Electropolishing of Niobium Superconducting Radio Frequency Cavities in Low-Viscosity, Water-Based, HF-Free Electrolyte: From Coupons to Cavities

The Path from Invention to Product: Electrochemical Technologies I

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October 6, 2014
Expo Center, 1st Floor, Universal 1 – Moon Palace
“Coupons to Cavities”

Nb Superconducting Radio Frequency (SRF) are required for the International Linear Collider as well as other high energy physics projects. To achieve required particle acceleration gradients, electropolishing is the final surface finishing operation;

9:1 H₂SO₄ (98%) : HF(48%) electrolyte (DC) – “viscous salt film” paradigm

Story of;

- Development of “eco-friendly” Nb SRF Cavity EP:
  - ~5% H₂SO₄ with Pulse Reverse Current (PRC) or BiPolar Pulses

Lessons regarding;

- Innovation / “Thinking outside of the Box”
- “Paradigm Shift” in the Thomas Kuhn sense of the phrase†
  - Resistance to ideas/observations which don’t conform to the current paradigm
- Believing / Building on observations even when they are in contrast to the current paradigm

†Thomas Kuhn, The Structure of Scientific Revolutions (1962).
Perspective/Origins

Faraday Technology Inc. was founded in 1991 to:
“...change the focus of electrochemical manufacturing/engineering processes from the use of multicomponent complex electrolyte chemistries to the use of simple electrolytes enabled by pulse/pulse reverse electric fields...”

Initial focus was:
Pulse/Pulse Reverse Current (PC/PRC) Electrodeposition/plating

PC/PRC plating not new, first(?) U.S. patent:

Many prior PC/PRC plating studies used the existing plating bath containing chemical additives optimized for the DC process:
1. Plating bath additives optimized for DC be optimum for PC/PRC?
2. Can a PC/PRC process enable a simple low or additive free electrolyte?
Pulse Current/Pulse Reverse Current Plating†

Cathodic Pulse
- Electrodeposition
  - Grain size, texture, internal stress

Anodic Pulse
- Electrodissolution / H⁺ generation

Off-time
- Replenish electroactive species

Pulse Frequency, $f = 1/(T)$

where $T$ is the pulse period

$T = t_{\text{cathodic}} + t_{\text{anodic}} + t_{\text{off}}$

Cathodic Duty Cycle, $D_{\text{cathodic}} = t_{\text{cathodic}} / T$

Anodic Duty Cycle, $D_{\text{anodic}} = t_{\text{anodic}} / T$

†J-C. Puippe, F. Leaman *Theory and Practice of Pulse Plating* AESF Orlando, FL (1986).
**Mass Transport in Pulse Plating**

**Direct Current**

\[ \delta \quad \text{hydrodynamic (Nernst) diffusion layer} \]

\[ \delta_p \quad \text{pulsating "electrodynamic" diffusion layer} \]

\[ \delta_s \quad \text{stationary diffusion layer} \]

**Pulse Current**

Electrodynamic diffusion layer:

\[ \delta_p \propto (2D \ t_{on})^{1/2} \]

Transition time:

\[ \tau \propto \pi((nF)^2 \ C_b \ 2D)/4 \ i_p^2 \]

\[ \Rightarrow \text{Mass transport control when } t_{on} > \tau \]

Guidance for Pulse Waveform Parameters†

Important pulse waveform parameters:
- Pulse times: Cathodic on-time, Anodic on-time, Off-time
- Pulse currents: Cathodic peak current, Anodic peak current

Secondary (derived) pulse waveform parameters:
- Pulse Frequency
- Cathodic Duty Cycle
- Anodic Duty Cycle

Current Distribution in Pulse Plating†

- Convert conformal hydrodynamic boundary layer to smaller conformal electrodynamic boundary layer
  ➡ Observe short pulses focus current distribution

- Convert non-conformal hydrodynamic boundary layer to conformal electrodynamic boundary layer
  ➡ Observe long pulses focus current distribution

Business Model Open Innovation

- Establish IP (26 patents issued/knowledge)
- Leverage Federal SBIR opportunities as non-equity technology funding
  - Retain IP rights
- Collaborate with universities and government laboratories
- Develop electrochemical engineering solutions based on PC/PRC processes
- Transition technology & competitive advantage to large companies via
  - Field-of-use licenses
  - Patent acquisition (8)

Detailed mechanistic understanding is not required; Development of robust process is critical!
Some PRC Plating Activities

- 2008: Sold patents related to PRC plating of copper interconnects for semiconductor application
  - Time reverse pulse to preferentially dissolve copper to level “dog-boning”
- PRC plating of tin for Pb-FREE solder for electronic applications
  - Tune forward pulse amplitude to control grain size and internal stress to eliminate whisker formation
- 2011: R&D 100 award for PRC plating of Co-Mn alloy interconnects for SOFCs
  - Control grain size and alloy composition
- 2013: Presidential Green Chemistry Challenge award for PRC plating of “functional” chromium coatings from Cr$^{+3}$ electrolyte
  - Generate H$^+$ during reverse pulse to enable thick chromium deposits

So...

*How did Faraday get involved in surface finishing in general and niobium electropolishing in particular?*
Deburring – Ford Motor Co.

- Cast iron (SAE 1010) planetary carrier
- Milling generates burrs in oil grooves
- Prior to 1996, manual burr removal
  - ~400 parts per hour
  - Tangible cost: $2,100,000 per year cost
  - Intangible cost: quality, worker injury

- Attempted electrochemical deburring
  - Used resistive electrolyte
    - ethylene glycol, ammonium salts, nitric acid, small water
  - Observed low tool life, high electrolyte maintenance cost anticipated
  - Required active chilling
  - Used expensive containment hardware e.g. stainless steel tanks

- During 35 minutes of pre-production trials, the process overheated, plastic tool coating melted and an ammonia odor was evident!
Deburring Paradigm

Current Focusing based on Primary/Geometric Current Distribution

- Low conductivity electrolytes
- Low temperature
  \(~ -40 \text{ to } 20^\circ\text{C}\)
- High differential resistance between peaks and valleys
- Focusing current on burrs or asperities using high resistivity electrolytes

\[ \Omega_{\text{surface}} > \Omega_{\text{burr}} \]
Recalled: Pulse Current Spot Plating†

Modeling & Experimental
- PC plating of gold and solder for electronic contacts
- Decreasing duty cycle at the same average current density → more non-uniform plating

From a current distribution perspective, deburring is essentially spot plating in reverse?

⇒ PC focusing current distribution for deburring in conductive electrolytes!

Deburring Bench-top – Ford Motor Co.

- Used same fixture / tooling as developed by Ford for ethylene glycol based process to optimize PC parameters
- Note stainless steel fixture

One Tool “Arm”
Pulse electrochemical deburring
- Aqueous NaCl/NaNO₃ electrolyte
- PLC driven machine†
  - eight stations processing,
  - eight stations unloading/loading
  - 45 second processing time
  - ~400 parts per hour
- Not chilled
- Makeup water twice a month
- Electrolyte replaced every six months
- Magnetic removal of iron hydroxide

$1,600,000 PLC machine:
estimate ~$400k savings with plastic tanks / elimination of chiller

Transition to Surface Finishing

With the success in deburring, we began to think of applications for Pulse/Pulse Reverse electrochemistry applications in the field of surface finishing, more specifically electropolishing†; An important industrial process!

Electropolishing occurs under diffusion limited conditions†

Buildup of reaction product “viscous salt film” in recesses

- Viscous, chilled electrolytes – thick boundary layers
- Promotes electropolishing

On-going debate regarding mechanistic specifics as a function of material ➔
Smooth, bright surface finish when dissolution rate is mass transfer limited!

- Salt Film Mechanism

- Anion Acceptor

- Microprofile Leveling (Large $\delta$)

- Water Acceptor
Electropolishing Paradigm (DC)

- **1st Issue**: Focusing current using viscous/chilled solutions:

  \[ M^0 \rightarrow M^+ + e^- \]

- **2nd Issue**: Polishing oxide forming materials:

  \[ xM + yH_2O \rightarrow M_xO_y + 2yH^+ + 2ye^- \]

  ➔ Chemically dissolve the passive films
  - challenging control issues/aggressive acids (HF)
  ➔ Non-aqueous electrolytes † < 5% H_2O
  - limited industrial implementation (NiTi stents?)

Electropolishing of Passive Materials.

Small Business Innovation Research (SBIR) Projects
- National Science Foundation Grant///Air Force Contract
- Directed towards EP of SS, Nickel alloys & Titanium alloys
  - Aqueous salt electrolyte (~15% NaCl/NaNO₃)
  - For passive materials; Anodic (Forward) only pulses (PC)†
    - Observed rougher surfaces,
    - Analogous to localized or pitting corrosion

**PRC electrodeposition with reverse (anodic) pulse** used to plate thick chromium deposits from a Cr³⁺ electrolyte to ameliorate “adverse H₂↑ evolution” effects by re-acidifying the interface!

- For electropolishing of passive materials, use reverse (cathodic) pulse to de-passivate the surface?

Analogous to Cr$^{+3}$ Plating

Plating of Low C.E. Deposits

DC: $\text{Cr}^{+3} + 3\text{e}^- \rightarrow \text{Cr}^0$
$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2 \uparrow$

Anodic Pulse “Tuned” to:
- H$^+$ generation/re-acidify surface

Cathodic Pulse “Tuned” to:
- Remove oxide/depassivate surface

Surface Finishing of Passive Materials

DC: $\text{M}^0 \rightarrow \text{M}^{+n} + n\text{e}^-$
$x\text{M}^0 + y\text{H}_2\text{O} \rightarrow \text{M}_x\text{O}_y + 2y\text{H}^+ + 2y\text{e}^-$
Electropolishing – Swagelok Corp.

- Stainless steel (300 Series)
  - Valves, Fittings & Tubular products
  - Semiconductor/biomedical
  - Required mirror-like finish

- Two step finishing process
  1. Abrasive flow media
     - faster than EP
     - tool line removal
     - but, expensive consumable
  2. Final EP: ~160 sec
     - concentrated sulfuric/phosphoric acid + “de-passivating additives”
     - chilled, expensive, difficult to control
Pulse Reverse Process

- Aqueous NaCl/NaNO₃ electrolyte
- Passive film
  - Forward (anodic) pulses
  - Reverse (cathodic) pulses
- One process: no front-end bulk
- Used EP apparatus
- Initial $R_a \sim 1 \mu m$
- After 30 sec $R_a \sim 0.2 \mu m$

- Continued Pulse Reverse EP
  - 120 sec; no improvement - $R_a \sim 0.2 \mu m$
  - Conformal etching?
Speculated - Sequenced† Waveform

Macroprofile \( \delta \sim r \)

Microprofile \( \delta >> r \)

Microprofile \( \delta >> r \)

Reverse pulses not shown for simplicity

Pulse/Pulse Reverse Sequence

- Initial $R_a \sim 1 \mu m$
- Assumed macroprofile
  - Short forward pulses
  - Reverse (cathodic) pulses
- After 30 sec $R_a \sim 0.2 \mu m$
- Assumed microprofile
  - Long forward pulses
  - Reverse (cathodic) pulses
- After additional 15 sec $R_a \sim 0.05 \mu m$
Small Business Innovation Research (SBIR) Projects:
- National Institutes of Health ➔ NiTi Shape Memory Alloy
- Department of Energy ➔ Nb for Superconducting Radio Frequency Cavities
- Both materials used concentrated viscous acids mixed with HF†
  - “Strongly” passive materials are those requiring Hydrofluoric acid during electropolishing
  - Generally, <-600 kJ/mol Ellingham Diagram (Nb, Ti, Ta, W)
  - Attempted PRC approach analogous to passive materials.

proved to be much more challenging than anticipated – initial attempts with aqueous salt solutions NOT successful?

Conventional Niobium EP

- Niobium
  - Superconducting Radio Frequency cavities ($T_{\text{crit}} \sim 10^0 \text{ K}$)
  - Particle accelerators/High energy physics
- Remove $\sim 130$ $\mu$m for SRF performance

- Two step surface finishing process
  1. Bulk: Buffered chemical polishing
     - $\sim 100$ $\mu$m removal at 0.5-1$\mu$m/min
     - $R_a \sim 2$ $\mu$m
     - 1:1:2 HNO$_3$(69%):HF(49%):H$_3$PO$_4$(85%)
  2. Final: Electropolishing
     - 17 V (cell voltage)
     - $\sim 25$ $\mu$m removal at $\sim 0.1-0.3$ $\mu$m/min
     - $R_a < 0.2$ $\mu$m
     - 9 parts H$_2$SO$_4$ (96%) to 1 part HF (49%)

$\Rightarrow$ Stringent safety protocols
$\Rightarrow$ 40 to 50% reject; metallurgy or EP?
Niobium EP Mechanism

- Nb EP for SRF “Cavities” → Nb₂O₅
- Soluble niobium fluorides and niobium oxyfluorides†:
  - Nb₂O₅ + 14HF → 2H₆NbO₂F₇ + H₂O
  - Nb₂O₅ + 12HF → 2HNbF₆ + 5H₂O
  - Nb₂O₅ + 10HF → 2NbF₅ + 5H₂O
  - Nb₂O₅ + 10HF → 2H₆NbOF₅ + 3H₂O
  - HNbF₆ + HF → H₂NbF₇
- Recent EIS studies consistent with EP paradigm

  Diffusion limited F⁻ to a compact ”salt” (oxide) film‡‡

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Pulse Reverse EP Process

Anodic Pulse “Tuned” to:
- Focus current distribution
  ➔ Eliminates need for viscous electrolytes

Cathodic Pulse “Tuned” to:
- Depassivate surface/remove oxide
  ➔ Eliminate need for HF, and/or low water content electrolytes

Off-Time “Tuned” to:
- Dissipate Heat
- Replenish reacting species
- Remove reaction products
Pulse/Pulse Reverse - coupons
  - Aqueous H₂SO₄ electrolyte (5 to 30%)
  - Strong Passive film
    - Forward (anodic) pulses
    - Reverse (cathodic) pulses
  - Fast Waveforms
    - Bulk removal (100 μm)
    - ~0.5-1 μm/min
  - Slower Waveforms
    - Final EP (25 μm)
    - ~0.03-0.3 μm/min
    - Ra ~0.05 μm (stylus)
  - Extremely clean surface (Dr. C. Reece, T. Jefferson lab)
    - “…comparable to standard HF EP…”

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o After *showing* a coupon to a colleague;
“...you can’t do that...” translate “…doesn’t fit EP paradigm…”

o Phase II DOE SBIR **NOT** awarded as the review stated just because EP demonstrated on coupons doesn’t imply success with SRF cavities;
  ➔ but, SRF cavities are currently processed with conventional EP and we are still doing EP?

  ➔ Paradigms “…do not go gently into the night!…”

o Awarded P.O. under the ARRA “Stimulus Act” from FermiLab to demonstrate “eco-friendly EP” of SRF cavities?
  ➔ Coupons 1”x1” (6.5 cm²) and 3”x3” (60 cm²) to
  ➔ Cavities (~2000 cm²)!
Niobium Oxide Removal

\[ 5\text{Nb} + 5\text{H}_2\text{O} \rightarrow \text{Nb}_2\text{O}_5 + 10\text{H}^+ + 10\text{e}^- \]

\[ \text{H}_2\text{O} \rightarrow \frac{1}{2}\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \]

Assumed dominant reactions?

\[ \Rightarrow \text{Transition from oxide formation to oxygen evolution?} \]


Anodic: 3V 2.5 ms
off: 1.0 ms
Cathodic: 9V 2.5 ms
Key observation:

Anodic current transition correlates with effective electropolishing!

**Mixed Metal Oxide Cathode**

- Parallel Plate/Coupon EP Cell
  - *Mixed Metal Oxide cathode exhibits a white coating.*
  - *Coating composition includes mainly Nb & O.*

⇒ ElectroPhoretic Collection of Niobium Oxide from EP

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<th>Element</th>
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<th>Location H</th>
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<tr>
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<td>32.1</td>
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<tr>
<td>Sodium</td>
<td>0.8</td>
<td>0.4</td>
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<td>Potassium</td>
<td>11.2</td>
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<td>Calcium</td>
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<td>Titanium</td>
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<td>Niobium</td>
<td>47.8</td>
<td>N/D</td>
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<td>Ruthenium</td>
<td>N/D</td>
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</tr>
<tr>
<td>Iridium</td>
<td>0.6</td>
<td>7.3</td>
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Off-times to minimize/eliminate heat build-up

“High Power” Waveform

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<th>$t_{off}$ (ms)</th>
<th>Total Time (min)</th>
<th>$T_i$ (°C)</th>
<th>$T_f$ (°C)</th>
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<td>0.3</td>
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<td>15</td>
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<tr>
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<td>14</td>
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<tr>
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<tr>
<td>5.0</td>
<td>560</td>
<td>16</td>
<td>19</td>
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Anodic: 30 V/0.06 ms
Cathodic: 35 V/0.2 ms

Off-Time “Tuned” to:
- Heat dissipation
- Replenish reacting species
- Remove reaction products

Excessive Heat During BiPolar EP?
EP SRF Cavities – Curved Sections?
Simulate Cavity Area Ratio and Gaps

- ARRA P.O. did not allow studies on curved cavity sections.
- Coupon studies used to simulate **area ratios** and **gaps** representative of the beam tube and equator.

### Beam Tube
- Gap – 2.25 cm
- Cavity to Cathode area – 2.4

### Equator
- Gap – 8.7 cm
- Cavity to Cathode area – 4.8

Observed: Anodic current transition correlated with effective EP!
- Increase coupon gap – decrease waveform frequency
- Increase coupon surface area – decrease waveform frequency

➡️ Cavity EP - slow frequency for anodic current transition
ARRA P.O. stipulated that EP studies be conducted in a cleanroom using the conventional EP tool:
- Horizontal
- 60% Volume Fill
- 1 rpm Rotation

Initial Pulse Reverse EP studies:
- Horizontal
- 60% Volume Fill
- 1 rpm Rotation
- 5-10 wt% H$_2$SO$_4$ in H$_2$O

After ~ 7 trials, no visual evidence of electropolishing!

Current cavity EP tool is based on work by Siemens$^\dagger$, so we re-visited.

Problem of ... 
“...electrolytic polishing hollow niobium bodies of a complicated geometrical structure...where development of gases...rise from the cathode...forming gas pockets...resulting in portions of the inside surface not polished...”

...is solved by...
“...horizontally orienting the hollow niobium body...partially filling said hollow body with polishing solution and slowly rotating said hollow body...”

Side Note; electrode “fins” to level current distribution disclosed – only recently considered by the particle physics community?

➔ Since our viscosity is much lower than conventional EP electrolyte, why would the same rotation rate be appropriate? Rather than conduct a rotation study; vertical orientation, no rotation, completely filled!
Subsequent Pulse Reverse EP Studies
- Vertical – actually “dump” mode
- 100% Volume Fill
- No Rotation
- 5-10 wt% \( \text{H}_2\text{SO}_4 \) in \( \text{H}_2\text{O} \)

\( \Rightarrow \) Analogous to plating of internal diameters
\( \Rightarrow \) Simpler/Industrial Compatible
Developmental Cavity – TE1NR001

Adjusted Waveform Timing to Observe Anodic Current Transition

Trial 12
Waveform:
Anodic: 4 V 20 ms
Off: 30 ms
Cathodic: 10 V 10 ms

Trial 14
Waveform:
Anodic: 4 V 140 ms
Off: 175 ms
Cathodic: 10 V 100 ms

Trial 13
Waveform:
Anodic: 4 V 140 ms
Off: 175 ms
Cathodic: 10 V 100 ms

Trial 15
Waveform:
Anodic: 4 V 140 ms
Off: 175 ms
Cathodic: 10 V 100 ms
Performance Cavity #1† – TE1DESYB5

“BiPolar EP” (PRC)
- Vertical
- 100% Volume Fill
- No Rotation
- 5 wt% H₂SO₄ in H₂O

⇒ 30 μm removed “light EP”
⇒ Cavity performed with a quench field about 31 MV/m with a low-field $Q_0$ of 2.0E*10 which is within the normal performance band of a cavity receiving standard EP.


“BiPolar EP” (PRC)
  - Vertical
  - 100% Volume Fill
  - No Rotation
  - 5-10 wt% H₂SO₄ in H₂O

→ 100 µm removed “bulk EP”
→ Cavity exhibited average performance as well as Q-disease which was alleviated after bake which is consistent with conventional bulk EP.


“BiPolar EP” (PRC)
- Vertical
- 100% Volume Fill
- No Rotation
- 10 wt% H$_2$SO$_4$ in H$_2$O

→ 20 µm removed “light EP”
→ Cavity did not exhibit Q-disease which is consistent with conventional light EP.


“BiPolar EP” (PRC)
- Vertical
- 100% Volume Fill
- No Rotation
- 10 wt% H$_2$SO$_4$ in H$_2$O

→ 25 µm removed “light EP”
→ Cavity achieved a maximum gradient of ~44 MV/m with a $Q_0$ of $1 \times 10^{10}$, the highest gradient observed at Fermilab in any cavity regardless of processing technique.


Summary

- Innovative BiPolar EP process demonstrated on Nb SRF cavities
  - Low-viscosity, water-based, HF-Free electrolyte!
- Observed anodic current response key to transition from coupons to cavities
  - Cathodic EP?
- Niobium oxide particles collected via electrophoretic deposition
- Additional mechanistic understanding should accelerate advancements in BiPolar EP
- Innovation requires a careful balance between current fundamental understanding combined with evolving observations which do not necessarily fit the current paradigm;

“...in order to create [innovate], one must first question that which exists...”

Acknowledgements

Co-authors and colleagues at Faraday!

Financial support:
1. Ford Motor Company
2. Swagelok Corp.
3. AF SBIR Program Office
4. NSF SBIR Program Office
5. National Institutes of Health SBIR Program Office
6. Department of Energy SBIR Program Office
7. Department of Energy FermiLab
8. Department of Energy T. Jefferson Lab
9. American Reinvestment Recovery Act (ARRA)

- SRF cavity measurements – Allan Rowe (FermiLab)
- AFM measurements of Nb coupons – Dr. Charles Reece (Jlab)

Thank-you!