavity polishing (Fig.7).

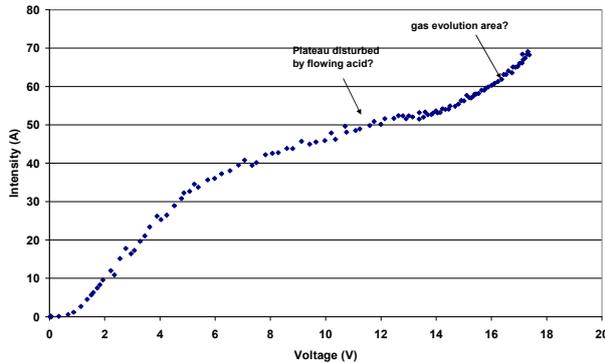


Fig.7: I(V) curve plotted on single-cell rotating CEBAF cavity. T=20 °C. 1 rpm. No clear plateau is observed.

In accordance with previous results on sample, no clear plateau is found. An inflexion point is noticed at 13.5 V prior to a fast increase in current. We have chosen to use a potential close to that point, but situated at lower potential to prevent from operating in the oxygen evolution area. We have observed a huge current density working at 12.5 V (~100 mA.cm⁻²) with a naked cathode. Wrapping the major part of the cathode was found to considerably decrease average current density (40 mA.cm⁻² were achieved). Three CEBAF cavities have been polished at Saclay and tested at JLAB [3, 6] as well as a TESLA shape cavity, C1-22 from CERCA Company, BEP-polished and tested at Saclay. C1-22 had a reference result: 22 MV/m, limited by quench. 50 μm were removed at 12.5 V and 30 °C. The RF tests (see Fig.8) showed a performance deterioration of the cavity due to an early Q-slope.

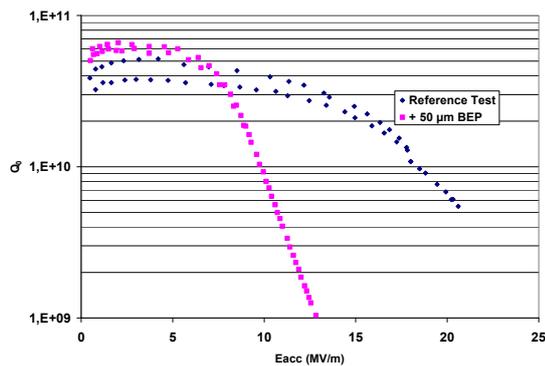


Fig.8: Q₀=f(Eacc) for C1-22 Tesla Shape cavity. Performances deteriorated after BEP with early Q-Slope.

It is not clear if bad performances might be attributed to the inappropriate quality of electrolyte (and the presence of carbide particles) or to different Electro-Polishing mechanisms responsible for modified surface and decreased RF performances. A too high fluorine mass transport to the surface during horizontal BEP is a possible origin of this phenomenon [4].

CONCLUSION

Experiments on flat samples prove that BEP differs from Standard EP from electro-chemical considerations. BEP is not limited by diffusion. Furthermore, EIS measurements indicate that a resistive surface film is likely to be formed at the niobium surface during BEP. Diffusion and electro-migration both directly govern current density. A uniform electric field is then necessary for uniform removal of niobium to achieve micro and macro polishing of the surface. In that way, improving the shape of cathodes is vital to reach that purpose.

Results obtained at Saclay on single-cell cavity after horizontal BEP are quite disappointing compared to those achieved at JLAB after vertical BEP. Early Q-slope might be attributed to the carbide particles present in the commercial electrolyte used. Increased fluorine content in the niobium might also be a possible cause for this decreased performance. SIMS measurements on samples are ongoing to evaluate this possibility.

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