Novel Characterization of the Electropolishing of Niobium with Sulfuric and Hydrofluoric Acid Mixtures

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Three-Electrode-Setup Improved Electrochemical Characterization of EP

Example:
- $V_{PwrSup} = 15\, \text{V}$
- $V_{\text{cathode}} : \sim 4\, \text{V}$
- $V_{\text{electrolyte}} : \sim 2\, \text{V}$
- $V_{\text{anode}} : \sim 9\, \text{V}$

Cathode: Al I-V
Anode: Nb I-V

Not Power Supply Voltage
MSE: Mercury / Mercurous Sulfate Reference Electrode

Separating impacts of individual components in EP system.

Emables enlightening study of temperature, flow, and composition dependent effects (electrolyte) in detail.

T = 31.5 +/- 0.5 °C
Ref electrode is nearby Nb.
Reactive area = 5.72 cm$^2$
Local Current Density Strongly Depends on Local Temperature

Past studies identified 25-35 °C for best EP gloss on Nb

For cavity EP, expect unstable temperatures when the electrolyte also serves as the process coolant, and particularly hot in no-flow condition and higher heat flux where flow rate is high, so non-uniform polishing effect is expected.
Anode Current Density Varies Linearly with HF Concentration

Different volume ratio of HF
HF (49%) & H₂SO₄ (96%)
1 : 9 ; 0.8 : 9.2 ; 0.6 : 9.4 ; 0.4 : 9.6 ; 0.2 : 9.8
Area ratio of Nb/Al = 10 : 1
T = 21.3 +/- 1.5 °C

Voltage (V) (vs. MSE)

Anode Current Density (mA/cm²)

Concentration of HF (by volume)

23.44 mA/cm²

5.27 mA/cm²

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What is Electrochemical Impedance Spectroscopy?

- Investigate the electrical dynamics of niobium-acid interaction during electropolishing.
- EIS: 10 mV variable-frequency ac superimposed on normal dc polarization voltage; record the impedance at the different frequency.

Nyquist Plot
- $\omega_{\text{max}} = \frac{1}{R_p C_{\text{dl}}}$
- $\omega = 0$
- $\text{arg} Z$
- $Z_l$
- $R_p$
- $R_s + R_p$
- $\text{Re} Z$
- $\text{Im} Z$

Equivalent Circuit of Nb-Acid Interface During EP
- $R_p$: Polarization Resistor
- $R_{\text{warburg}}$: Diffusion Resistor
- $R_s$: Solution Resistor
- $C_{\text{dl}}$: Capacitor of Electrode Surface
- Nb
- Ref. Elec.
EIS Study of Constant Current Density

Area Ratio of Nb/Al = 10 : 1
(Nb : 26.035 cm$^2$; Al : 2.6035 cm$^2$)
Ref electrode & Thermal Couple nearby Nb (< 5 mm)

Anode Current Density (mA/cm$^2$)

Anode Potential (V)

$T = 21.5 \, ^\circ C$

$T = 5.5 \, ^\circ C$, along the plateau region @ different potential, No agitation
HF : H2SO4 = 1:9

$R_p$ increases with the potential

$R_s$ remains constant

$Z_{real} (\Omega)$

$Z_{imag} (\Omega)$

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EIS Study of different flow rates

Static (triangle) vs. Agitation (dot)
flow rate ~ 4 ~ 5 cm/sec
T = 9.2 ± 0.1 °C

Rs @ at different flow condition remains as constant
R_p decreases with increasing flow
What We have Learned from EIS Studies?

Constant $R_s$ @ different potential regions and flow condition rules out the “porous salt film” model.

$R_p$ ↑ @ different potential regions is inconsistent with the “adsorbates acceptor” model.

$C_{dl}$ ↓ @ different potential regions & $C_{dl}$ ↑ @ different flow conditions is consistent with the “compact salt film” model.

<table>
<thead>
<tr>
<th>Characteristic feature @ the high frequency</th>
<th>Salt Film Models</th>
<th>Adsorbates Acceptor Model</th>
</tr>
</thead>
<tbody>
<tr>
<td>( * C = constant )</td>
<td></td>
<td></td>
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<tr>
<td>Porous Film</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$R_s$</td>
<td>$R_p$</td>
<td>$C_{dl}$</td>
</tr>
<tr>
<td>Different Potential (↑)</td>
<td>↑</td>
<td>C</td>
</tr>
<tr>
<td>Different Rotation (↑)</td>
<td>↓</td>
<td>↓</td>
</tr>
</tbody>
</table>

$T = 9.0 \pm 0.2 \degree C$

Without agitation

with agitation (flow rate: $v \sim 4 \sim 5$ cm/sec)
Sulfuric tends to anodize the Nb under polarization potential producing the "compact salt film"- "Nb$_2$O$_5$".

HF tends to dissolve the Nb oxide under kinetic control with the "at the surface" concentration of F$^-$.  

F$^-$ concentration “at the surface” is limited by how fast it diffuses through the electrolyte - thus the plateau current.

The local gradient in F$^-$ concentration produces the desired polishing action.
Thank You
Preliminary Small Sample EIS Study for Implication

There is a signature difference in EIS response between rough and smooth surfaces. Potentially useful for on-line process feedback.

WEP04 "Surface Roughness Characterization of Niobium Subjected to Incremental BCP and EP Processing Steps"
H. Tian, et. al.

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Future Work on Small Sample EP

- EIS study with different concentration HF
- Monitor polishing effect with different concentration HF
- Monitor polishing effect with different flow rate
- Monitor polishing effect with different temperature electrolyte
- Simulation