FEATURES

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Sustainable Green Processes Enabled by Pulse Electrolytic Principles

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Electrochemical and solid state science, engineering, and technology have an important role to play in society’s sustainable future. Early discussions of the potential environmental contributions by academic, government, and industrial electrochemists were presented in Electrochemistry of Cleaner Environments (1972), Electrochemistry for a Cleaner Environment (1992), and Environmental Aspects of Electrochemical Technology (2000). Some important electrochemical technologies include batteries and fuel cells for mobile (electric vehicle) power and stationary energy storage (wind, solar), conversion and capture of greenhouse (carbon dioxide) gases, contaminate destruction (PFAS), and electrochemical recycling of electronics in support of a circular economy among others. Additionally, many have noted that electrochemical processes are inherently environmentally friendly as “electrons are green.” While we agree with this notion, we also note that many electrochemical processes based on direct current (DC) electrolysis, such as electrodeposition (plating) and surface finishing (electropolishing and electrochemical machining), use environmental and worker “unfriendly” electrolytes. By altering the electrochemical paradigm from one based on DC electrolysis to one based on pulse/pulse reverse current (P/PRC) electrolytic principles, simpler electrolytes with favorable manufacturing/worker and environmental impacts may be accrued. After a brief introduction to the author’s perspective, we present examples of sustainable technologies enabled by P/PRC electrolysis: 1) green electrodeposition of chromium for functional applications, 2) worker friendly electropolishing of niobium for particle accelerator applications, and 3) zero-discharge electrochemical machining of cannon barrels.

Perspective and Introduction to Pulse/ Pulse Reverse Current Electrolysis

The authors’ perspective is generally based on their experiences at an electrochemical research, development, and engineering company, Faraday Technology, Inc. Faraday was founded in 1991 to invent, develop, and commercialize novel electrochemical technologies based on pulse/pulse reverse current electrolytic principles. Faraday often leverages federally funded Small Business Innovative Research (SBIR) and Small Business Technology Transfer (STTR) grants’ contracts to demonstrate novel electrochemical technologies based on P/PRC. Once the technologies are patented, they are adapted to client specific needs with client funds and ultimately licensed to the client.

The concept of pulse reverse current electrolysis is not new and was first reported in the early part of the nineteenth century for electrolysis/recovery of metals from alloys. The main principles of pulse current and pulse reverse current plating, presented in 1986 in the classic compendium, Theory and Practice of Pulse Plating, are still relevant today. A more recent review of pulse current plating is also available.

A generalized P/PRC waveform may consist of a cathodic or anodic pulse followed by an off-time, followed by an anodic or cathodic pulse followed by a second off-time. The cathodic peak current density ($i_{\text{cathodic}}$), cathodic on-time ($t_{\text{cathodic}}$), cathodic off-time ($t_{\text{off,cathodic}}$), anodic peak current density ($i_{\text{anodic}}$), anodic on-time ($t_{\text{anodic}}$), and anodic off-time ($t_{\text{off,anodic}}$) are additional variables for process control compared to DC electrolysis. Additionally, P/PRC waveforms may 1) be net cathodic for plating or net anodic for surface finishing, 2) eliminate one or both off-times, or 3) consist of only cathodic or anodic pulses.

The sum of the cathodic on-time, anodic on-time, and off-time(s) is the period (T) of the pulse and the inverse of the period is the frequency (f) of the pulse:

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

$$f = (1/T)$$

The cathodic duty cycle ($\gamma_{\text{cathodic}}$) is the ratio of the cathodic on-time to the pulse period, and the anodic duty cycle ($\gamma_{\text{anodic}}$) is the ratio of the anodic on-time to the pulse period. The average current density ($i_{\text{average}}$) is given by:

$$i_{\text{average}} = (i_{\text{cathodic}} \cdot \gamma_{\text{cathodic}} + i_{\text{anodic}} \cdot \gamma_{\text{anodic}})$$

Even though P/PRC waveforms may contain off-times and reverse (anodic or cathodic) periods, the electrochemical process rate is typically the same or higher than the corresponding DC process due to enhanced mass transport effects. Current distribution and grain size are also strongly influenced by the P/PRC waveform parameters.

In spite of numerous theoretical and experimental studies characterizing pulse current processes, generally directed towards plating, most of the studies used the existing electrolytes containing harsh chemicals and/or chemical additions optimized for the corresponding direct current (DC) process. In pursing novel applications of P/PRC electrolytic processes, we considered two questions:

1. Why should one expect that electrolytes containing harsh chemicals and/or chemical additions optimized for the corresponding DC process be optimum for a P/PRC process?
2. More importantly, can P/PRC enable simpler electrolytes without harsh chemicals and/or chemical additions and thereby lead to an environmentally and more robust process?

Consequently, when investigating novel P/PRC electrochemical processes, we focus on simple electrolytes devoid of harsh chemicals and/or chemical additions, i.e., “Breaking the Chemical Paradigm in Electrochemical Engineering.”

Green Electrodeposition of Chromium for Functional Applications

Chrome coatings plated from a hexavalent chromium electrolyte are widely used in both military and commercial markets due to their functional properties, such as hardness, sliding wear, and abrasion resistance. The U.S. Environmental Protection Agency (EPA), the Department of Defense (DoD), most states, and the European Union have recognized the need to minimize and preferably eliminate the use of hexavalent chromium plating due to adverse effects from worker exposure and discharge to the environmental. Specifically, the EPA lists hexavalent chromium as a “hazardous air pollutant” because it is a human carcinogen, a “priority pollutant” under the Clean Water Act (enacted 1972), and a “hazardous constituent” under the Resource Conservation and Recovery Act (enacted 1976). In addition, the Secretary of Defense referred to the need to minimize/eliminate the use of hexavalent chromium and to aggressively mitigate the unique risks to DoD operations posed by hexavalent chromium use. Alternative technologies, such as High Velocity Oxygen Fuel (HVOF), have undergone extensive evaluation by the DoD as a replacement for
hexavalent chromium plating. The HVOF process produces high velocity molten particles resulting in a dense coating layer. However, HVOF is a line-of-sight method and is not applicable to components with internal diameters. Consequently, hexavalent chromium plating, which is applicable to internal diameters, is still conducted at DoD and commercial facilities for functional applications.

Plating from trivalent chromium plating baths has been commonly practiced for decorative coating applications, such as car bumpers, plumbing fixtures, hubcaps, and the like. Trivalent chromium is found naturally in the environment and is not a known carcinogen. Furthermore, trivalent chromium is not listed as a chemical of concern by the EPA and is not on the European Union’s Registration, Evaluation Authorization and Restriction of Chemical substances (REACH) list. For decorative applications, the plated chrome coating is thin, typically <10 μm. In contrast, functional chrome must be thick (~100 μm) in order to provide the desired functional properties, such as wear resistance. Previously, plating from trivalent chromium electrolytes was found to be self-limiting and thick coatings were not possible. Consequently, trivalent chrome plating was not pursued for the development of an alternative to hexavalent chromium plating for functional applications.

Chromium plating from a trivalent chromium electrolyte generally has a <20% faradaic efficiency (Eq. 4) with >80% (Eq. 5) of the current resulting in hydrogen evolution:

\[
\begin{align*}
\text{Cr}^{3+} + 3\text{e}^- &\rightarrow \text{Cr}^{0} \\
2\text{H}^+ + 2\text{e}^- &\rightarrow \text{H}_2 \uparrow
\end{align*}
\]

We speculated that the self-limiting nature of trivalent chrome plating was related to the increasing pH at the interface due to the hydrogen evolution reaction (Eq. 5). In order to electrodeposit thick chromium coatings from trivalent chromium electrolytes, we hypothesized that by using an appropriately designed pulse reverse waveform, the pH excursion at the interface could be avoided. Specifically, during the anodic reverse pulse nascent hydrogen oxidation (Eq. 6) or oxygen evolution (Eq. 7) would occur:

\[
\begin{align*}
\text{H}_2 &\rightarrow 2\text{H}^+ + 2\text{e}^- \\
\text{H}_2\text{O} &\rightarrow \frac{1}{2}\text{O}_2 \uparrow + 2\text{H}^+ + 2\text{e}^-
\end{align*}
\]

In either case, the interface would be re-acidified and chromium electrodeposition could continue as illustrated in Fig. 1.

Some earlier work by researchers at the National Institute of Standards and Technology (NIST) reported a trivalent chromium plating process based on direct currents or cathodic pulse currents (no reverse). As we understand, the NIST process required a high temperature (~800°C) post-plating heat treatment to obtain the desired hardness and has not been commercialized.

With funding from several EPA SBIR programs, as well as the National Center for Manufacturing Science (NCMS), we demonstrated the ability to electrodeposit thick chromium coatings from a trivalent chromium electrolyte using the pulse reverse current (PRC) approach. For some electrolytes, the plating rate and current efficiency was considerably higher than that for hexavalent chromium plating. Similar to hexavalent and other plating systems, the pulse reverse trivalent chromium plating process is amenable to internal diameters.

The technology is the subject of a recently issued patent and the basis for the 2013 Presidential Green Chemistry Challenge Award. Current development activities are supported by the U.S. Army and are directed toward extensive material testing at Faraday and other locations. A summary of some of the properties of the trivalent chrome coating are presented in Table I. The remaining challenges include developing a plating bath maintenance protocol in collaboration with our chemical formulator (Coventya, Inc.) and demonstrating an equivalent microstructure.

Regarding the microstructure, chromium plating from a hexavalent electrolyte exhibits discontinuous microcracks. In contrast, chromium plating from a trivalent electrolyte exhibits continuous through-cracks. While the properties of the trivalent plated chromium do not appear to be adversely impacted by the continuous-through-cracks, the different visual appearance presents cause for concern, particularly for aerospace applications. The discontinuous microcracks in hexavalent-plated chrome have long been associated with internal stress. We assumed that the continuous through-cracks observed in trivalent chromium deposits was also related to internal stress.

We collaborated with Prof. S. Brankovic and PhD candidate Kamyar Ahmadi at the University of Houston (UH) to understand the stress buildup during plating and translate that knowledge to a practical solution for trivalent chromium electrodeposition. Using a cantilevered laser apparatus, UH studied the build-up of stress during the initial plating of chromium from hexavalent and trivalent electrolytes, respectively. For the hexavalent electrolyte, a large tensile stress appears as the first few microns of chrome are deposited. As the electrodeposition continues, stress-relieving cracks occur resulting in discontinuous microcracks. In contrast, trivalent chromium electrodeposition exhibits a large compressive stress. The stress relieving cracks occur after plating resulting in continuous through-cracks. By conducting pulse current experiments during trivalent chromium electrodeposition, UH researchers demonstrated that stress-relieving cracks would form during plating for pulse off-times ~5 to 7X longer than the pulse on-times. Based on the knowledge gained from the UH activity, we have produced chromium coatings from trivalent electrolyte with improved wear resistance and reduced the number and volume of cracks. Further optimization efforts are underway for the most demanding functional chrome coating applications. We are currently optimizing the pulse reverse waveform parameters to relieve the stress during electrodeposition to form discontinuous microcracks. The process is being commercialized through our licensee Coventya.

In summary, we have shown that with the use of pulse reverse current electrodeposition one can deposit functional chromium coatings using a much more benign trivalent chromium electrolyte compared to the traditional hexavalent chromium plating electrolyte.

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**Fig. 1.** Pulse reverse current waveform for chrome plating from a trivalent electrolyte.
Worker Friendly Electropolishing of Niobium for Particle Accelerator Applications

Electrochemical surface finishing preferentially removes metal from the asperities of a surface by anodic dissolution:

$$M^0 \rightarrow M^{\text{aq}} + n e^- \quad (8)$$

The selection of the appropriate surface finishing electrolyte to focus the current on the asperities is dependent, in part, on the initial roughness of the surface. For relatively large asperities (arbitrarily >1 µm)32, low conductivity electrolytes are used to magnify the voltage gradient between the asperities and the recesses of the surface. Under primary current distribution control, the asperities are preferentially anodically removed. Low conductivity electrolytes are generally used for applications, such as deburring. For relatively small asperities (arbitrarily <1 µm), high viscosity electrolytes are used to create a thick boundary layer. Under tertiary current distribution control, the limiting currents are higher at the tip of asperities than in the recesses and the asperities are preferentially anodically removed. Jacquet24 was the first to report that the optimum region for electropolishing is in the mass transport or current limited plateau in the polarization curve based on a “viscous salt film” model.

During anodic metal dissolution (Eq. 8) some metal surfaces can form a passive oxide film, generally described as:

$$M + n H_2O \rightarrow M(OH)_n + 2nH^+ + 2ne^- \quad (9)$$

For strongly passivating metals, electropolishing under direct current (DC) electric fields in a simple electrolyte can lead to a roughened surface similar to pitting corrosion. Aggressive chemicals are therefore added to the electrolyte to remove the passive film from the surface and enable uniform polishing.29 For example, hydrofluoric acid and/or fluoride salts, not desirable from a worker safety and environmental point of view, are added to traditional electropolishing electrolytes to depassivate the surface for strongly passive metals such as niobium.29

Niobium is used to fabricate Superconducting Radio Frequency (SRF) cavities used in particle accelerators, such as the Large Hadron Collider and the planned International Linear Collider. For the final fabrication step, the interior surface of the cavities must be electropolished to a microscale roughness. Conventional DC electropolishing of niobium is conducted in a viscous electrolyte consisting of nine parts sulfuric acid (96%) to one part hydrofluoric acid (48%). This electrolyte represents an extreme hazard to workers41, requires costly safety protocols with extensive worker protection (Fig. 2)23, and imposes additional costs related to waste treatment. Furthermore, the viscous electrolyte necessitates the use of a horizontally rotating cavity which is partially filled with electrolyte to enable the escape of hydrogen gas generated at the cathode tool to escape and avoid streaking of the internal surface. This requires elaborate sealing equipment, and limits the industrial implementation of cavity electropolishing.

In order to eliminate the need for concentrated viscous acids with fluoride or hydrofluoric acid additions during electropolishing, we hypothesized that an appropriately designed pulse reverse waveform could remove the surface oxide during the cathodic reverse pulse as illustrated in Fig. 3.

With initial funds from the DOE SBIR program, we developed a pulse reverse process to electropolish niobium coupons in aqueous electrolytes of 5-10 wt% sulfuric acid—devoid of hydrofluoric acid, as shown in Table 1. Chrome Characteristics Plated from a Trivalent Electrolyte.

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**Table 1. Chrome Characteristics Plated from a Trivalent Electrolyte**

| Property                  | Value       |
|---------------------------|-------------|
| Thickness                 | Equivalent to Cr<sup>6</sup> |
| Porosity                  | Equivalent to Cr<sup>6</sup> |
| µ-Hardness                | Hardness increases with Temperature |
| Bath pH                   | 5.3         |
| Bath pH                   | 5.3         |
| Substrate                 | 4130 Steel/15CVD6/300M |
| Current Efficiency        | ~9%         |
| Visual Appearance         | Bright      |
| Adhesion (ASTM B 571)*    | Yes (after bake) |
| Pulse Reverse Plating from Trivalent Chromium Electrolyte |

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**Fig. 2. Safety protocols associated with conventional (DC) electropolishing of niobium cavities.**

...as shown in Table 1. Chrome Characteristics Plated from a Trivalent Electrolyte...

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**Fig. 3. Pulse reverse current waveform for electropolishing of passive materials.**

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(continued on next page)
fluorides, or other chemical additions. The surface roughness was comparable to that observed under conventional DC electropolishing of niobium coupons. The coupon work was transitioned to single cell niobium cavities and the RF performance (~45 MV/m accelerating gradient at quality factor of 1x10^8) was the highest observed at the DOE’s Fermi National Accelerator Laboratory. Due to the avoidance of the safety burden associated with the sulfuric-hydrofluoric acid electrolyte, the capital and operating costs of the pulse reverse process were considerably less than the conventional electropolishing process. More specifically, assuming production of ~4,000 cavities per year, the annual electrolyte cost was reduced from $11.2 M to $1.1 M. The process was validated on nine-cell niobium SRF cavities, patented and transitioned to the DOE’s Thomas Jefferson National Accelerator Facility under a Cooperative Research and Development Agreement (CRADA). As illustrated in Fig. 4, the pulse reverse electropolishing approach requires “ordinary” laboratory safety precautions in contrast to those required for conventional DC cavity electropolishing (Fig. 2). In addition, due to the low viscosity electrolyte, the pulse reverse electropolishing is processed in an industrially compatible manner: vertical, filled, and without rotation.

In summary, pulse reverse electropolishing enables the use of low concentration aqueous electrolytes devoid of hydrofluoric acid. In addition to electropolishing of niobium cavities, the pulse reverse approach was successfully licensed to a company for electropolishing of stainless-steel valves and for electropolishing nickel titanium (Nitinol) alloys for medical devices and implants.

Zero-Discharge Electrochemical Machining for Cannon Rifling Applications

Electrochemical machining (ECM) is a manufacturing technology that allows metal to be precisely removed by electrochemical oxidation or dissolution. As illustrated in Fig. 5, the workpiece is the anode and the tool is the cathode in an electrochemical cell. By relative movement of the shaped tool into the workpiece, the mirror image of the tool is “copied” or machined into the workpiece. Compared to traditional machining processes, ECM has numerous advantages: 1) applicability to hard and difficult to cut materials, 2) no tool wear, 3) high material removal rate, 4) smooth bright surface finish, and 5) production of parts with complex geometry. Consequently, ECM has strong utility as a manufacturing technology for fabrication of a wide variety of metallic parts.

While electrochemical machining can utilize aqueous salt electrolytes for many applications, harsh electrolytes such as hydrofluoric acid or perchlorates, undesirable chemicals from a worker safety, environmental, and associated costs point of view, are required for many alloys of interest for advanced engineering applications. Analogous to electropolishing, we have developed pulse reverse waveform electrochemical machining processes using aqueous salt or low concentration acid electrolytes.

A major impediment to wider implementation of electrochemical machining is the large amount of sludge generated during the process. Specifically, during electrochemical machining, the material removed from the work piece forms an insoluble metal hydroxide and/or hydrated metal oxide sludge. This metal containing sludge must be filtered, dried, and shipped to third party vendors for landfilling and/or recycle, although recycling of the sludge is often cost prohibitive. In addition, as many materials contain chromium, chromium-containing sludge imparts an additional cost burden on landfilling.

In a study of an electrochemical machining process for boring and rifling a 5-inch gun barrel, ~4.1 L of metal was removed generating ~1,325 L of centrifuged sludge. This enormous quantity of sludge represents a >325X volume increase relative to the solid metal removed. As currently practiced, electrochemical machining is inconsistent with the Army’s “Vision for Net Zero” management of natural (metals, water, energy) resources.

In order to eliminate the large amount of sludge generated during electrochemical machining operations and recover/recycle materials, we hypothesized that an appropriately designed electrolyte and pulse reverse waveform could electrochemically machine the metals from a workpiece, while leaving them in soluble form and avoid plating out on the cathode tool. The soluble metals would then be recovered in electrowinning cells using pulse electrolysis.

With SBIR funding from the U.S. Army Benet Labs, we have demonstrated a recycling electrochemical machining process for current and future cannon materials, including high strength gun steel, chrome-copper alloy, cobalt-chrome alloy, and nickel alloy. A recycling electrochemical machining system (Fig. 6) capable of processing up to 0.5 m^3/yr. of material has been delivered to Benet Labs cited at Watervliet Arsenal. The process recovers valuable metals such as nickel and copper; is estimated to reduce water consumption from ~85,000 gal to 3,000 gal; and is estimated to eliminate ~ 500 metric tons of sludge.

In summary, pulse/pulse reverse current enable an environmentally friendly electrochemical machining/electrowinning process, which recovers metals, reduces water usage, and eliminates sludge. Two patents have issued directed to the recycling electrochemical machining process and apparatus.
Electrochemical and solid state science, engineering, and technology have an important role to play in society’s sustainable future. In particular, electrochemical manufacturing processes are deemed inherently environmentally friendly, as “electrons are green.” However, as traditionally practiced using direct current (DC) electrolysis, processes such as electrodeposition (plating) and surface finishing (electropolishing and electrochemical machining) often use harsh chemicals and reagents, which are not environmentally or worker “friendly.” In this article, we suggest that by altering the electrochemical paradigm from one based on DC electrolysis to one based on pulse/pulse reverse current (P/PRC) electrolytic principles, simpler electrolytes with favorable worker and environmental impacts may be accrued. In addition, we have found that the P/PRC processes are generally more robust and economical. Three tangible examples of sustainable technologies enabled by P/PRC electrolysis were presented: 1) green electrodeposition of chromium for functional applications, 2) worker friendly electropolishing of niobium for particle accelerator applications, and 3) zero-discharge electrochemical machining of cannon barrels.

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**Timothy D. Hall** is the laboratory manager at Faraday Technology, Inc., where he oversees the company’s experimental activities directed towards developing innovative pulse and pulse reverse electrolytic processes. In addition to numerous presentations and publications, he is an inventor on many patents. Hall is part of a team that received a 2011 R&D 100 award for developing a novel pulse reverse deposition process for an alloy coating, won the 2013 Presidential Green Chemistry Challenge awards for trivalent chromium plating, and was a finalist for the 2016 R&D 100 award for niobium electropolishing. He has been a member of the ECS for over 15 years and is active in the Electrodeposition (ELDP) Division. He may be reached at timhall@faradaytechnology.com.

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**E. Jennings (EJ) Taylor** is the founder and CTO of Faraday Technology, Inc., a small business focused on developing innovative electrochemical processes and technologies based on pulse and pulse reverse electrolytic principles. He leads Faraday’s business, technology, and commercialization strategy. In addition to 200+ technical publications and presentations, Taylor is an inventor on over 50 patents. He was part of the team that won the 2013 Presidential Green Chemistry Challenge awards for trivalent chromium plating and a finalist for the 2016 R&D 100 award for niobium electropolishing. Taylor has been a member of ECS for 42 years. He is an ECS fellow, past treasurer, and currently serves as chair of the Interdisciplinary Science and Technology Subcommittee. He may be reached at jennings@faradaytechnology.com.

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