

# Electropolishing (EP)

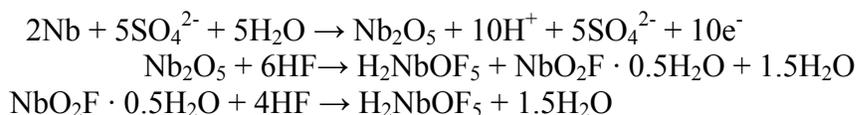
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## Introduction:

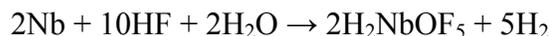
In order to achieve good performance in a cavity, a defect and impurity free metal surface is essential. After fabrication, the inner surface of scrf cavities needs to be cleaned to remove the damage layer and any surface roughness or impurities that could cause field emission (FE) or premature breakdown of superconductivity (quench). Besides, a smooth surface provides less magnetic field enhancement on grain boundaries, which results in smaller surface resistivity and higher quality factor Q. It is now known that EP produces better results and is superior to the most common surface treatment for scrf cavities, buffered chemical polishing (BCP), when trying to achieve high accelerating fields (gradients) [1]. EP is an electro-chemical method of removing thin layers of metal from a surface by an anodic dissolution. An EP system consists of two metals, an anode and a cathode, immersed in an electrolytic solution with an applied electric potential to begin the polishing process.

## Niobium Chemistry:

When a voltage is applied between the anode and cathode the polishing process is activated. Current first oxidizes the niobium surface at peaks because of field enhancement, then hydrofluoric acid (HF) solutes these oxides [2]. This occurrence is explained by the leveling mechanism [3]. This mechanism states that an electro-chemical reaction generates a liquid layer by viscous complex salt near the surface. At peaks, the anode current concentrates due to smaller electrical resistivity with the liquid layer. This liquid layer is thickest over micro depressions and thinnest over micro projections. Electrical resistance is at a minimum wherever the liquid layer is thinnest (high electric field), resulting in the greatest rate of metallic dissolution [4]. The chemical processes of EP on niobium using a mixture of sulfuric and hydrofluoric acid are [5]:



Therefore the overall chemical reaction is:



Since the reaction taking place is known, the amount of energy that is released (per mole) can easily be calculated using heats of formation ( $\Delta H_f$ ).

Species	$\Delta H_f$ (Kcal/mol)
Nb	0
HF	-75.75
H <sub>2</sub> O	-68.3174
NbF <sub>5</sub>	-433.22
H <sub>2</sub> NbOF <sub>5</sub> *	-501.5374
H <sub>2</sub>	0

\*There is no physical data on H<sub>2</sub>NbOF<sub>5</sub>. Since pentafluoxyniobic acid is the hydrated form of NbF<sub>5</sub>; just add the heats of formation of NbF<sub>5</sub> and H<sub>2</sub>O together.

$$\Delta H = \sum \Delta H_{f \text{ products}} - \sum \Delta H_{f \text{ reactants}}$$

$$\Delta H = -108.94 \text{ Kcal/mol}$$

$$\Delta H = -456.11 \text{ KJ/mol}$$

It is easy to see that HF is the determinative chemical in the electrolyte. Oxidation of Nb metal is caused by anodic polarization of the cavity which produces Nb<sup>5+</sup>. HF provides F<sup>-</sup> ions which complex the Nb<sup>5+</sup> ions and forms a compound soluble in water. H<sub>2</sub>SO<sub>4</sub> acts as a buffer with high viscosity which is known to improve surface state because it is often used as a brightening agent [6,7]. The cathode and the cavity (anode) should be the only metallic parts that come in contact with the acid mixture. All other parts that come in contact with the acid solution must be made out of chemically inert plastics such as PFA, PVDF or PTFE.

### **Cathode Material:**

The most common electrolyte solution that is currently being used is an acid mixture that contains 9 parts of 96 wt% sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) and 1 part of 46 wt% hydrofluoric acid (HF) [2,8,9]. Nonetheless there are many more recipes (although some less studied) that can also be used. In EP of niobium for scrf cavities niobium plays the role of the anode, the site where oxidation occurs. The cathode should be made out of a material that is as inert as possible to the electrolytes involved. Ideally, gold and platinum would be the best materials to use because of their resistance to taking part in chemical reactions; unfortunately these materials are quite expensive. An inert and relatively inexpensive cathode material must be chosen. Stainless steel could be used but it creates comparatively large holes sporadically throughout the niobium surface [10]. If using a copper cathode, the copper becomes passivated when the current is flowing. When the current is stopped, copper ions precipitate on the cavity surface creating impurities on the niobium [8]. Choosing pure aluminum as the cathode is the best and most inexpensive option available for this electrolyte composition because it does not generate a chemical reaction when in contact with the acid mixture. The electro-chemical series shows that aluminum is less noble than niobium; therefore the concentration of aluminum impurities on the niobium surface is prevented [9]. Better results can be obtained if the cathode is shaped in such a way that gives a more uniform distance between cathode and anode. This helps to achieve uniform etching rates over the entire surface of the cavity.

## Optimum Conditions for EP:

During EP, depending on applied voltage and sample geometry, a typical sample may experience etching, periodic oscillation of anode current density, polishing (plateau of current density), and then gas evolution on the cavity surface. Depending on what recipe is used for the electrolyte mixture, periodic oscillation may occur before or after polishing. EP was originally invented by P.A. Jacquet in 1935. He discovered that the plateau in current density was the optimum region for EP [11].

There are several methods of EP to obtain better results in scrf cavities. The first method was developed by Siemens, and they found that the optimum EP condition was not in the plateau of current density but in current oscillation [3]. When current oscillation is reached, there are two processes taking place: dissolution of the oxide film by hydrofluoric acid and re-oxidation by sulfuric acid [4,8,12]. The current can oscillate continuously for as long as 3 hours. The key is to maintain a constant acid temperature and a continuous mild agitation (laminar flow) of the acid solution. The laminar acid flow assists the dissolution process and a balance between building up and dissolution processes is reached. Oscillation amplitude and frequency can both be altered by changing cell voltage, acid temperature or agitation speed. The best results were received for oscillation amplitude of 10-15% around the mean value [4,8]. This method allows for a lower content of hydrogen on the surface of the cavity as well as represses all grain boundaries and even results in a higher Q.

More recently K. Saito at KEK has developed a continuous process that controls only current density and temperature. According to Saito [3], the optimum EP condition is not always in current oscillation but current density of 30-100 mA/cm<sup>2</sup> and acid temperature between 20°C and 35°C. He believes current density is the most important parameter for achieving gradients over 35 MV/m; therefore the cell voltage can be ignored. Hydrogen absorption and consequently Q-disease do not occur with this method due to the continuous potential barrier. This method is better suited for cavities that need large amounts of material removed from the inner surface.

The polishing current is a critical parameter needed for optimization of the EP process. The polishing current can easily be calculated by multiplying the total surface area of the cavity by the limiting current density [10]. The polishing rate is a valuable piece of information needed to know approximately how long the process will take to remove a specific amount of material. Weigh the samples before and after polishing, this confirms how much material was dissolved over the period of time EP was occurring. The density of niobium is 8.57 g/cm<sup>3</sup>, thus the polishing rate in units of μm /min can be calculated [10]. A simple correlation between time, thickness of the etched niobium layer, and current density can be written in the form of the following equation [9]:

$$d [\mu\text{m}] = 0.811 \cdot j [\text{mA}/\text{cm}^2] \cdot t [\text{h}]$$

Given a niobium sample's dimensions, it is possible to calculate the amount of energy released for every 1 μm etch that goes into solution. For a 40 mm by 40 mm niobium sample, 67.276 J of energy is released per 1 μm etch.

Acid temperatures above 40°C must be avoided as they will create etching pits on the niobium cavity. Ideally, the acid temperature should be kept between 35°C and 20°C. A constant temperature distribution inside the cavity is needed for uniform removal.

### **Comparison with BCP:**

A damage layer of about 100  $\mu\text{m}$  is created during fabrication of niobium scrf cavities [4,8]. The goal of chemical surface treatments is to remove this damage layer and obtain as smooth a surface as possible. K. Saito quantitatively evaluated the required surface smoothness by analyzing Q-slope. From his analysis he deduced that the surface roughness required to achieve rf superconductivity depends on the rf frequency of the cavity [3]. For example, a required surface roughness of less than 2  $\mu\text{m}$  is needed to prevent field enhancement problems in a scrf cavity (made of 1300 MHz single cells). After 150  $\mu\text{m}$  of niobium is removed by EP, the surface roughness of a sample will drop below 1  $\mu\text{m}$ . This thickness correlates to the damage layer created by sheet rolling of the niobium. Therefore, at least 100  $\mu\text{m}$  must be removed to achieve a smooth surface (less than 2  $\mu\text{m}$  roughness) and removal of the damage layer [3]. Typically, chemically etched surfaces are at least one order of magnitude rougher than electropolished surfaces [8]. From the viewpoint of surface quality, the main difference between EP and BCP is that EP produces smoother ridges at the grain boundaries [4,8]. EP will also provide smoother surfaces and better cavity performance such as higher Q and higher gradients [1], as well as reduce steps and avoid magnetic field enhancements at grain boundaries. Results from the KEK/Saclay collaboration demonstrate that EP raises the gradient by more than 7 MV/m when compared to BCP while electropolished cavities endure clear degradation when subjected to a following BCP [13]. Although many labs have fabricated electropolished cavities with gradients greater than 35 MV/m, high gradient niobium cavities are limited to around 40 MV/m by a fundamental limitation known as the superheating field [3].

One disadvantage of using EP is that it is more complex and slower than BCP (a step size of 1  $\mu\text{m}$  is obtained by EP compared to 5  $\mu\text{m}$  by using BCP) [14]. Another disadvantage is a higher probability of provoking heavy Q-disease (degradation of quality factor) caused by hydrogen absorption in the cavity surface resulting in increased surface resistance.

### **Hydrogen Absorption:**

Hydrogen absorption occurs when niobium is in contact with the acid solution without an applied voltage. Niobium has a natural 5 nm thick passive oxide film ( $\text{Nb}_2\text{O}_5$ ) on its surface, with other oxides and sub-oxides below it [8]. This oxide layer is protective against hydrogen absorption but it is destroyed by halogen ions such as  $\text{F}^-$ . Once the oxide film is depassivated by  $\text{F}^-$  ions, hydrogen is absorbed into the niobium surface and precipitation of hydrides is favored. Keeping a continuous voltage between the cavity and cathode will not allow  $\text{H}^+$  ions to be picked up by niobium due to the potential barrier (both the cavity and  $\text{H}^+$  ions are positively charged).

When cooling a cavity down to get superconductivity, precipitation of dissolved hydrogen (hydrides) occurs around 100 K. This increases the surface resistance of the cavity – an effect known as hydrogen Q-disease. Hydrogen in metals has a tendency to interact with crystal defects such as impurity atoms, dislocations, and grain boundaries forming an area of concentrated dissolved hydrogen that can reach hydride precipitation [6]. This is even more sensitive in very pure metals because there are fewer crystal

defects inside the crystal lattice and the surface remains as the principal defect. Since most of the hydrogen is trapped on surface defects, it is possible to assume that the number of hydrogen atoms is proportional to the number of defects [15]. Hydrogen is not really trapped in the sense, but concentrated near the defect. Hydrogen contamination inside the niobium metal is only in the form of interstitial atoms, so  $H_2$  is not the only possible contamination source [6]. Some species such as  $H_2O$ ,  $OH^-$ , and  $H^+$  are more likely to lead to hydrogen absorption. Since acid mixtures are being used, high concentrations of  $H^+$  ions are present which are directly absorbed into the niobium surface (when voltage is not applied).

Oxidizing conditions result in the dissociation of hydrides and the formation of an oxide layer. During EP, oxidization occurs once an electric voltage is applied [7]. The EP acid mixture does not contain any chemicals that function as an oxidizer (unlike BCP), suggesting that the oxidation prevents hydrogen absorption. In the presence of a strong oxidant such as  $NO_3^-$ , one of the products formed is  $H_2O$  instead of  $H_2$  [6]. This fact explains why  $H_2$  evolution is not seen in BCP and why chemically polished cavities contain less hydrogen than electropolished ones. For this reason, K. Saito and T. Higuchi [15] propose that adding a small amount of nitric acid ( $HNO_3$ ) to the EP acid will result in continuous oxidation so as to prevent any hydrogen absorption. However, this results in Q-slope (degradation of Q at high fields). Saito and Higuchi think that it may be due to the addition of nitric acid and are trying to find the optimum amount of nitric acid that will cure Q-disease and also prevent Q-slope.

Most systems used for EP of a cavity operate using a horizontal orientation because the gases produced are promptly removed from the wetted cavity surface. A porous PTFE bag placed around the cathode will prevent bubble traces and hydrogen gas from the cathode coming in contact with the cavity surface, which will result in less dissolved hydrogen in the niobium. If a vertical system (cavity upright) is used, gas bubbles produced from the cathode would travel up along the surface of the niobium cavity creating axial wells.

### **Heat Treatments:**

Heavy Q-disease and hydrogen contamination are especially problematic with electropolished cavities. Heat treatments are used to expel any hydrogen out of the niobium. There are currently two heat treatments being used at various labs to combat these problems. A low temperature baking will eliminate hydrogen contamination because Nb hydrides dissociate over 100-150°C as long as  $[H]/[Nb]$  is under 60%. However, if too much hydrogen is dissolved in the niobium Q-disease will result. Regardless if Q-disease is the result, baking will improve the cavities performance. The mechanism by which low temperature baking occurs is stated in the following: a niobium surface that has been electropolished is lightly coated by  $NbO_x$  ( $x < 1$ ) and  $Nb_2O_{5-y}$  covered with hydrogen bonded  $H_2O/C_xH_y(OH)_z$ . This type of surface deteriorates surface resistance at high fields by interface tunnel exchange (ITE) of conduction electrons in  $NbO_x$  between localized states of  $Nb_2O_{5-y}$  and states of niobium, in which the result is Q-slope. After baking, oxygen diffuses through the London penetration depth  $\lambda_L$  (50-100nm). This causes  $Nb_2O_{5-y}$  to become thinner and  $NbO_x$  precipitation into niobium. This results in the disappearance of Q-slope [16]. Unfortunately baking does not

eliminate Q-disease because the protective passive oxide film can remain until 250-300°C. It is known that hydrogen in niobium bulk can be easily degassed at temperatures over 600°C [16]. Therefore, a mild temperature annealing of 2 hours at approximately 750-800°C seems to be the most effective treatment. This treatment has several advantages: reduction of crystalline defects, less hydrogen absorption, and enhanced thermal conductivity at 2 K [6].

### **Stability to Exposure to Air:**

The ability of a scrf cavity to tolerate being in a particle accelerator for long periods of time is a very important concern. At Saclay [13] a test was conducted to show the effect of long time air exposure to electropolished cavities since it was believed that exposing a cavity to air could be a possible cause of degradation of the gradient. After a bake out, a polished single-cell cavity was introduced to clean air. No significant change was found in the cavities behavior even after the niobium cavity was exposed to air for two months.

### **Conclusion:**

In recent years, electropolishing has proved to be superior to BCP and is now the forefront of surface treatments for scrf cavities. Gradients above 35 MV/m are now possible but are limited to 40 MV/m by a fundamental limitation: the superheating field. Using heats of formation it is calculated that 456.11 KJ of energy is given off (per mol) when this reaction proceeds. The cathode material should be carefully chosen so as to not react with any of the ingredients in the electrolyte recipe. Two different methods to EP niobium are currently being used. The current oscillation method allows lower hydrogen content, no grain boundaries, and a higher Q. Saito's method is more ideal for cavities that require heavy surface material removed and prevents any hydrogen absorption as well due to its continuous potential barrier. The surface roughness of a cavity that has undergone EP is generally one order of magnitude smoother than one that has undergone BCP. Hydrogen absorption is caused by F<sup>-</sup> ions from the electrolyte solution destroying the niobium's natural oxide film when no voltage is applied. Q-disease is all but uncommon with electropolished cavities but can be easily treated with an annealing of 2 hours at 750-800°C. A mild heat treatment of 130°C for 48 hours can be effective by eliminating hydrogen contamination and reducing the degree of Q-disease. However, this will not cure Q-disease and should therefore be used in conjunction with a PTFE cathode bag for maximum protection. When exposed to clean air for long periods of time, electropolished cavities show no significant change in performance. For a 40 mm by 40 mm niobium sample, 67.3172 J of energy is released by the chemical reaction for every 1 μm etch. Once the EP of small niobium samples is finished, data analyzed, and conditions optimized, work will then begin on electropolishing half cells and dumbbells for CKM scrf cavities

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