SULFUR RESIDUES IN NIOBIUM ELECTROPOLISHING*

L. Zhao, M. J. Kelley, the College of William and Mary, Williamsburg, VA 23187, U.S.A.
H. Tian, C. E. Reece[#], JLab, Newport News, VA 23606, U.S.A.

Abstract

Electropolishing (EP) in sulfuric/hydrofluoric acid mixtures affords significantly greater surface smoothness than the incumbent buffered chemical polishing (BCP), making it attractive as the future baseline technology for SRF cavity manufacture. However, reported observations of particulate sulfur residues raise concern. One hypothesis is sulfate reduction to elemental sulfur at the cathode, where the measured potential drop is thermodynamically sufficient. We explored these possibilities under standard EP conditions in a small three-electrode laboratory cell. Hydrogen generated on the cathode also plays an important role as a strong reductant. We varied aluminum cathode area to obtain different current densities (and thus overpotentials) at constant cell current. We substituted platinum, an excellent hydrogen activating catalyst, for aluminum in some experiments. Surface of cathodes was examined with Scanning Electron Microscope (SEM). Surface composition was analyzed by Energy Dispersive X-Ray Spectroscopy (EDS) and X-Ray Photoelectron Spectroscopy (XPS).

INTRODUCTION

In Nb EP process, the main reaction at the cathode is hydrogen evolution: $2H^+ + 2e^- \leftrightarrow H_2$. However, the large amount of concentrated sulfuric acid in the electrolyte cannot be neglected when considering chemical reactions. The form of sulfur species in the solution varies under different combinations of pH and potential (E), as shown in the E-pH diagram in Figure 1.
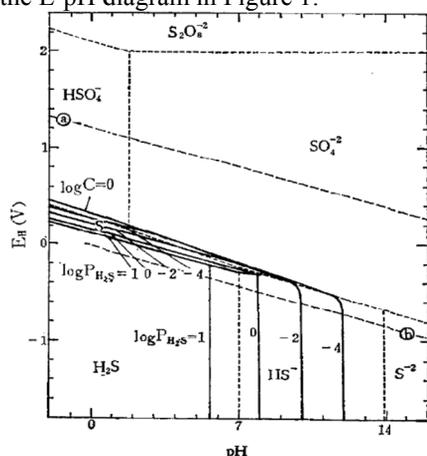
Figure 1: E-pH diagram of S-H_2O system at 25°C [1].

As the potential at the cathode becomes more negative, assuming the pH is near 0 or negative in the highly acidic

solution, H_2S is more stable than other forms of sulfur species in the system.

H_2S is produced from H_2SO_4 reacting with the H_2 generated from the main reaction:

$H_2SO_4 + 4H_2 \rightarrow 4H_2O + H_2S$
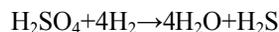
H_2S can produce elemental sulfur and SO_2 by reacting with H_2SO_4:

$H_2SO_4 + H_2S \rightarrow 2H_2O + SO_2 + S$ [2]

In terms of kinetics, potential (E) drives the reaction, and current density (i) indicates how fast the reaction runs. The slope and intercept of i-E curve can be related to the resistance of a reaction [**1**].

According to existing reports, sulfur species was found on Nb coupons, in cavity EP tubing [3] and Teflon mesh wrapped around Al cathode [4**]**. No existing report used a technique giving chemical state information indicating it is elemental sulfur, sulfate or sulfide. Analysis indicates that sulfur species generate near the cathode and travel along with the electrolyte. However, the focus of existing studies is on either Nb anode [5] or the electrolyte [6, 7], no detailed characterization on Al cathodes has been reported. We carried out a series of experiments to help understand how different cathode sizes and materials affect sulfur generation and the mechanism behind it, so as to find ways to reduce it. The range of surface area ratio of anode and cathode we studied covered the typical ratio (about 10) for elliptical shaped 9-cell SRF cavities.

EXPERIMENT

Nb anode was fine grain square with reactive surface area of 3.6 cm^2 fully immersed into the electrolyte. The reactive size of Nb anode was the same for all of the experiments. Three different sized Al samples were used as the cathode. The area ratio between Nb and Al were 0.6, 9 and 18, named Al0.6, Al9 and Al18 in this paper. Pt was also used as cathode for comparison study, and the area of Nb vs. Pt was 18, named Pt18 in this paper. For potential measurement three-electrode setup was used with a saturated mercury mercurous-sulfate electrode (MSE, 0.65V vs. NHE) as reference electrode (RE). The distance between anode and cathode was 7 cm, and 0.5~1 cm between the cathode and the RE. The electrodes were immersed in 300 ml electrolyte (HF: H_2SO_4=1:10, vol.%).

An Agilent E3634A DC power supply was used to apply voltage to the EP cell. A Keithley 617 Programmable Electrometer and a HP 3478A multimeter were used to measure potential and current respectively. Current-potential (I-E) curves of the cathode were recorded when applying 0~15 V voltage to the two electrodes, the voltage step was 0.25 V and time interval between data points was about 5s. Current-time (I-t) curves of EP process were recorded, with 14 V power

supply, room temperature, for 90 minutes. After EP the samples were rinsed with de-ionized water till pH value is neutral and then air dried. The surface topography and chemical information of the Al and Pt samples were studied by SEM/EDS and XPS.

RESULT AND DISCUSSION

Electrochemical Properties of Different Sized Cathodes

For Al cathodes, the cathode size has no significant influence on the total current (Fig 2(a)) and the position of i-E curve (Fig 2(b)) (the cathode reaction mechanism is not changed). The current density and potential drop (Fig 2(b)) on the cathode is apparently increased with decreasing cathode size (with the same amount of voltage applied).

The potential on cathode is -1.7 V vs. NHE for Al0.56, and even more negative for the other two sizes. All of them fall into the range where H_2S is more favorable than H_2SO_4 according to the E-pH diagram in Figure 1. Therefore we can predict that H_2S is produced in all these cases. And that can explain why H_2S is smelled when cleaning cavity EP apparatus.
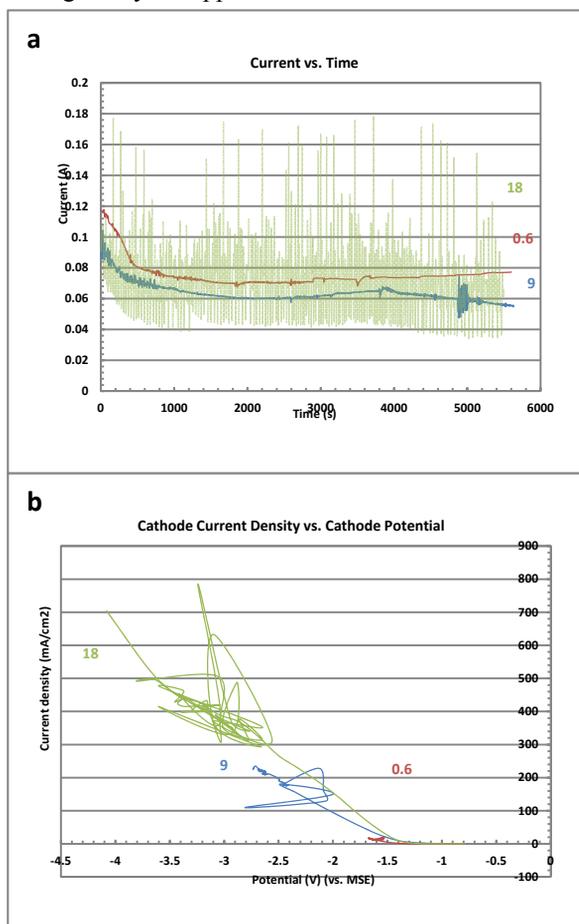
Figure 2: Electrochemical behavior of three sized Al cathodes. (a) Current-Time; (b) Cathode current density-Cathode potential.

Electrochemical Properties of Different Cathode Materials

Using a Pt cathode instead of the same sized Al cathode introduced no significant change in the total current (Fig 3(a)) and the cathode current density. Pt causes less potential drop (Fig 3(b)) on the cathode than Al (with the same amount of voltage applied). The current on Pt cathode climbs up at an earlier stage than Al and for the same amount of potential drop Pt cathode needs larger current density, i.e., i-E_curve (Fig 3(b)) is shifted upwards.
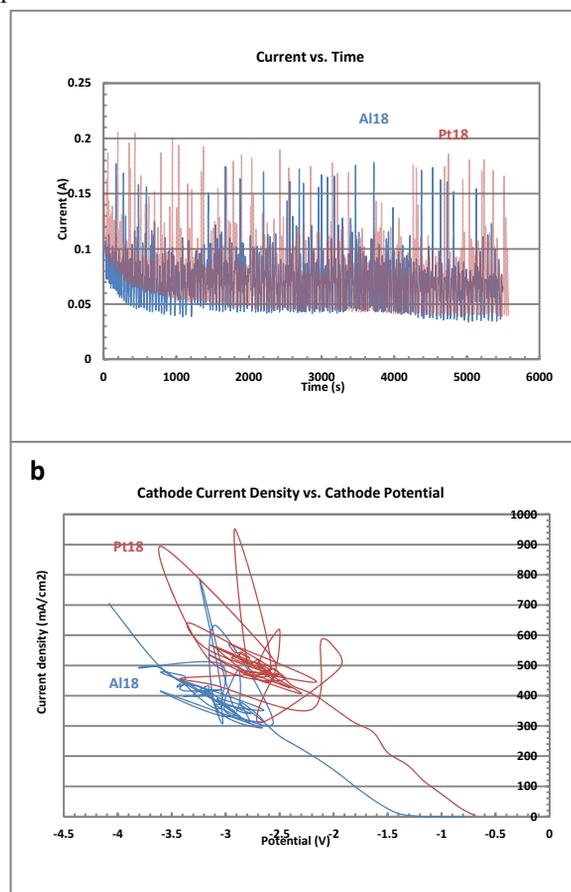
Figure 3: Electrochemical behaviour of Al18 and Pt18. (a) Current-Time; (b) Cathode current density-Cathode potential

Pt is known to have lower over-potential for hydrogen evolution than other metals. It is also a good absorbent for hydrogen. And this seems to apply in Nb EP system as well. We chose Pt as an alternative cathode material hoping that the low hydrogen evolution over-potential will reduce the generation of sulfur. However, from the XPS analysis shown below, Pt may not be a good candidate for this purpose.

Characterization of Cathodes with SEM/EDS and XPS

EDS is not a surface sensitive technique. It explores elemental information of 1 um thick under the surface [8] and a sensitivity of 1% ~ 2%. In our study a high

resolution SEM Hitachi-4700 with an energy dispersive x-ray detector was used. EDS spectrum was taken under 15 kV acceleration voltage. EDS analysis shows that noticeable amount of sulfur residue is found only on Al18, where oxygen peak is also very strong, as shown in Figure 4(left). The surface shows a crystal structure. The sulfur content on Al0.6 and Al9 was below the EDS sensitivity. Considering the difficulty of separating S from Pt peaks using EDS, and the lack of chemical state information, XPS was used to obtain more surface

sensitive (3-10 nm under the surface [8]) and chemical state information.

Survey scans shows that significant amount of sulphur species presents on Al18 and Pt18, as shown in Figure 4 (middle) and Figure 4 (right). From high resolution scan of S2p peak we found that the sulfur residue on Al18 was actually sulfate, consistent with the strong oxygen peak in EDS. On Pt18 both sulfate and sulfur exist. Only about 1% atm sulfate was found on Al0.6 and Al9, also in the form of sulfate. It seems that small sized cathode increases the possibility of sulfur residue.
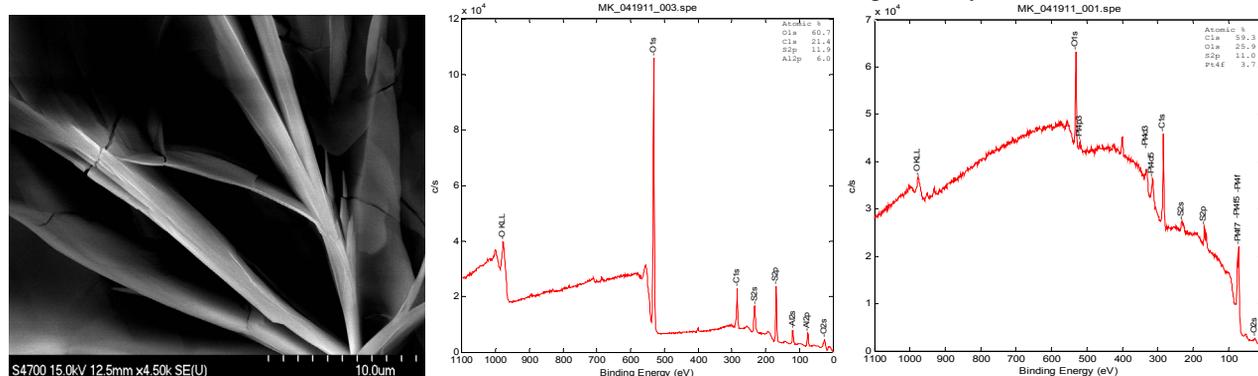
Figure 4: SEM images of Al18 (X4500) (left) and XPS survey spectra for S2p on Al18 (middle) and Pt18 (right). 10.3 atm% of S was found with EDS. 12 atm% of S was found in sulfate form with XPS.

Elemental sulfur was found only on Pt may relate to higher reactivity of H_2 on Pt. Pt is known as a good catalyst for reactions involving hydrogen, by keeping H in an active state [9]. This increased the chance of reaction between H_2 and H_2SO_4, consequently more H_2S and S can be generated. The results suggest that cathode with larger surface area and reduced contact between H_2 and electrolyte can help reduce sulfur residue.

CONCLUSION

Cathode potential measured on all the cathodes we used were in the range where thermal equilibrium favors H_2S instead of H_2SO_4. Total current is not affected by cathode size as predicted. Smaller cathode introduces larger potential drop on the cathode. SEM and XPS study shows that significant amount of sulfate was found covering the smallest Al cathode after EP for 90 min at room temperature with a 1:18 anode and cathode surface area ratio, both sulfate and sulfur presents on the same sized Pt cathode. On larger Al cathodes only hint of sulfate were found. It provides evidence for the hydrogen reduction sulfur generating mechanism. Pt causes less potential

drop than Al, but it may not help much in reducing sulfur generation.

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