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Electropolishing of Nitinol Stents in Aqueous, Acid-Free Solutions

Phase I Final Report

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EXECUTIVE SUMMARY

1) How the Research adds to the Understanding of the Area Investigated

Faraday Technology proposed to demonstrate the feasibility of an innovative stent manufacturing process with the overall aim of addressing technological innovation in the U.S. manufacturing economy consistent with Executive Order "Encouraging Innovation in Manufacturing".[1] Currently, all stents manufactured must undergo an electropolishing process that is commonly done in high concentration acid mixtures of sulfuric/phosphoric/hydrofluoric acid. The proposed process uses simple aqueous pH neutral electrolytes, eliminating process control difficulties and high reject rates (up to 40-50%[2]) associated with current practice, reducing environmental and OSHA challenges, and therefore reduce cost and improving reproducibility. Initial commercialization is envisioned to occur via the replacement of the current electropolishing process with the acid free FARADAYIC®,[3] ElectroPolishing process.

2) Technical Effectiveness and Economic Feasibility

- In the Phase I program, three different bench scale processing apparatus were designed/built for polarization/ flat coupon studies, for straight wire processing studies, and for loop clip processing studies.
- The FARADAYIC® ElectroPolishing Process was tuned to achieve surface roughness (Ra) values as low as 0.16 μm using a salt solution consisting of 25 g/L KNO_3 and 150 g/L Na_2SO_4 at an as-mixed pH of 5.88 when processing and 1" x 1" Nitinol coupons. The industrial benchmark for Ra is less than 0.2 μm, and based on the results enclosed herein we anticipate lower values will be obtained with further development.
- Nitinol wires and loop clips provided by industrial partners were polished and showed the potential to achieve the desired finish required by the medical industry. This program demonstrated a non-toxic aqueous pH neutral electrolyte that is simpler to control and more environmentally friendly as compared to the concentrated sulfuric acid/phosphoric acid electrolyte used by the current state-of-the-art electropolishing technology.
- An α-scale high-throughput stent finishing apparatus was designed within the Phase I program and will be built at the onset of the Phase II program.
- Faraday installed onsite a high-throughput reel-to-reel strand electropolishing system designed by a commercial client for processing straight wire. Through commercial contributions, the system will be retrofitted to allow streamline processing medical device wires.
- Faraday compiling a manufacturing process flow and economic assessment.

3) How the Project Benefits the Public

This project meets the NIH mission by developing an innovative stent manufacturing process with the overall aim of addressing technological innovation in the U.S. manufacturing economy consistent with Executive Order "Encouraging Innovation in Manufacturing". This technology will enable a rapid, high yield, cost-effective manufacturing process for Nitinol stents, and will be compatible with stents and other medical devices fabricated from a wide variety of materials. Stents represent one of the fastest growing segments of the medical device market. From their introduction in 1990, the stent market has grown to over $5 billion in 2011.

1. INTRODUCTION AND BACKGROUND INFORMATION

1.1 Purpose of the Phase I Research

The overall objective of the Phase I program was to demonstrate the feasibility of using aqueous pH neutral electrolytes in conjunction with the FARADAYIC® Process to electropolish biological implant materials, and eliminate the process control difficulties and high reject rates associated with state-of-the-art practices. The Specific Aims to be addressed in the Phase I program include:

1. *Optimize the FARADAYIC® ElectroPolishing Process on Nitinol stents, including the preliminary development of a library of waveform parameters to achieve the desired surface finish for a variety of stents of interest to industry.*
2. *Design an α-scale pilot manufacturing apparatus for demonstration of continuous, industrial-scale processing of stents. This apparatus would be built and validated in Phase II.*
3. *Initiate steps for transitioning the technology to industry partners.*

1.2 Background and Significance

There is a need for robust, non-toxic, low-cost manufacturing of medical devices and implants such as stents (Figure 1), fabricated from materials such as Nitinol. Specifically, ***there is a need to reduce exposure to occupational hazards such as toxic chemicals during manufacturing of these devices. If manufacturing yield can also be improved, this will positively impact device performance and lower cost.***

Figure 1. Various stent products made by Memry Corp.

The stent, a tubular scaffold that exerts a radial force against the vessel wall to keep it open and functional, expands the lumen of a body passageway for 1) preventing recurrence of restenosis, 2) use in passageways such as the left main coronary artery, 3) preventing passageway recoil, 4) expansion to a variable size preventing passageway rupturing.[4,5,6] While many stents are stainless steel or cobalt chrome, self-expanding Nitinol stents[7] have captured a significant portion of the market. Nitinol is a nickel-titanium shape memory alloy with the ability to recover deformation by changing crystalline phase upon heating or cooling. Nitinol stents are tuned to recover their intended shape in vivo at the body's temperature.[8] Stent fabrication involves laser cutting a designed pattern into drawn thin walled Nitinol tubes (~300-760 μm dia., Figure 2). Issues/problems with this method include:

- Local heating associated with the laser cutting process causes a recast/damaged layer of metal oxides on the stent surface, which must be removed.
- The stent is then electropolished to smooth/passivate the surface. Conventional direct current (DC) electropolishing uses a concentrated acid mixture that can include hydrofluoric, sulfuric and phosphoric acids. These chemicals must be completely removed due to their incompatibility with the body and disposed of appropriately. Worker safety issues with highly concentrated acid solutions, and the need for targeted waste treatment, increase the device cost while reducing throughput.

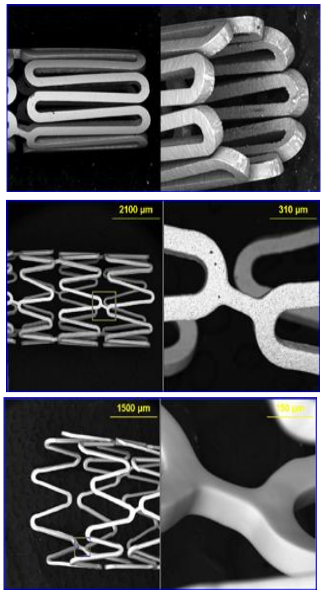


Figure 2. Nitinol stent top) as cut; mid) oxide removed; bottom) after electropolishing.

Due to thermal damage to the stent associated with laser cutting and the requirement for the difficult to control steps of descaling and strong acid electropolishing, the reject rate for Nitinol stents is up to 40-50%,[2] resulting in a huge waste in material and manufacturing throughput, increasing cost and decreasing device reliability. While new laser cutting methods are being developed that do not cause as much surface damage, we understand from our commercial partners that electropolishing will still be needed for the final surface finish, with associated process control difficulties and reject rates. Alternative cutting processes such as electric discharge machining[9] require descaling/electropolishing, and thereby suffer from a similarly high reject rate.

The Problem Being Addressed: The technology under development addresses two major problems with current manufacturing methods for stents:

1. Use of highly concentrated acid solutions, including mixtures of sulfuric, phosphoric, perchloric and hydrofluoric acids, for the final electropolishing step, which pose a significant worker safety hazard.
2. Reject rates of up to 40-50%[2] after completion of the strong acid electropolishing process.

The FARADAYIC® ElectroPolishing Process will impact the stent manufacturing process by replacing conventional electropolishing, done in a highly concentrated mixed acid environment, with a robust, pH neutral aqueous salt-based FARADAYIC®,[10] Electropolishing process. As a drop-in replacement for conventional electropolishing, the necessary changes would be substitution of a high acid concentration electrolyte with a simple pH neutral aqueous salt electrolyte, and substitution of a DC power supply with a pulse/pulse reverse power supply. While the rectifier would require moderate capital investment, this would be offset by reduced chemical cost and waste treatment costs, and improvement in yield/reduction in reject rate, and the return on investment would be swift.

Faraday has successfully transitioned the FARADAYIC® ElectroPolishing processes for stainless steel semiconductor valves to Swagelok, who use the process in their manufacturing plants. A similar technology transition for the stent industry is anticipated. Faraday has had preliminary discussions with a number of companies in the stent industry, and all have expressed strong interest in the technology. This process would be applied to stent fabrication, to lower reject rates, improve worker safety, and improve manufacturing throughput while lowering cost. The FARADAYIC® ElectroPolishing process represents a new paradigm[11] in electrochemical processing and is readily adaptable to other materials of potential interest to medical researchers and clinicians.

2. TECHNICAL APPROACH

The FARADAYIC® Process is a non-contact electrolytic, metal finishing process. The novel aspect of this technology is the sophisticated manner in which the power is transferred to the workpiece. In lieu of the constant electric fields often applied in electrolytic processing, the FARADAYIC® Process utilizes an asymmetric electric field. This enables one to effectively tune the process to a particular application, instead of relying on complex chemical additives that are consumed during the polishing process, resulting in a difficult to control process. The main advantages, as compared to conventional direct current (DC) polishing, are:

- Enhanced process control: As the process proceeds only under the electric field influence, the processing time is exact and uniform across the part.
- Enhanced uniformity: The FARADAYIC® process parameters can be selected to favor uniform polishing.
- High surface quality: The final geometry will exhibit high levels of surface integrity that are needed in complex medical implants and devices.
- Safety: Metal removal is driven via an external power source, eliminating the use of aggressive chemicals.

2.1 ElectroPolishing

Conventional Electropolishing Processes

Electropolishing is an industrially important edge and surface finishing technology. Conventional surface finishing utilizes high viscosity electrolytes, such as concentrated acids (e.g. phosphoric, sulfuric) and non-aqueous solutions (ethylene glycol, methanol-sulfuric acid).[12] For strongly passive materials (e.g. titanium alloys and niobium), hydrofluoric acid is added to the electrolyte to depassivate the surface.[13,14,15] Alternatively, some have suggested electropolishing strongly passive materials in acid-alcohol electrolytes with low water content[16] or organic solutions containing fluoride salts.[17] Due to the nature of conventional surface finishing electrolytes, process control and robustness are difficult[18] and reject rates are often as high as 40 to 50%.[2,19]

A critical process step in conventional stent manufacturing is electropolishing in a sulfuric/phosphoric acid electrolyte. Faraday has considerable experience in electropolishing materials in simple aqueous electrolytes using pulsed electrolytic fields tuned to the material of interest to achieve the desired surface finish.[20,21] This process has been applied to a number of advanced engineered materials including stainless steel semiconductor valves and nickel and titanium based aerospace turbine components.[22] Recently, Faraday has begun exploring the application of the FARADAYIC® ElectroPolishing Process for surface finishing of medical devices.[23,24,25] Faraday's patents are frequently cited related to pulsed/pulsed reverse electrochemical engineering. The U.S. Patent & Trademark Office recently cited Faraday art during the examination of a stent electropolishing patent (Pat. No. 7,153,411) issued to Boston Scientific Scimed, Inc.[26] Specifically, the patent examiner limited the scope of the electropolishing claims directed to the use of pulsed/pulsed reverse electric fields as obvious (35 .S.C. 103(a)) in view of Faraday prior art (Pat. No. 6,558,231).[27]

As depicted in Figure 3a, on some scale, all surfaces are rough. Electropolishing is the process whereby the asperities are preferentially removed by an electrolytic reaction (Figure 3b), generally represented as:

$$M^0 \rightarrow M^+ + e^- \qquad (1)$$

As Figure 4 shows, high viscosity electrolytes, used in conventional electropolishing, focus the electric field on surface asperities. For given electrolyte agitation conditions, the diffusion layer thickness (δ) is proportional to the electrolyte viscosity. For diffusion layers thicknesses greater than the characteristic dimension of the surface roughness, under mass transport control, the currents will be higher at the asperities than the recesses and the asperities are preferentially removed. Jacquet first reported that the optimum region for electropolishing is the mass transport/current limited plateau in the polarization curve.[28] Wagner reported "microprofile" leveling under mass transport limited conditions for large diffusion layers.[29] The diffusion limited process has been attributed to diffusion of the dissolved metal ion away from the polished surface[30] or the diffusion of an "acceptor ion" or complexing species to the surface.[31] These diffusion limited processes are further hindered, and hence electropolishing improved, by the formation of a viscous salt film in the recesses of the surface.[12] During anodic metal dissolution (eq. (2) some metal surfaces can form a passive oxide film, generally described as:

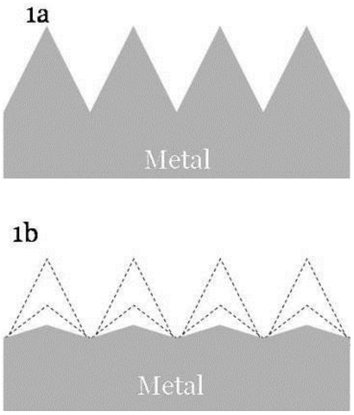


Figure 3. Generalized surface roughness (a) and electropolishing by removal of asperities (b).

$$M + xH_2O \rightarrow M(O_x) + 2xH^+ + 2xe^- \quad (2)$$

For these strongly passivating metals (e.g., stainless steel, titanium, nickel and their alloys), continued electropolishing leads to a roughened surface similar to pitting corrosion. Consequently, for some of these materials, hydrofluoric acid is added to the electrolyte to depassivate the metal surface by forming soluble metal fluorides and/or metal oxiflourides.[13,14] Considerable process control issues as well as safety issues are associated with managing and handling these hydrofluoric acid containing electrolytes. In the case of Nitinol stents, the reject rates associated with the conventional electropolishing process are as high as 40-50%.[2] There is a need for an electropolishing process using non-viscous, aqueous electrolytes devoid of hydrofluoric acid or other difficult to control additives.

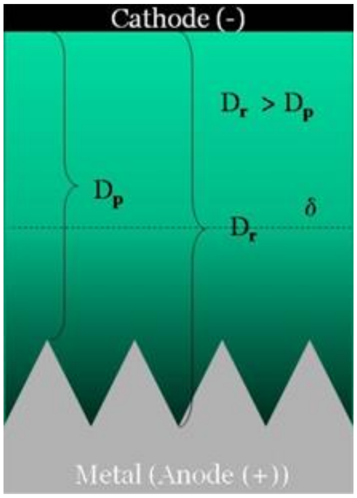


Figure 4. Focusing electric field on surface asperities in high viscosity electrolytes.

FARADAYIC® Electropolishing in Non-Viscous Electrolytes

Figure 5 is a generalized FARADAYIC® Waveform. Applied to FARADAYIC® ElectroPolishing, the anodic pulse is tuned (pulse-time/peak voltage) to enhance mass transport and control current distribution. The cathodic pulse is tuned to depassivate the surface, eliminating the need for hydrofluoric acid or other depassivating agents. An off-time may be inserted between the pulses to facilitate replenishment of reacting species and removal of byproducts and heat. The instantaneous anodic pulse current is much higher than the steady state current obtained under DC conditions and compensates for off-times and cathodic periods such that the average material removal rate is equivalent to or greater than DC electropolishing. Key to the development of the pulse/pulse reverse waveform is the "tuning" of the anodic and cathodic pulses (pulse time and amplitude) as well as the duration of the off-times. While FARADAYIC® waveform parameters cannot be selected *a priori*, we have developed guiding principles for optimizing the FARADAYIC® ElectroPolishing process parameters for a particular application.

In electropolishing, the diffusion layer thickness is relevant in context with the surface roughness scale (Figure 6). For a microprofile, the diffusion layer thickness is larger than the roughness scale. For electrolysis under microprofile conditions and mass transport control, the peaks are preferentially removed relative to the recesses and electropolishing is achieved. In a macroprofile, the diffusion layer thickness is less than or equal to two times the roughness scale and consequently the diffusion layer follows the surface contour. For electrolysis under macrop_rofile conditions and mass transport control, the peaks and recesses are equally removed and the surface roughness generally remains unchanged. That is, electropolishing is not accomplished. Whether or not the electropolishing process is under mass transport control is determined by the relationship between the pulse-time (t_p) and the transition time (τ).[32] Although originally developed for electrodeposition, for electropolishing the transition time may be thought of as the time for the dissolved metal to reach its solubility limit at the electrode surface.

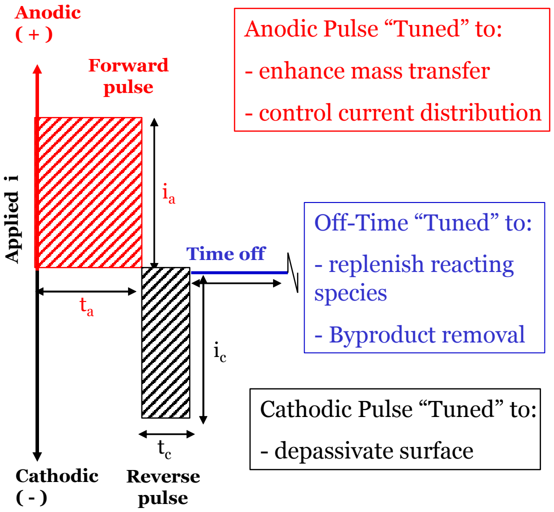


Figure 5. Generalized FARADAYIC® ElectroPolishing waveform.

We assume that the relationships from single pulse studies are applicable to anodic and anodic/cathodic pulse waveforms with off-times. For electropolishing under macroprofile conditions, the pulsed anodic waveform converts the macroprofile diffusion layer to a smaller electrodynamic macroprofile diffusion layer (Figure 6). For shorter anodic pulse-times, the electrodynamic macroprofile diffusion layer will be smaller, as shown in equation 3:

$$\delta_p = 2((Dt_p)/\pi)^{1/2} \qquad (3)$$

where D is the diffusion coefficient. The inner pulsating layer (δ_p)[32,33,34] the "electrodynamic diffusion layer",[35] is proportional to the pulse-time (t_p), and may be adjusted by the pulse-time. In electropolishing, the diffusion layer thickness is relevant to the roughness scale (Figure 6). Therefore, at the same material removal rate, the contribution of mass transport will be less for the smaller electrodynamic macroprofile and material removal will occur preferentially at the peaks. This is due to the process being less influenced by mass transport so the current distribution is more non-uniform, all else being equal.[36]

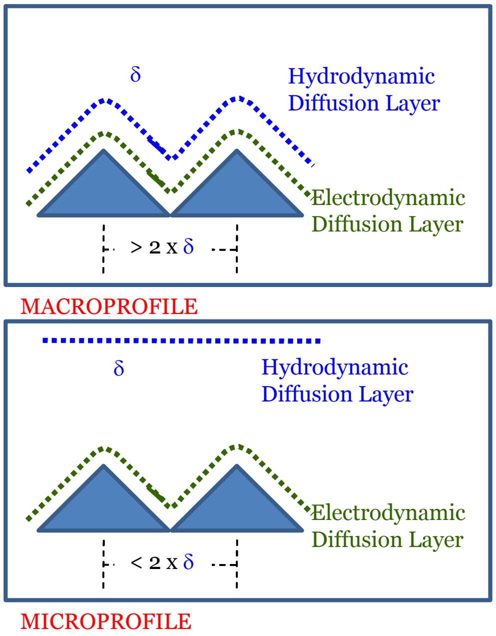


Figure 6. Hydrodynamic and electrodynamic diffusion layers for a macroprofile and a microprofile.

For electropolishing under microprofile diffusion layer conditions, the pulsed anodic waveform converts the microprofile to a smaller microprofile or a macroprofile (Figure 6). We have generally found for cases where a microprofile is converted to a smaller microprofile, it is desirable to have relatively high peak current densities in order to have relatively short transition times. In this manner, we maintain mass transport control and the current distribution is more non-uniform and preferentially focused on the peaks. We have generally found for cases where a microprofile is converted to a macroprofile, it is desirable to maintain relatively low peak current densities in order to have relatively long transition times. In this manner, we remove mass transport control and the current distribution is more non-uniform and preferentially focused on the peaks. A macroprofile diffusion layer situation is more likely to occur at the beginning of the electropolishing process and a microprofile diffusion layer occurs as the electropolishing process progresses. An understanding of these effects provides the user with a set of guiding principles to optimize the waveform parameters of the electropolishing process for a given application.

The final consideration for developing a FARADAYIC® ElectroPolishing waveform is for the case of passive materials, for which anodic only pulses lead to a rougher surface due to the non-uniform breakthrough of the passive film.[37,38] To depassivate the surface, we intersperse cathodic pulses within the anodic pulses, with or without off-times.[39,40,41] In a general sense, we assume the cathodic pulse removes the oxide film and restores the metal surface as the reverse of eqn (2). The cathodic pulse amplitude is selected to remove the passive oxide film and is material specific. For metals with strong oxide films, higher cathodic amplitudes are required. Some have suggested using non-aqueous or low water content electrolytes to remove the source of oxygen (eq. (2)) leading to the formation of the passive film.[42] From an industrial implementation perspective, these processes are difficult to control due to the resistivity and hydroscopic nature of the non-aqueous electrolyte.

3. PHASE I RESULTS AND DISCUSSIONS

In this section, the work performed to achieve the Specific Aims of the Phase I program is described. It will be shown that technical feasibility was demonstrated during this project, and the results will be summarized in relation to the Phase I Specific Aims.

1. *Optimize the FARADAYIC ElectroPolishing Process on Nitinol tubular stents, including the preliminary development of a library of waveform parameters to achieve the desired surface finish for a variety of stents of interest to industry.*

   Milestone 1. Design/construct bench-scale apparatus for electropolishing stents.
   Milestone 2. Refine electrolyte selection to optimize salt concentration for Nitinol and other materials
   Milestone 3. Apply the FARADAYIC® ElectroPolishing process to industry-supplied Nitinol stents, targeting a mirror like finish (Ra of $\leq$0.2 μm).
   Milestone 4. Evaluate FARADAYIC® ElectroPolishing for other materials of interest to industry.

2. *Design an α-scale pilot manufacturing apparatus for demonstration of continuous, industrial-scale processing of stents. This apparatus would be built and validated in Phase II.*

   Milestone 5. Design the α-scale pilot manufacturing apparatus, based on the requirements of our industrial partners. Such requirements may include range of stent sizes, stent throughput, and overall apparatus footprint.

3. *Initiate steps for transitioning the technology to industry partners.*

   Milestone 6. Compile manufacturing process flow, economic assessment and quality plan.
   Milestone 7. Develop documentation, processes and procedures for compliance with FDA regulations.
   Milestone 8. Interface with collaborators, and generate further interest via commercialization activities.

3.1: Electrochemical Apparatus Design and Build for Coupons, Wires, and Shape Sets

Faraday has considerable experience in bench-scale and pilot-scale fixtures for demonstrating and validating FARADAYIC® manufacturing processes. In this program, Faraday designed and built three electrochemical cells to assess the effect of electrolytes, FARADAYIC® Processing parameters, electrical connection, and material shape on the quality of the polished Nitinol surface.

Flat 1” x 1” Coupon Studies
Nitinol coupons, 1” x 1” x 0.063” were purchased from the Nitinol Development Corporation. The as received coupons had an average surface roughness, Ra = 3.0 ± 0.5 μm, and the Nitinol compositional analysis provided was within ASTM F 2063 specification for Wrought Nickel-Titanium Shape Memory Alloys for Medical Devices and Surgical Implants.[43] Figure 7 shows a photograph (left) and a cross-sectional AutoCAD drawing (right) of a flow channel cell that accommodates 1 in^2 flat coupons. The working (anode) and counter (cathode) electrodes face each other and are separated by an adjustable gap where the electrolyte flows from bottom to

top. This cell allowed the study of FARADAYIC® ElectroPolishing of Nitinol at different anode to cathode distances, as well as different electrolyte velocities, concentrations, and mixtures. The flexibility inherent within this cell design enabled an investigation of the effect of primary current distribution in conjunction with the FARADAYIC® Process for electropolishing of Nitinol substrates in acid free electrolytes.

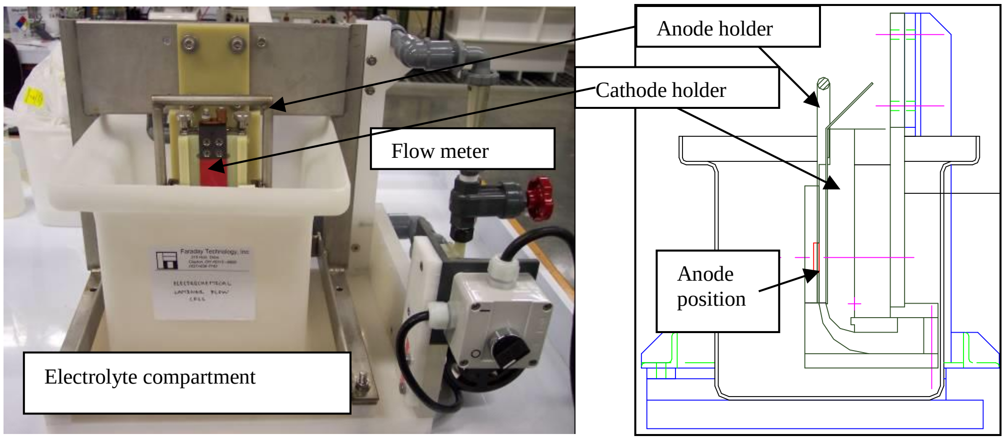


Figure 7. Photograph (left) and side view AutoCAD drawing (right) of a flow channel cell used for waveform development on 1 in² flat Nitinol coupons.

Wire Length Apparatus

Wire electropolishing tests were facilitated with an electrochemical cell and a specially designed sample holder (Figures 8 through 10). The holder enables Faraday to process stationary lengths of wire and utilizes a round mixed metal oxide cathode through which the Nitinol wire is secured. The holder also incorporates offset shielding to concentrate the electric field and adjust the exposed wire length, if needed. The Nitinol wire was used in this apparatus was provided at no cost to the program by Fort Wayne Metals.

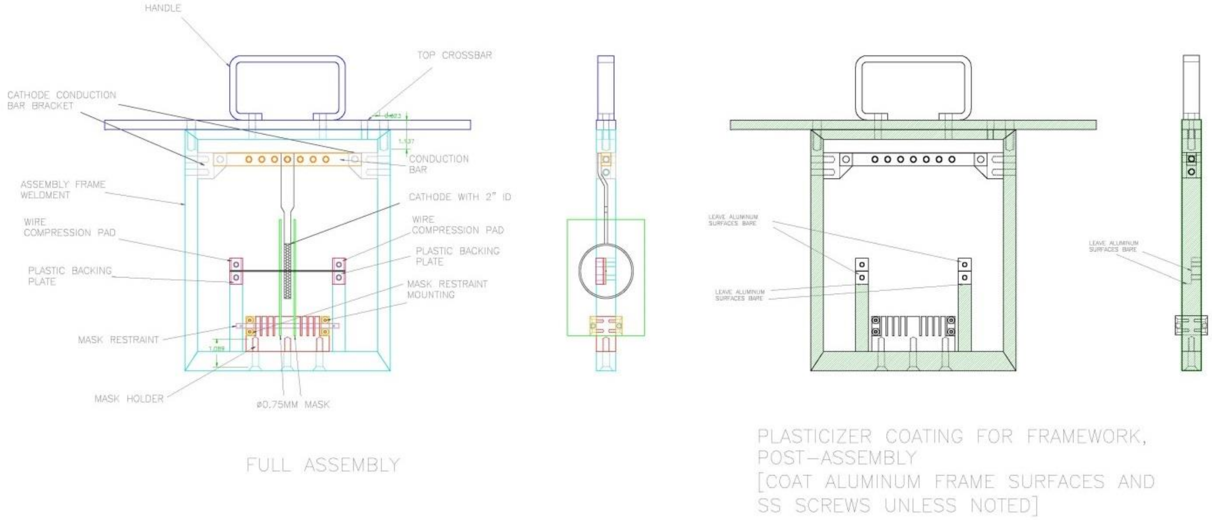


Figure 8. CAD drawing of the wire holder used in preliminary work to process stationary straight lengths of wire.

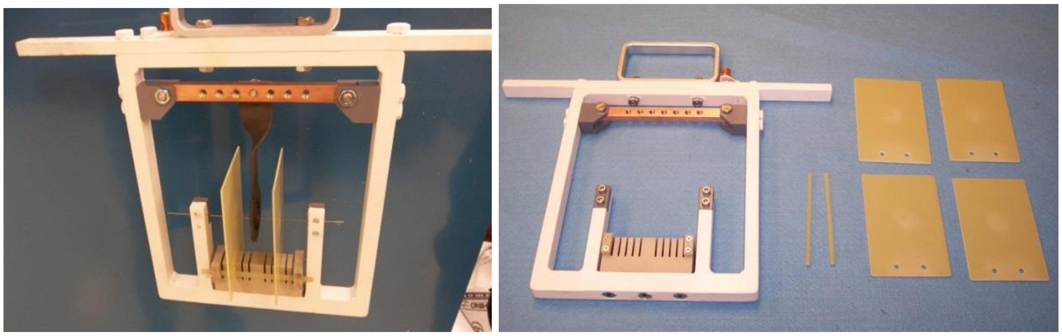


Figure 9. Photographs of the wire holder used in preliminary work to process stationary straight lengths of wire.

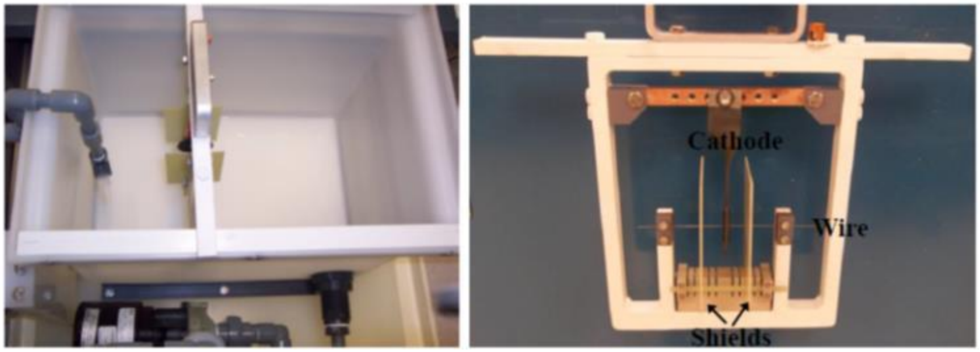


Figure 10. Flow cell and specially designed wire holder used for electropolishing trials.

Loop Clip Apparatus

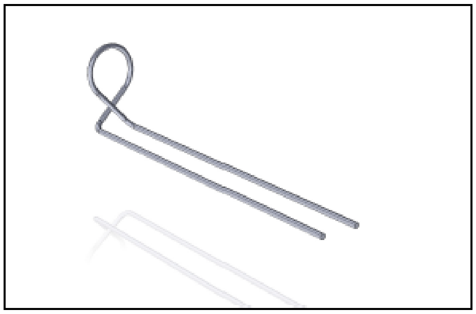


Figure 11. Photograph of loop clip.

Loop Clip electropolishing tests were facilitated with a simple beaker electrochemical cell. Figure 11 shows a photograph of the loop clip provided by Faraday's commercial partner, Fort Wayne Metals, at no cost to the program. Figure 12 shows the beaker cell used for the experiment. A mixed metal oxide mesh cylinder served as a cathode. Figure 13 shows the mixed metal oxide part holder, used to immerse the loop clip in the electrolyte, while making an electrical connection. The loop clip was affixed to the holder, that was twisted to hold the part, and the connection area was covered in insulating tape to minimize parasitic current during electropolishing experiments. Agitation during the test was achieved with a simple stir plate and magnetic stirrer, held constant at 360 RPM.

Figure 12. Beaker cell for electropolishing of loop clips; cathode is shown.

Figure 13. Mixed metal oxide piece used for anode connection, A) showing connection to loop clip with dark oxide finish, and B) entire piece covered in insulating tape.

3.2: FARADAYIC® Electropolishing Results

3.2.1: Electrolyte Selection

The objective of the early trials was to identify the appropriate pH neutral electrolyte composition and concentration for FARADAYIC® ElectroPolishing process development. Development of the FARADAYIC® Process typically begins with the polarization curve (Figure 14), which is a plot of the anode voltage, E, as a function of anodic current density, i, and provides information on active and passive regions of materials in the different electrolytes.[44] Curve 1 shows the behavior of a metal in an active electrolyte (NaCl), and Curve 2 shows the behavior of a metal in a passive electrolyte (Na_2SO_4). Before the electric field is applied, a metal anode immersed in an electrolyte has a steady-state potential (E_{ss}). When the power is applied, the electrode potential shifts positively from E_{ss} to E_{ab} (breakdown potential). Above E_{ab}, the current density rises abruptly due to the dissolution reactions occurring on the anode (region AB). The dissolution rate of the anode stops increasing when a limiting current density i_{lim} is reached (BC region), where the metal atoms form metal ions and compounds with the activating anions and pass into the electrolyte. The limiting current density i_{lim} and the ratio of ΔI to ΔE

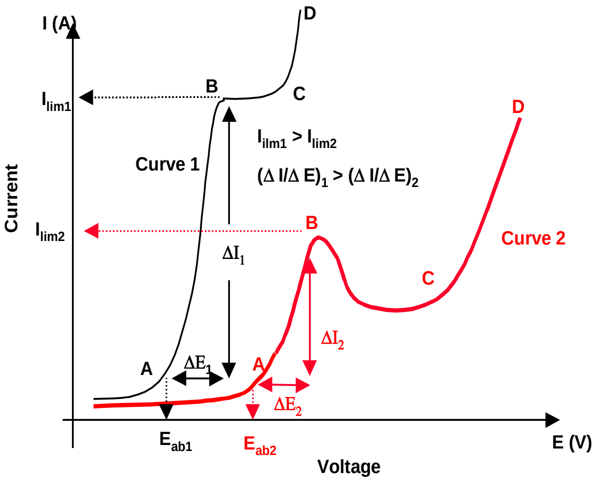


Figure 14. Typical polarization curves for metal in different electrolytes.

(the slope of AB on the polarization curve) can be defined as the metal dissolution rate and current efficiency in the electrolyte, respectively. The electrolyte which has a high ratio of ΔI /ΔE indicates a fast and efficient metal dissolution process. In region BC, the current density remains constant (curve 1) or drops to a lower value (curve 2) indicating mass transport phenomena that limit the rate of metal ion removal. If the metal dissolution is conducted in a passive electrolyte, the passive film can grow faster than metal ions pass into the electrolyte, with the result that the current density falls to lower values (curve 2). When the anode potential increases to region CD of the polarization curve, the higher potential can breakdown or remove the passive film and deposits, and increase the ionization rate of the metal to increase the current density. The optimal polarization curve should 1) indicate a low breakdown potential (E_{ab}), 2) have a high ratio of ΔI to ΔE, and 3) a smooth and shiny surface. As a simple, efficient, and cost-effective screening method, the polarization curve can be used to select candidate electrolytes.

Figure 15 shows two-electrode DC polarization curves that were produced with the goal of identifying the electrochemical activity of each salt electrolyte as it pertains to Nitinol electropolishing. The electrolytes tested were NaH_2PO_4 (200 g/L), Na_2SO_4 (150 g/L), $NaNO_3$ (200 g/L), NaBr (200 g/L), NaCl, (100 g/L), KNO_3 (200 g/L), and some mixtures of these constituents, *i. e.* $NaNO_3$/NaCl (200/25 g/L) or Na_2SO_4/KNO_3 (150/25 g/L). Table 1 lists the pH and conductivity of all the electrolytes tested for Nitinol electropolishing. As shown in Table 1, pH values ranged between 5 and 7.5, with the exception of the 260 g/L NaH_2PO_4 electrolyte, which had a slightly acidic pH of 3.8. The conductivity of the electrolytes varied between 60 and 172 mS.

Table 1. Measured pH and conductivity of the solutions tested for Nitinol electropolishing.

Electrolyte	pH	Conductivity (mS)
260 g/L NaH_2PO_4	3.8	60.0
200 g/L NaBr	5.1	172.0
100 g/L NaCl	4.9	140.0
200 g/L $NaNO_3$	7.3	150.0
200 g/L $NaNO_3$ + 25 g/L NaCl	7.5	160.8
200 g/L KNO_3	6.1	171.5
150 g/L Na_2SO_4	5.6	101.5
150 g/L Na_2SO_4 + 25 g/L KNO_3	5.9	106.2

The polarization tests were performed at room temperature (~70°F). A mixed metal oxide coated titanium flat substrate was used as the cathode. This mixed metal oxide (typically iridium or ruthenium oxide) coated electrode is commonly known as a dimensionally stable anode, or DSA. At Faraday we have successfully used it as a cathode, due to its excellent electrochemical stability and because it minimizes side reactions, thereby limiting possible parasitic currents.

A Dynatronix power supply (Model DPR-40/30/100) was used to raise the cell voltage by increments of 1 volt every 0.5 minutes. Total currents were read from the Dynatronix feedback loop. The DC polarization behavior also provided the $\Delta I/\Delta E$ ratio (slope of the polarization curve) and breakdown voltages (E_{ab}, Figure 14). Based on the E_{ab} value of the Nitinol substrates in the different electrolytes, we were able to estimate starting potentials for electropolishing trials. The surface appearance of the substrate after the polarization tests was also informative for electrolyte selection and subsequent waveform development.

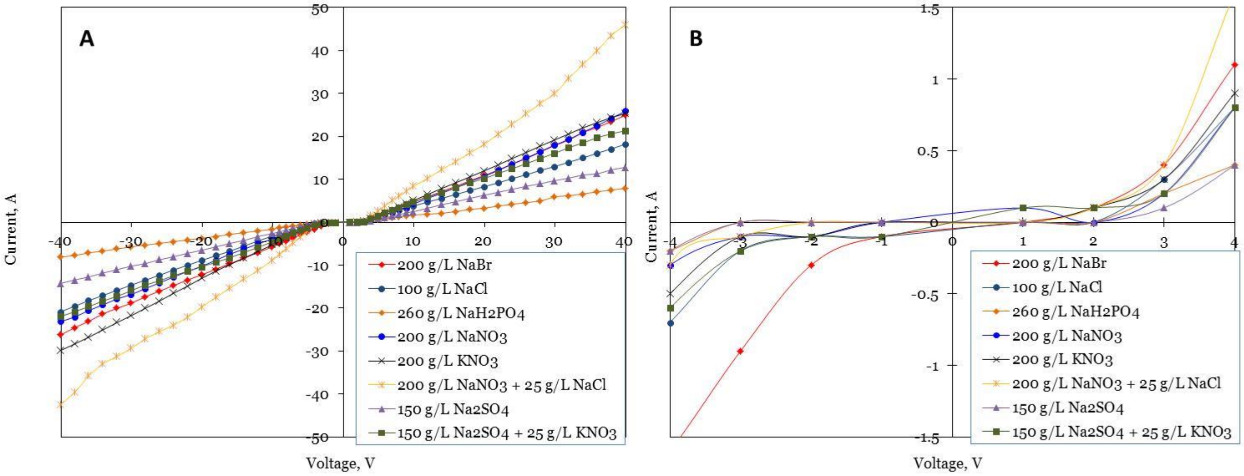


Figure 15. Polarization curves performed on Nitinol substrates at different cell voltages and different electrolyte compositions. A) Shows the full polarization curve, B) shows a reduced scale view of the same curve that is used to better identify variations in the breakdown voltage.

Breakdown Voltage: As shown in Figure 15B, each of the electrolytes exhibited breakdown voltages between 2 and 3 V. Equal or higher voltages were considered as the starting point for waveform development.

Current: Figure 15A showed variations in the rate of current change with respect to the voltage ($\Delta I/\Delta E$), which is associated with the rate of electrochemical activation (i.e. material removal). In general, an electrolyte with a higher $\Delta I/\Delta E$ ratio will tend to remove metal more quickly than one with a low $\Delta I/\Delta E$ ratio. The binary $NaNO_3/NaCl$ electrolyte showed the steepest $\Delta I/\Delta E$ slope, followed by the nitrate (KNO_3 or $NaNO_3$) and NaBr electrolytes, which exhibited comparable $\Delta I/\Delta E$ ratios. The flattest slopes were observed for NaH_2PO_4, Na_2SO_4, NaCl and KNO_3/Na_2SO_4.

Summary: The $\Delta I/\Delta E$ data shown in Figure 15A would suggest that $NaNO_3/NaCl$, KNO_3, $NaNO_3$, and NaBr would be the ideal electrolytes for rapid material removal. However, the measured current is a function of the relative contributions of:

- Nitinol dissolution reaction,
- Parasitic side reactions such as water electrolysis at each electrode (minimized at the cathode through the use of a DSA electrode), and
- Higher electrolyte conductivities that enable the passage of more current through the solution for a given voltage via Ohms law (V = I x R).

The $NaNO_3$/NaCl, KNO_3, $NaNO_3$, and NaBr electrolytes had higher conductivities (Table 1), which may have contributed more to the total measured current than the other electrolytes. However, it is difficult to parse out the relative contributions of all of the reactions to the total current based on the limited data that we generated in the Phase I program. Furthermore, extremely rapid material removal may not be a strong requirement of the final process, so a higher $\Delta I/\Delta E$ slope may not necessarily be advantageous. Finally, rapid metal removal does not necessarily correlate with an improved final surface finish. Therefore, the following conclusions may be made from the electrolyte selection study:

- All of the electrolytes showed electrochemical activity for Nitinol,
- Similar breakdown voltages were observed for all electrolytes,
- There were a range of currents measured across all of the electrolytes, for a given voltage, suggesting (but not confirming) varying rates of material removal, and
- This data suggests considerable flexibility when choosing an electrolyte, which is likely to be of interest to our customers.

3.2.2: FARADAYIC® Process Development

Flat Coupon Studies

The polarization curve studies suggested a wide range of electrolytes that may be useable for Nitinol electropolishing. However, the data did not indicate the ability to achieve a desirable surface finish, nor specific rates of material removal. Therefore, a preliminary investigation into the effect of FARADAYIC® Processing parameters for all of the electrolytes was done, in order to narrow the electrolyte selection criteria.

Initial development of the FARADAYIC® Processing parameters for electropolishing Nitinol in the electrolytes listed in Table 1 was done on flat 1 in^2 coupons using the cell shown in Figure 7. Table 2 shows the number of FARADAYIC® Processing conditions evaluated for each electrolyte, as well as the maximum material removal rate and minimum Ra obtained within this preliminary study. (For reasons of brevity, the results are summarized for each electrolyte across all of the process parameters tested, rather than specifically detail the hundreds of tests that were performed). Additionally, Table 2 indicates the feasibility of the evaluated electrolyte to produce the desired Ra values within the parameter evaluated within this study.

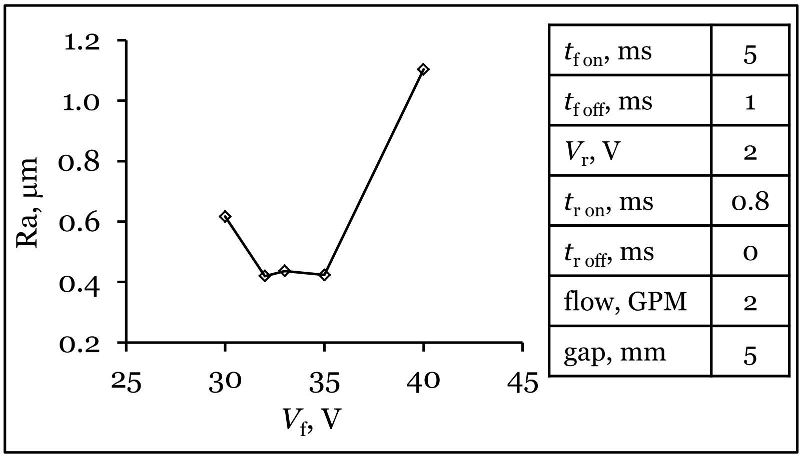
Table 2. Observed performance of each electrolyte for electropolishing Nitinol using a range of FARADAYIC® Processing parameters, with maximum material removal rates and best surface finish.

Electrolyte	# of processing conditions tested	Max. material removal rate (μm/min)	Min. Ra (μm)	Electrolyte feasibility
260 g/L NaH_2PO_4	5	0	NA	Not Feasible
200 g/L NaBr	59	100	1.32	Not Feasible
100 g/L NaCl	79	90	0.94	Not Feasible
200 g/L $NaNO_3$	176	140	0.25	Feasible
200 g/L $NaNO_3$ + 25 g/L NaCl	65	9	0.32	Feasible
200 g/L KNO_3	57	44	0.21	Feasible
150 g/L Na_2SO_4	40	3	0.25	Feasible
150 g/L Na_2SO_4 + 25 g/L KNO_3	33	3	0.16	Feasible

As shown in Table 2, three of the electrolytes tested (260 g/L NaH_2PO_4, 200 g/L NaBr, and 100 g/L NaCl) did not demonstrate the potential to adequately produce the Ra values that tending toward ~0.2 µm and were eliminated from further consideration. The nitrate (NO_3^-) and sulfate (SO_4^{2-}) based electrolytes showed the potential to produce an Ra close to the desired finish, and were investigated in more detailed FARADAYIC® Process parameter studies, as described below.

a) FARADAYIC® Process development in nitrate electrolytes.

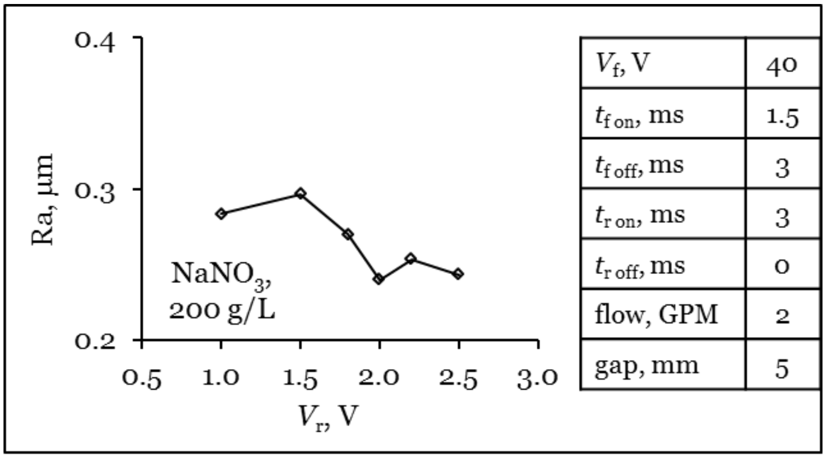
Figure 16 presents the surface finish (Ra) as a function of the applied anodic pulse voltage, V_f, for the 200 g/L $NaNO_3$ electrolyte, for the specific set of FARADAYIC® Processing conditions listed therein. The data indicates that the anodic voltage can potentially have a strong effect on the efficiency of the process to electropolish. Specifically in this case, the Ra seems to be improved when V_f was between 32 and 35 V, at which time Ra values of ~0.4 µm were measured (Fig. 16). When the V_f values were outside of this window, substantial increases in Ra were observed. We anticipate that this behavior could be shifted to other anodic voltage ranges that have reduced Ra values by changing other processing conditions like the anodic duration ($t_{f\ on}$) or cathodic voltage (V_r).



$t_{f\ on}$, ms	5
$t_{f\ off}$, ms	1
V_r, V	2
$t_{r\ on}$, ms	0.8
$t_{r\ off}$, ms	0
flow, GPM	2
gap, mm	5

Figure 16. Ra as a function of anodic peak voltage, V_f, in 200 g/L $NaNO_3$.

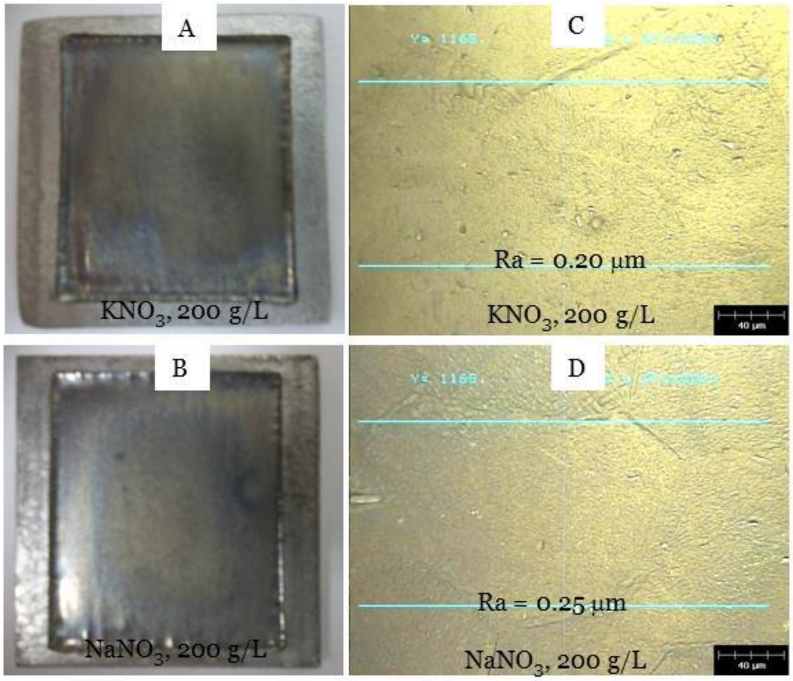
Figure 17 suggests that the applied cathodic voltage, V_r, has a minimal influence on Ra at the conditions tested. As the cathodic voltage increases, the Ra decreases slightly. The magnitude of this effect, and possible ways to enhance it, would be studied in a Phase II program.



V_f, V	40
$t_{f\,on}$, ms	1.5
$t_{f\,off}$, ms	3
$t_{r\,on}$, ms	3
$t_{r\,off}$, ms	0
flow, GPM	2
gap, mm	5

Figure 17. Ra as function of the reverse (cathodic) voltage, V_r, in 200 g/L $NaNO_3$ solution.

Figure 18 shows surface images and the FARADAYIC® Processing conditions that exhibited the highest potential to electropolish Nitinol coupons and achieve a low Ra in the sodium and potassium nitrate electrolytes. Figure 18A/C shows the Nitinol coupon that was electropolished in 200 g/L KNO_3 to achieve an Ra value of 0.2 µm. Figure 18B/D shows a similar surface for the Nitinol coupon that was electropolished in 200 g/L $NaNO_3$ to achieve an Ra value of 0.25 µm. After polishing in these electrolytes, the surfaces showed a visibly bluish discoloration (Figure 18A/B), and some surface defects (scratches/pits) were still present on the polished areas as indicated by optical microscopy images (Figure 18C/D). The average material removal rate was comparable for the best FARADAYIC® Processing conditions used in either of the nitrate solutions tested, e. g. 27.9 µm/min with 200 g/L KNO_3 and 17.3 µm/min with 200 g/L $NaNO_3$.



V_f, V	40
$t_{f\,on}$, ms	0.8
$t_{f\,off}$, ms	1.2
V_r, V	2.4
$t_{r\,on}$, ms	1
$t_{r\,off}$, ms	0.8
flow, GPM	2
gap, mm	5

V_f, V	40
$t_{f\,on}$, ms	1.5
$t_{f\,off}$, ms	3
V_r, V	2.4
$t_{r\,on}$, ms	3
$t_{r\,off}$, ms	0
flow, GPM	1.5
gap, mm	5

Figure 18. Nitinol coupons electropolished in A) KNO_3, or B) $NaNO_3$, electrolytes, at the conditions listed. C and D, optical microscopy images of coupons A and B, respectively.

b) FARADAYIC® Process development in sodium nitrate and sodium chloride mixed electrolytes.

The results in Section 3.2.2 a demonstrate the potential of nitrate based electrolytes to produce relatively low Ra values with some visible surface discoloration (Figure 18B). Therefore, as a test case, 25 g/L NaCl was added to the 200 g/L $NaNO_3$ electrolyte with the goal of avoiding the discoloration effects observed with the baseline $NaNO_3$ electrolyte.

Figures 19 and 20 shows the effect of specific FARADAYIC® Processing variables on the measured Ra in the binary $NaNO_3$/NaCl electrolyte. Figures 19 A and B demonstrate the effect of the applied anodic (forward) voltage (V_f), and applied cathodic (reverse) voltage (V_r) on the measured Ra. The observed behavior of Figure 19 A is comparable to the behavior observed in the pure $NaNO_3$ bath (Figure 16), although the trend in Figure 21 A is slightly shifted to the left relative to Figure 16. This result was expected since the major constituent in the binary solution is $NaNO_3$, thus, underlying electropolishing behavior ought to be comparable to that for the pure $NaNO_3$ bath. Figure 19B indicates that the cathodic voltage (V_r) could potentially have a strong effect on the efficiency of the process to electropolish Nitinol; this result is unlike that previously observed for the pure $NaNO_3$ electrolyte (Fig. 17). In this case, the Ra seems to be improved when V_r values were between 18 and 23 V.

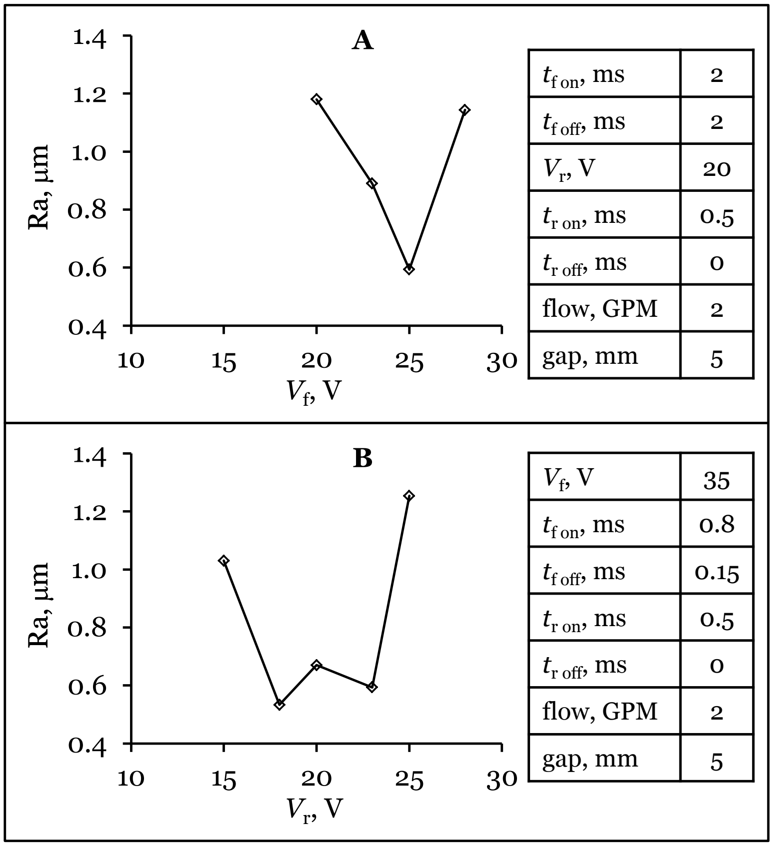
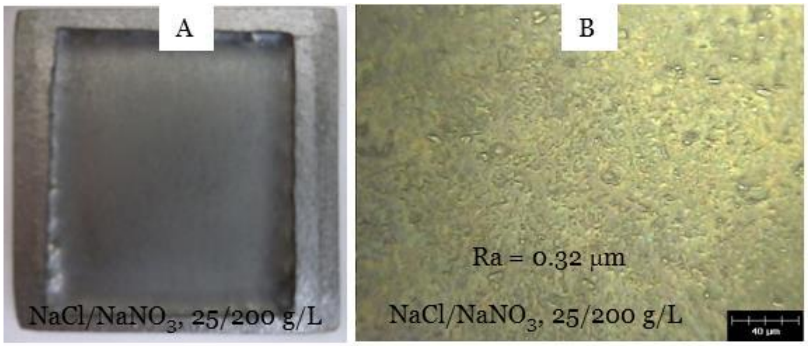


Figure 19. Ra versus forward (anodic) voltage, A, and reverse (cathodic) voltage, B, in the $NaNO_3$/NaCl 200/25 g/L solution.

Figure 20 shows two surface images and the FARADAYIC® Processing conditions that exhibited the highest potential to electropolish Nitinol coupons and achieve a low Ra in a sodium nitrate and sodium chloride mixed electrolyte. This mixed electrolyte visibly reduced the discoloration on electropolished substrates (Figure 20A); however after looking into the effect of various FARADAYIC® Processing parameters on Ra, no improvements in Ra were seen with respect to the pure $NaNO_3$ solution. Furthermore, the lowest observed Ra for the $NaNO_3$/NaCl electrolyte system was 0.32 μm, where the optical microscopy image of this coupon (Figure 20B) still shows a surface with more defects than observed with the base electrolyte (Fig. 18B).



V_f, V	35
$t_{f\,on}$, ms	0.8
$t_{f\,off}$, ms	0.15
V_r, V	20
$t_{r\,on}$, ms	0.5
$t_{r\,off}$, ms	0
flow, GPM	2
gap, mm	5

Figure 20. Nitinol coupon electropolished in 200 g/L $NaNO_3$ and 25 g/L NaCl solution, at the conditions listed. B, optical microscopy images of the coupon.

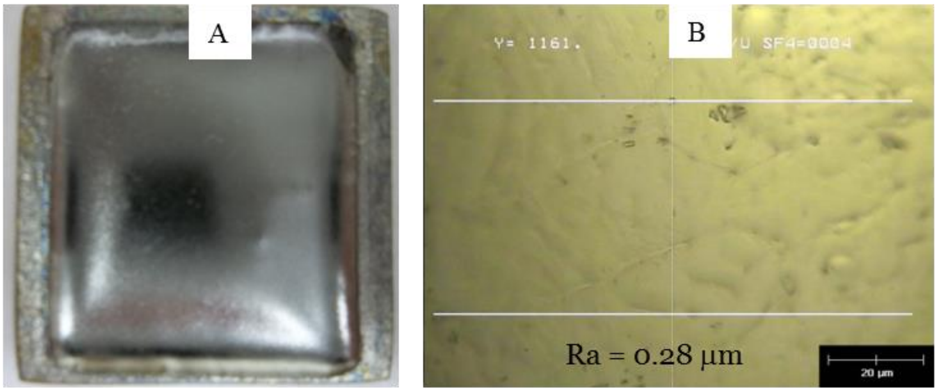
c) FARADAYIC® Process Development in Na_2SO_4 and KNO_3/Na_2SO_4 electrolytes.

Electropolishing studies with Nitinol coupons continued with the 150 g/L Na_2SO_4 based electrolytes. These electrolytes exhibited lower ΔI/ΔE ratios than NaBr or NaCl electrolytes (Figure 15), thus, comparatively lower material removal rates were expected. In contrast to the previously discussed nitrate-based electrolytes, with the 150 g/L Na_2SO_4 electrolyte visually bright surfaces with a metallic appearance were obtained using a range of FARADAYIC® Processing conditions. Additionally, as detailed in Table 3, the Na_2SO_4 electrolyte also showed the potential to generate surface finishes with Ra values ranging between 0.28 and 0.34 μm using various anodic voltages and FARADAYIC® Processing parameters. The material removal rates of tests listed in Table 3 in the 150 g/L Na_2SO_4 solution ranged between 1.2 and 1.9 μm/min, and were lower than those observed using the NaCl, NaBr, $NaNO_3$, KNO_3 or $NaNO_3$/NaCl electrolytes.

Table 3. Some of the waveforms tested in the 150 g/L Na_2SO_4 solution for electropolishing Nitinol coupons.

V_f, V	$t_{f,on}$, ms	$t_{f,off}$, ms	V_r, V	$t_{r,on}$, ms	$t_{r,off}$, ms	Material removal rate, μm/min	Final Ra, μm
20	1.5	0	30	0.5	0	1.2	0.34
23	1.5	0	30	0.5	0	1.4	0.29
30	1.0	0	30	0.5	0	1.9	0.29
40	0.75	0	30	0.5	0	1.3	0.28

Figure 21 shows the surface and the FARADAYIC® Processing conditions that produced the highest potential to electropolish Nitinol coupons and achieve a low Ra in a sodium sulfate electrolyte. This surface was more uniformly polished than that previously obtained with the other electrolytes, as shown in the optical microscopy image (Figure 21B), which shows a clean surface without defects. Additionally, the surface was without discoloration (Fig. 21A) and a Ra value of 0.28 μm was obtained.



V_f, V	40
$t_{f\,off}$, ms	0.75
$t_{f\,off}$, ms	0
V_r, V	30
$t_{r\,on}$, ms	0.5
$t_{r\,off}$, ms	0
flow, GPM	2
gap, mm	5

Figure 21. Nitinol coupon electropolished in 150 g/L Na_2SO_4, A, at the conditions listed. B, optical microscopy image of coupon A.

In order to increase the relatively low material removal rates (~1.6 μm/min, Table 3) and improve the surface finish with less discoloration, 25 g/L of KNO_3 was added to the 150 g/L Na_2SO_4 electrolyte. The presence of KNO_3 slightly increased the material removal rates (~2 μm/min) with respect to the pure Na_2SO_4 solution, while also improving the achievable surface finish, as shown in Table 4. Additionally, as detailed in Table 4, the mixed electrolyte of Na_2SO_4 and KNO_3 showed the potential to generate surface finishes with Ra values ranging between 0.16 and 0.31 μm using various anodic on times. The material removal rates of tests listed in Table 4 ranged between 1.8 and 2.5 μm/min, and were faster than those observed using the pure Na_2SO_4 electrolytes.

Table 4. Some of the waveforms tested in the 150 g/L Na_2SO_4 and 25 g/L KNO_3 solution for electropolishing Nitinol coupons.

V_f, V	$t_{f,on}$, ms	$t_{f,off}$, ms	V_r, V	$t_{r,on}$, ms	$t_{r,off}$, ms	Material removal rate, μm/min	Final Ra, μm
40	0.65	0	5	2	0	2.5	0.31
40	0.55	0	5	2	0	2.2	0.16
40	0.45	0	5	2	0	1.8	0.2

Figures 22A and 23A include photographs of coupons with bright and metallic appearances and exhibiting Ra values between 0.16 and 0.20 μm that were electropolished using the KNO_3/Na_2SO_4 electrolyte. The surface was reflective enough to show the dark eye of the camera used to take the photo reflected in the center of the coupon. The processing conditions for either coupon shown were nearly identical (e. g. V_f = 40 V, $t_{f,off}$ = 0 ms, V_r = 5 V, $t_{r,on}$ = 2 ms, $t_{r,off}$ = 0 ms, flow rate = 2 GPM, anode : cathode gap = 5 mm), except the $t_{f,on}$, which was 0.55 and 0.45 ms in Figures 22 and 23, respectively. Optical microscopy images (panels B of Figures 22 and

23) also present clean surfaces and absence of defects. Subtle variations in the forward time on, $t_{f,on}$, caused small differences in material removal rates and Ra values as shown in Figure 22 A (Ra = 0.2 μm) / Figure 23 A (Ra = 0.16 μm), which achieved material removal rates of 2.2 and 1.9 μm/min, respectively. Figures 22 and 23 also include SEM scans and grain structure of respective coupons; SEM images (panels C) again show clean and electropolished surfaces in the microscale, whereas panels D suggest a comparable granular structure for both coupons. Panels E and F present the Ni and Ti detection obtained from EDS analysis of the scanned area, and indicate that Ti-rich points coincide with Ni-deficient spots and higher defect points on the polished substrate (encircled areas in panels E and F).

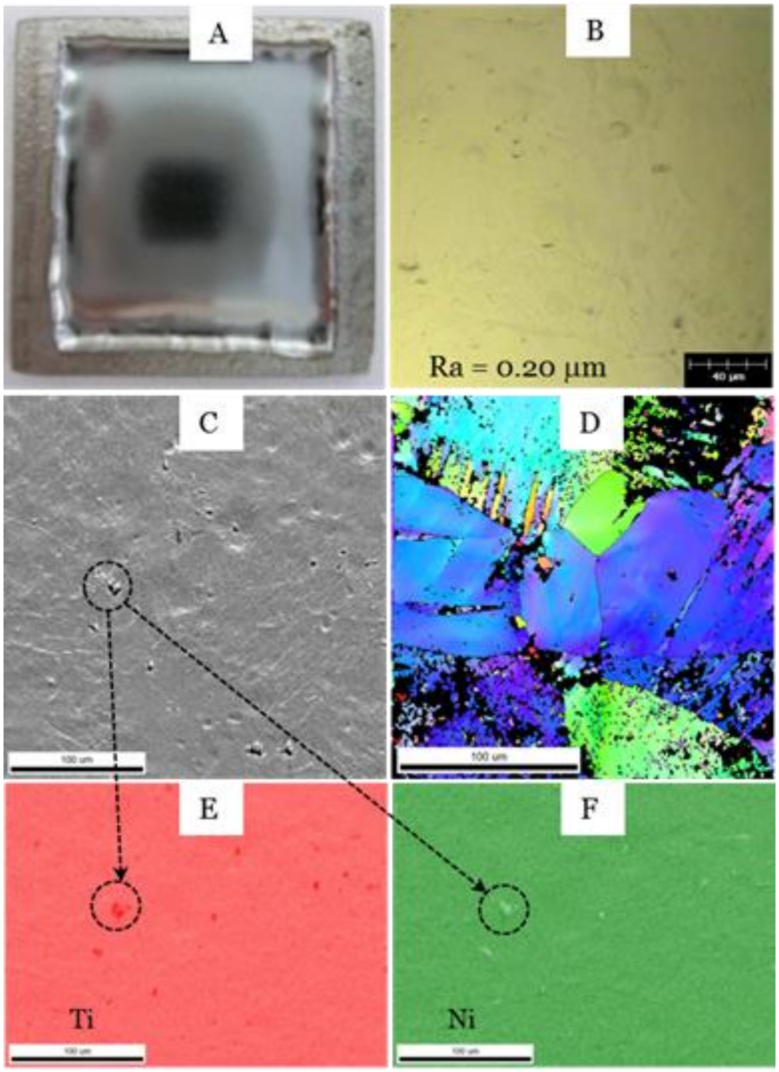


Figure 22. A, Nitinol coupon electropolished in KNO_3/ Na_2SO_4, 25/150 g/L . B, optical microscopy image, and SEM/EDS scans, C-F, of coupon A. $t_{f,on}$ = 0.45 ms.

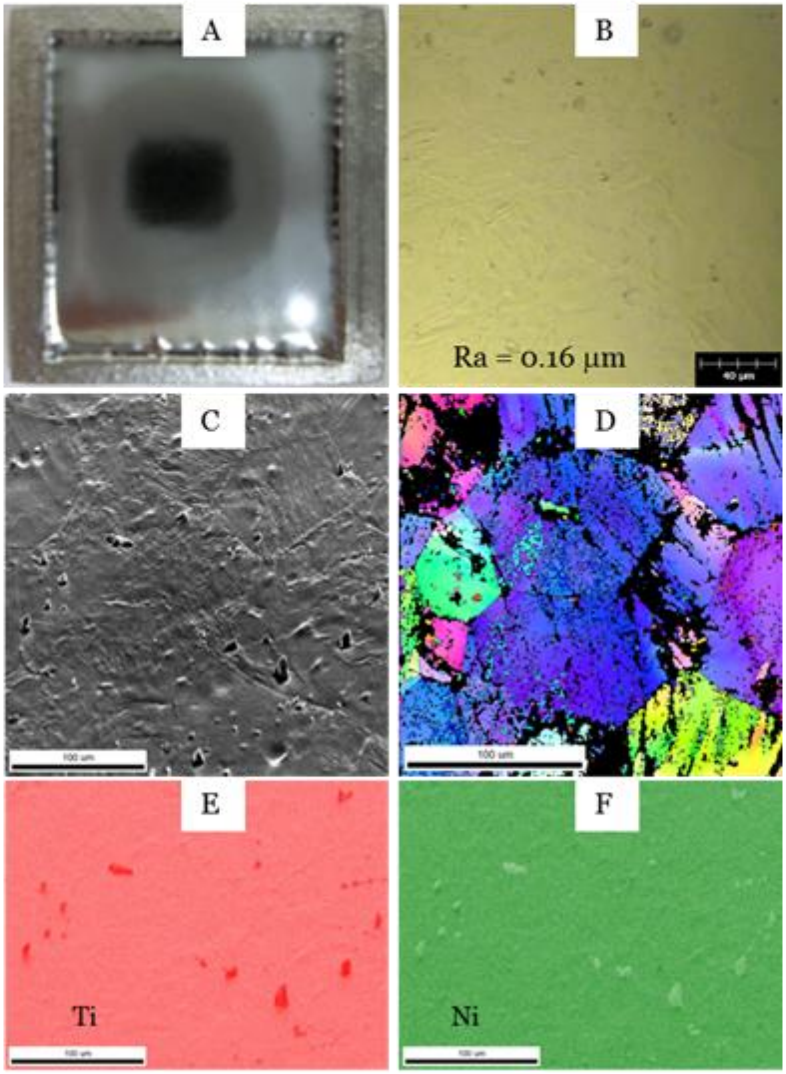


Figure 23. A, Nitinol coupon electropolished in KNO_3/ Na_2SO_4, 25/150 g/L . B, optical microscopy image, and SEM/EDS scans, C-F, of coupon A. $t_{f,on}$ = 0.55 ms.

d) Summary of FARADAYIC® Process development on 1 in² coupons.

Faraday investigated electropolishing of 1 in² Nitinol coupons; over 600 tests were run. The desired surface finish is proprietary within industry, but is generally thought to be an Ra ≤ 0.2 µm. Both 200 g/L NaBr and 100 g/L NaCl were very aggressive electrolytes that removed material in a relatively short time. However, the surfaces were very rough, and did not approach the desired finish of 0.2 µm. 260 g/L NaH_2PO_4 was very slow to polish, and there were no improvement in surface finish, even after 1 hour. Based on these results, these 3 single electrolytes were not examined further.

Table 5 gives the best data from the other single component and mixed electrolytes, describing the initial and final Ra for a given waveform and polishing time. The best result in a single test was in 200 g/L KNO_3, in which we were reduced the Ra from 2.86 to 0.21 µm in 20 minutes. In the other electrolytes, 2 or 3 individual tests are listed in a sequence that would achieve the desired Ra of close to or less than 0.2 µm. For example, in 200 g/L $NaNO_3$ we should be able to achieve 0.13 µm in ~25 minutes, using three sequenced waveforms. The use of waveform sequencing is easily done by programming the pulse reverse rectifier to deliver each waveform for a specific period of time. We did not test the waveform sequencing specifically in Phase I, but will investigate this method in the Phase II. In 150 g/L Na_2SO_4 + 25 g/L KNO_3, we were able to achieve an Ra of 0.18 µm, but the processing time was considerably longer. In 150 g/L Na_2SO_4 and 200 g/L $NaNO_3$ + 25 g NaCl, we got down to 0.25 and 0.32 µm respectively, and it may be possible to achieve the desired surface finish with additional investigation. These results show that we can achieve an order of magnitude change in Ra and the desired surface finish using a variety of electrolytes, which gives flexibility for our customers.

The single component electrolytes containing KNO_3 and $NaNO_3$ polished quickly (2 to 30 min). However, at the completion of the process we observed a blue surface hue. This may be eliminated using a waveform sequence, but there was insufficient time in the Phase I to investigate that possibility. The Na_2SO_4 and Na_2SO_4 + KNO_3 electrolyte polished more slowly, but the surface was very shiny and smooth without a blue hue. The typical initial Ra for Nitinol wire may be less than we used, which would decrease the required polishing time. The coupons were sent for analysis to Fort Wayne Metals, but we have not yet received feedback.

Table 5. Best results from FARADAYIC® Electropolishing coupon studies on Nitinol, showing initial and final Ra as a function of chemistry, waveform and polishing time.

Chemistry	**$Ra_{initial}$ µm**	**Ra_{final} µm**	**Waveform**	**Polishing Time (min)**
200 g/L KNO_3	2.86	0.21	V_{for} = 40 V for 0.8 ms, Off_{for} for 1.2 ms V_{rev} = 2.4 V for 1.0 ms, Off_{rev} for 0.8 ms	20
200 g/L $NaNO_3$	3.01	0.31	V_{for} = 40 V for 2.0 ms, Off_{for} for 3.0 ms V_{rev} = 2.4 V for 1.0 ms, Off_{rev} for 0.8 ms	5
	0.31	0.24	V_{for} = 40 V for 1.5 ms, Off_{for} for 3.0 ms V_{rev} = 2.5 V for 3.0 ms, Off_{rev} for 0 ms	5
	0.22	0.13	V_{for} = 5 V for 1.0 ms, Off_{for} for 0 ms V_{rev} = 40 V for 0.5 ms, Off_{rev} for 0 ms	15
150 g/L Na_2SO_4 + 25 g/L KNO_3	3.32	0.23	V_{for} = 40 V for 0.45 ms, Off_{for} for 0 ms V_{rev} = 5 V for 2.0 ms, Off_{rev} for 0 ms	180
	0.23	0.18	V_{for} = 40 V for 0.45 ms, Off_{for} for 0 ms V_{rev} = 5 V for 2.0 ms, Off_{rev} for 0 ms	80
150 g/L Na_2SO_4	1.95	0.29	V_{for} = 30 V for 1.0 ms, Off_{for} for 0 ms V_{rev} = 30 V for 0.5 ms, Off_{rev} for 0 ms	120
	0.29	0.25	V_{for} = 40 V for 0.75 ms, Off_{for} for 0 ms V_{rev} = 30 V for 0.5 ms, Off_{rev} for 0 ms	60
200 g/L $NaNO_3$ + 25 g NaCl	3.59	0.59	V_{for} = 35 V for 0.8 ms, Off_{for} for 0.15 ms V_{rev} = 20 V for 0.8 ms, Off_{rev} for 0.5 ms	10
	0.60	0.45	V_{for} = 35 V for 0.8 ms, Off_{for} for 0.15 ms V_{rev} = 20 V for 0.8 ms, Off_{rev} for 0 ms	20
	0.45	0.32	V_{for} = 35 V for 0.8 ms, Off_{for} for 0.15 ms V_{rev} = 20 V for 0.8 ms, Off_{rev} for 0 ms	10

Based on the results from the above coupon study, electrolytes and waveforms were selected for the subsequent electropolishing studies with straight wires and shape sets due to their observed Ra and surface coloration, these are shown in Table 6.

Table 6. Best FARADAYIC® Processing conditions for electropolishing Nitinol coupons that were selected for straight wires and shape sets in the 150 g/L Na_2SO_4 and 25/150 g/L KNO_3/Na_2SO_4 electrolytes.

Electrolyte	V_f (V)	$t_\text{f on}$ (ms)	$t_\text{f off}$ (ms)	V_r (V)	$t_\text{r on}$ (ms)	$t_\text{r off}$ (ms)	Final Ra (µm)	Appearance
Na_2SO_4	20	1.5	0	30	0.5	0	0.34	Metallic Finish
	23	1.5	0	30	0.5	0	0.30	Metallic Finish
	23	1.5	0	30	0.5	0.5	0.32	Metallic Finish
	30	1.0	0	30	0.5	0	0.29	Metallic Finish
	40	0.7	0	30	0.5	0	0.25	Metallic Finish
KNO_3/Na_2SO_4	40	0.45	0	5	2	0	0.16	Metallic Finish
	40	0.55	0	5	2	0	0.20	Metallic Finish
	40	0.60	0	5	2	0	0.31	Metallic Finish

Straight Wire Studies

Figure 24. Top) unprocessed and bottom) electropolished wire after 100 secs in 150 g/L Na_2SO_4 + 25 g/L KNO_3.

Wire electropolishing tests were facilitated with a simple flow cell and a specially designed sample holder (Figures 8-10). The holder utilizes a mixed metal oxide cathode ring with a 1-in internal diameter through which the wire is secured, and also incorporates off-set shielding to concentrate the electric field, if needed. These tests were conducted using the 150 g/L Na_2SO_4 and 25/150 g/L KNO_3/Na_2SO_4 electrolytes using the conditions from Table 6. The Nitinol wire for this work was provided by Fort Wayne Metals (Fort Wayne, IN) at no cost to the program. These tests were conducted using Nitinol wires that were pretreated with a sulphamic etch or were untreated and coated in a blue oxide. Fort Wayne Metals requested that we develop a single step that removes the blue oxide and polishes the surface, negating the need for the pretreatment. We used sodium sulfate electrolytes as these were able to remove the oxide and polish the surface in a single step. Figure 24 shows one of the wires electropolished in 150 g/L Na_2SO_4 + 25 g/L KNO_3 electrolyte, while the luster of the surface after electropolishing is difficult to see, one can clearly observe the removal of the oxide layer, and reduction in tool lines. Seventeen additional wire samples were sent to our commercial partner for additional analysis; we have yet to receive the results from their analysis.

Loop Clip Studies.

Electropolishing of loop clips coated with a dark oxide was performed using the experimental set-up shown in Figures 12 and 13 in the 150 g/L Na_2SO_4 solution and for a time shorter than one minute, as suggested by time studies with wires, described above. Figure 25 presents substrates with a bright metallic surface finish; each panel includes both, as-received (unprocessed) and electropolished loop clips (left and right, respectively). Loop clips shown in panels LC1-LC5 were electropolished for 42 seconds, and showed that within this period the dark oxide coating was removed throughout the surface, except within the point of intersection. Removal of the oxide in this region was greatly aided by twisting the loop clip in a way to avoid electrical contact at the point of intersection and prior to electropolishing, and increasing the experiment time to 48 seconds. Panel LC6 shows a loop clip that was processed for 48 seconds using identical conditions used to process LC4, and showing no oxide left at the intersection point.

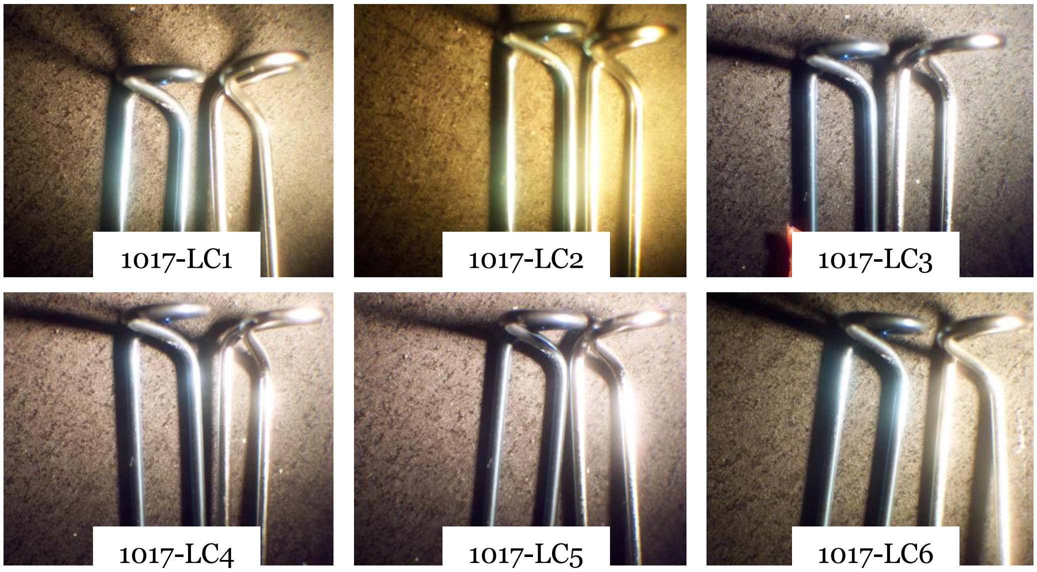


Figure 25. Nitinol loop clips electropolished in 150 g/L Na_2SO_4, at V_f = 20 (LC1), 23 (LC2 and LC3), 30 (LC4) or 40 V (LC5), $t_{f\,on}$ = 1.5 (LC1-LC3), 1.0 (LC4) or 0.7 ms (LC5), $t_{f\,on}$ = 0 ms, V_r = 30 V, $t_{r\,on}$ = 0.5 ms, $t_{r\,off}$ = 0 (LC1, LC2, LC4 and LC5) or 0.5 ms (LC3) , stirring rate = 360 rpm.

Additional Material of Interest to Commercial Team Members

Fort Wayne Metals has a strong interest in electropolishing of cobalt chrome alloys, specifically 35N LT wires. Faraday electropolished these wires in a 150 g/L Na_2SO_4 electrolyte using a variety of waveform conditions and the same processing apparatus shown in Figures 8-10. As shown in Figure 26, the material showed a metallic, bright and electropolished surface. Samples have been sent to Fort Wayne Metals for analysis, but the data has not yet been received.

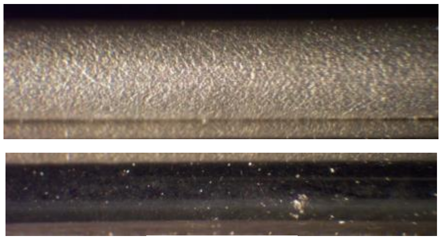


Figure 26. 35N LT wire electropolished in 150 g/L Na_2SO_4 Top) unprocessed and bottom) electropolished wire after 10 min processing.

3.3 Alpha Scale Stent Processing Apparatus

The second Specific Aim of this Phase I program was to *design an α-scale pilot manufacturing apparatus for demonstration of continuous, industrial-scale processing of stents.* While Faraday's initial market target were laser cut stents, we adjusted our primary market target to electropolishing Nitinol wire, based on industry direction. During Phase I, Fort Wayne Metals delivered (at no cost to the program) a prototype wire processing apparatus capable of processing a wire product, with let-off and take-up spools (Figure 27). This apparatus was originally designed for chemical polishing in aggressive electrolytes. Rather than design and build a wire processing apparatus from scratch, Faraday will work with Fort Wayne Metals to modify their apparatus for FARADAYIC® Electropolishing, based on the parameters developed in this program. Fort Wayne Metals will assist Faraday with the setup and operation of the apparatus and wire handling equipment, and visited Faraday in April 2014 to continue these developments and discuss future activities.

Figure 27. Wire processing apparatus, delivered to Faraday by Fort Wayne Metals, at no cost to the program.

Figure 28 shows a preliminary concept design of the planned modifications for implementing FARADAYIC® Electropolishing within the apparatus supplied by Fort Wayne Metals. This will enable medical grade wires to be electropolished continually via a high-throughput reel-to-reel process. The process flow allows the wire to be guided into the electrolyte via anode rollers (that are electrically connected to the rectifier) that are external to the electrolyte, then guided within the electrolyte by insulated rollers that are fully immersed in the electrolyte. The electrically connected wire can then be driven at a constant rate through a mesh cathode tube (Figure 29), fabricated from a mixed-metal oxide. The dwell time required for the desired level of electropolishing would define a) the length of the cathode tube, b) the rate of travel, and/or c) the number of anode pairs/cathode. The length of wire that could be done in one day, i.e. throughput, could be optimized based on the residence time and the desired footprint of the operation.

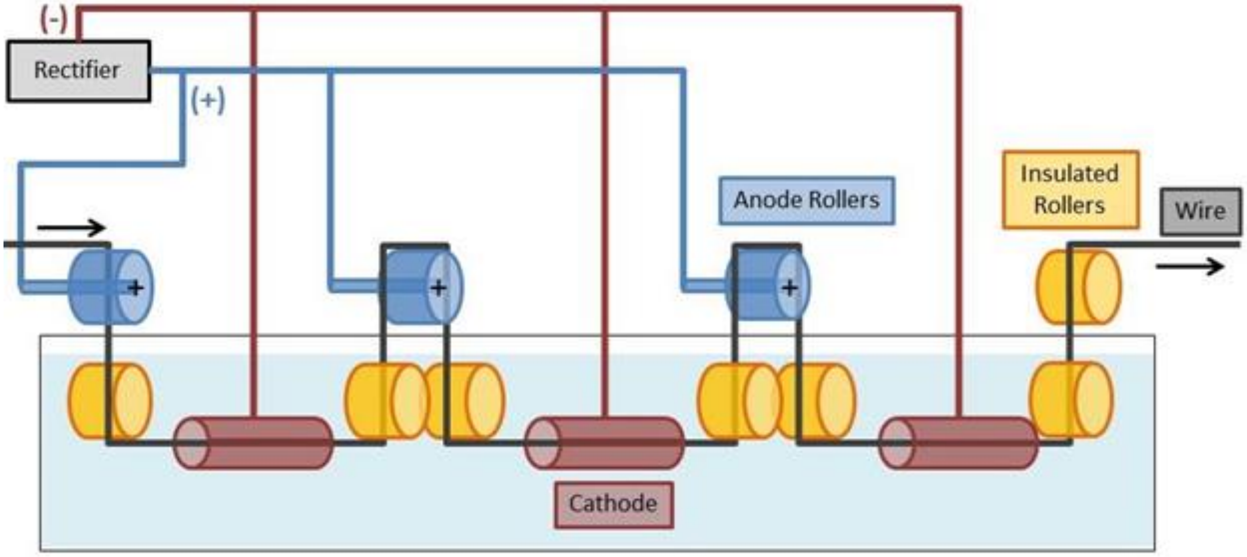


Figure 28. Design concept for anode-cathode and wire configuration modifications to the Fort Wayne Metals wire polishing apparatus.

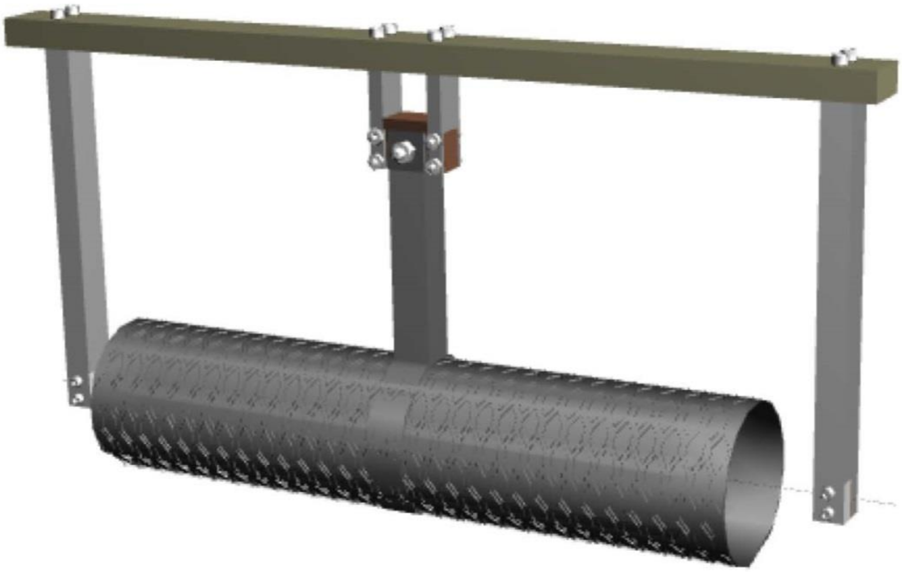


Figure 29. Design concept for cathode for the Fort Wayne Metals wire polishing apparatus.

3.4: Manufacturing Process Flow and Economic Assessment

Current Technology Status and Preliminary Economic/Commercialization Analysis
In Phase I, we demonstrated the feasibility of FARADAYIC® ElectroPolishing for cost effective surface finishing of medical grade wires and shape sets. A variety of pH neutral electrolytes for Acid-Free FARADAYIC® ElectroPolishing development were identified, and an order of magnitude change in surface finish, with a final Ra of ~0.2 µm or less (mirror-finish), was achieved in 3 salt-based electrolytes. A spool wire processing apparatus was obtained from Fort Wayne Metals, and will be modified in Phase II for electrochemical processing. Preliminary technology transition steps are underway.

Faraday attracted the interest of a number of medical device/ implant companies, as well as raw material suppliers such as Fort Wayne Metals, who may participate in future efforts by supplying test samples and post-process evaluation. This collaboration will enable Faraday to develop and commercialize the technology in line with industrial needs.

According to a recent Wall Street Journal article,[45] the current medical stent market is approximately $5.1 billion with a projected annual growth rate of ~2.6%. Within this market, w*e estimate* the current overall cost of stent fabrication at ~$100 million annually - ~2% of the total stent market. In addition, while stent electropolishing is the focus of future work, the FARADAYIC® ElectroPolishing process will be applicable to surface finishing of any metallic medical device or implant. The market for medical devices and implants is much larger than for stents, estimated to be ~$92 billion,[46] so the potential impact of this technology is very high.

Faraday's marketing/sales strategy is to commercialize its FARADAYIC® ElectroPolishing process through these key supply chain companies, such as Fort Wayne Metals. This market entry approach addresses the "sweet spot" in the current manufacturing process in terms of 1) lack of robustness, 2) high reject rate, 3) worker exposure to hazardous chemicals. In addition, as the FARADAYIC® ElectroPolishing process does not represent a "substantial" change to the current electropolishing process, according to our industrial partners the need for FDA preclinical trials is eliminated.[47] Technical certifications are, however, required by our customers. These certifications include corrosion and dimensional stability and are generally covered by ASTM standards such as F2129-0848 and F2081-0649, respectively. In addition, each customer has a surface roughness requirement which is generally maintained as proprietary.

Income from modifications to existing apparatus are based on the implementation of a continuous FARADAYIC® ElectroPolishing line. The cost basis for said apparatus modifications is based on Faraday's experience in the printed circuit board industry employing continuous production lines. The cost elements associated with the FARADAYIC® ElectroPolishing line modifications are presented in Table 7.

Table 7. Estimated Cost Elements associated with FARADAYIC® ElectroPolishing of Wire

Wires/Line	1
Line Length / feet	50
Number of Lines	8
Processing Time (min)	2
Total Feet of Wire/Hr	12000
Processing Hrs/Day	8
Wire Feet/Processing Day	96000
Processing Days/Year	300
Wire Feet/Line/Year	28,800,000
Materials	
Water Cost	$0.004/gal.
Water/Line	100 gallons
Water Consumed/Line/Year	30,000 gallons
Water Cost/Line/Year	$ 120.00
Rinse Water/Line	300 gallons
Rinse Water Consumed/Line	90,000 gallons
Rinse Water Cost/Line/Year	$ 360.00
Total Water cost/stent	$ 0.000
Chemical Cost (150 g/L Na2SO4)	$0.45/lb.
Chemicals/Line	125.3 lb.
Chemicals/Line/Year	3,007.1 lb.
Chemical Cost/Line/Year	$ 1,353.20
Chemical Cost/Stent	$0.000
Labor	
Operator cost/hr	$ 40
Operator cost/yr	$ 96,000
Operator cost/stent	$ 0.003
Electricity	
Current/Wire Foot	5 Amps
Potential/Wire Foot	40 V
Power/Wire Foot	200 W
Power/Wire Foot @ 50% efficiency	400 W
Energy/Wire Foot	0.03 kWH
Cost per kWH	$ 0.06
Energy cost/Wire Foot	$ 0.002
Total ElectroPolishing Cost per Wire Foot	**$ 0.005**

Income from sale of rectification equipment for delivery of the pulse/pulse reverse FARADAYIC® ElectroPolishing parameters is estimated at 25% of rectifier sales based on Faraday's current vendor relationship with Dynatronix, a leading rectifier manufacturer. This decreased reject rate provides both operating and capital cost saving throughout the process and does not include the further intangible benefit associated with elimination of worker exposure to strong acids. According to Table 8, by 2019 Faraday will take in Net Annual Revenues of ~$1.1M. However, our strategic partner(s) will save ~$6.7 million annually of the cost of wire fabrication, through implementation of the FARADAYIC® ElectroPolishing process. This savings is partially due to the reduced chemical cost, reduced waste treatment cost, and improvement in worker safety associated with eliminating high concentration acid mixtures, and primarily due to the reduction in reject rate down to at least 5% that will be obtained when implementing FARADAYIC® ElectroPolishing.

Pro Forma data and assumptions are conservatively estimated for implementation at, at least, our early adopter facilities. More widespread implementation of the technology throughout the medical device and implant industry would obviously result in much higher revenues. Assumptions are given below:

Table 8. Pro Forma for FARADAYIC® ElectroPolishing Process.

		2015	2016	2017	2018	2019
1	Medical Grade Nitinol Wire Market @ 4% Growth	$300,000,000	$312,000,000	$324,480,000	$337,459,200	$350,957,568
2	Estimated Price per Wire Foot	$9	$9	$9	$9	$9
3	Feet of Wire Produced	33,333,333	34,666,667	36,053,333	37,495,467	38,995,285
	P&L: Strategic Partner					
	Revenues:					
4	% Market Penetration	15%	15%	15%	20%	25%
5	Wire Feet Produced	5000000	5200000	5408000	7499093	9748821
6	Total Sales	$45,000,000	$46,800,000	$48,672,000	$67,491,840	$87,739,392
	COGS: Conventional Electropolishing with 15% Reject Rate					
7	Wire Fabrication Cost as % of Price	25%	25%	25%	25%	25%
8	Wire Fabrication Cost	$2.25	$2.25	$2.50	$2.50	$2.50
9	Reject Rate	15%	15%	15%	15%	15%
10	Wire Fabrication Cost Normalized by Reject Rate	$2.65	$2.65	$2.94	$2.94	$2.94
11	Conventional Wire Fabrication Cost	$13,235,294	$13,764,706	$15,905,882	$22,056,157	$28,673,004
12	% Electropolishing Cost of Fabrication	5%	5%	5%	5%	5%
13	Electropolishing Cost per Wire Foot	$0.13	$0.13	$0.15	$0.15	$0.15
14	Conventional Electropolishing COGS	$661,765	$688,235	$795,294	$1,102,808	$1,433,650
	COGS: Staged Implementation of FARADAYIC® ElectroPolishing with 2% Reject Rate					
15	Wire Fabrication Cost as % of Price	25%	25%	25%	25%	25%
16	Wire Fabrication Cost	$2.25	$2.25	$2.25	$2.25	$2.25
17	Total Electropolishing Lines	8	8	9	10	12
18	FARADAYIC® ElectroPolishing Lines	0	0	1	6	12
19	Adjusted Reject Rate	15%	15%	14%	9%	5%
20	Wire Fabrication Cost Normalized by Reject Rate	$2.65	$2.65	$2.61	$2.47	$2.37
21	Wire Fabrication Cost - Impact of Reduced Reject Rate	$13,235,294	$13,764,706	$14,130,581	$18,541,714	$23,089,314
22	Wire Produced using Conventional Electropolishing	5000000	5200000	4807111	2999637	0
23	Wire Produced Using FARADAYIC® ElectroPolishing	0	0	600,889	4,499,456	9,748,821
24	FARADAYIC® ElectroPolishing Cost/Wire	$0.005	$0.005	$0.005	$0.005	$0.005
25	Electropolishing Cost - Impact of FARADAYIC® Process Cost	$661,765	$688,235	$709,931	$463,607	$48,715
26	No. of ElectroPolishing Lines Modified for FARADAYIC® Process (@ $10k ea.)	0	0	1	5	6
27	Total Cost of Modification	$0	$0	$10,000	$50,000	$60,000
28	No. of Rectifiers ($20k ea.)	0	0	1	5	6
29	Total Rectifier Cost	$0	$0	$20,000	$100,000	$120,000
30	FARADAYIC® ElectroPolishing Implementation COGS	$661,765	$688,235	$739,931	$613,607	$228,715
31	**COGS Savings By Implementation of FARADAYIC® ElectroPolishing**	**$0**	**$0**	**$1,830,665**	**$4,003,644**	**$6,788,626**
	P&L: Faraday					
	Revenues: Implementation of FARADAYIC® ElectroPolishing					
32	% Royalty on Cost Savings from FARADAYIC® ElectroPolishing	0%	0%	15%	15%	15%
33	Royalty from FARADAYIC® ElectroPolishing	$0	$0	$274,600	$600,547	$1,018,294
34	Line Modification Income	$0	$0	$10,000	$50,000	$60,000
35	Rectifier Income	$0	$0	$20,000	$100,000	$120,000
36	Total Revenues	$0	$0	$304,600	$750,547	$1,198,294
37	COGS: Implementation of FARADAYIC® ElectroPolishing					
38	Royalty	$0	$0	$0	$0	$0
39	Rectifier @ 80%	$0	$0	$16,000	$80,000	$96,000
40	Total COGS	$0	$0	$16,000	$80,000	$96,000
41	**Net Income to Faraday Before Taxes & Depreciation**	**$0**	**$0**	**$288,600**	**$670,547**	**$1,102,294**
42	Margin	0%	0%	95%	89%	92%

1. Market estimate based on fraction of stent market. Wire market assumed to be less than stent market.
4. Assumed conservative estimate of market penetration by strategic partner(s), increasing with time.
8. Assumed conservative estimate of wire fabrication cost.
9. Assumed reject rate after completion of electropolishing step, conservatively estimated to be considerably less than that for finished stents
12. Assumed estimate of electropolishing cost, as a percentage of total wire fabrication cost (including increased costs associated with reject rate).
17. Assumed number of lines used by strategic partner(s). Based on wire produced per line, per Table 7.
18. Potential staged implementation rate of FARADAYIC® ElectroPolishing process.
19. Adjustment to overall reject rate, based on conservative reject rate of 5% after FARADAYIC® ElectroPolishing process. We will aim to be much lower than this in the program.

23,25. Total wire produced per year using a line implementing the FARADAYIC® Process and the remaining wire produced using the conventional process.

24. Estimated cost of FARADAYIC® ElectroPolishing process.
27. Estimated costs for modification of existing apparatus, based on Faraday experience.
29. Rectification costs based on Faraday experience with pilot-scale facility build.
31. COGS Savings to our partner, based on staged implementation of FARADAYIC® ElectroPolishing.
32. Royalty rates estimated at 15% of COGS savings.
39. 25% royalty rate based on existing vendor relationship between Faraday and rectifier manufacturers.

4. COMPARISON OF ACCOMPLISHMENTS WITH THE SPECIFIC AIMS

The overall objective of the Phase I effort was to demonstrate the feasibility of an innovative acid free electropolishing process for the cost effective finishing of stents made from Nitinol or other alloys. The experimental approach and major results of the program have been described above. The Phase I Specific Aims are given verbatim, and answers given to each objective:

1. *Optimize the FARADAYIC ElectroPolishing Process on Nitinol tubular stents, including the preliminary development of a library of waveform parameters to achieve the desired surface finish for a variety of stents of interest to industry.*

The milestones of this task were 1) Design/construct bench-scale electropolishing system, 2) Conduct polarization studies for electrolyte selection, 3) Optimize pulse/pulse reverse electropolishing conditions to achieve a finish of ≤ 0.2 μm, and 4) Evaluate other material of interest to industrial partners. All the four milestones were successfully completed.

Three different bench scale processing apparatus were designed/built for polarization/ flat coupon studies, for straight wire processing studies, and for loop clip processing studies. While Faraday's initial market target were laser cut stents, we adjusted our primary market target to electropolishing Nitinol wire, based on direction from industry. Subsequent markets include Nitinol shape sets, including stents, and other materials. In Phase I, we demonstrated the feasibility of FARADAYIC® ElectroPolishing for cost effective surface finishing of medical grade wires and shape sets. A variety of pH neutral electrolytes for Acid-Free FARADAYIC® ElectroPolishing development were identified, and an order of magnitude change in surface finish, with a final Ra of ~0.2 μm or less (mirror-finish), was achieved in 3 salt-based electrolytes. An Ra value of <0.2 μm is below the industrial benchmark, and based on the overall results we anticipate lower values with further development. Additionally, straight Nitinol wires were polished using similar conditions and are being evaluated by our commercial partner, Fort Wayne Metals. Furthermore, Nitinol loop clips provided by Fort Wayne Metals were electropolished and showed the potential to achieve the desired finish. This program has demonstrated a non-toxic aqueous near pH neutral electrolyte that is simpler to control and more environmentally friendly as compared to the concentrated hydrofluoric/sulfuric acid/phosphoric acid electrolytes used by the current state-of-the-art electropolishing technology.

2. *Design an α-scale pilot manufacturing apparatus for demonstration of continuous, industrial-scale processing of stents, to be built and validated in Phase II.*

The milestone of this task was to design an alpha scale pilot manufacturing apparatus, and this was successfully completed. While Faraday's initial market target were laser cut stents, we adjusted our primary market target to electropolishing Nitinol wire, based on industry direction. During Phase I, Fort Wayne Metals delivered (at no cost to the program) a prototype wire processing apparatus capable of processing a wire product, with let-off and take-up spools. This apparatus was originally designed for chemical polishing in aggressive electrolytes. Rather than design and build a wire processing apparatus from scratch, Faraday will work with Fort Wayne Metals to modify their apparatus for FARADAYIC® Electropolishing, based on the parameters developed in this program.

3. Initiate steps for transitioning the technology to industry partners.

The milestones of this task were 1) Compile manufacturing process flow, 2) Validate compliance with FDA regulations, and 3) Interface with collaborators. All the three milestones were successfully completed.

Faraday installed onsite a high-throughput reel-to-reel strand electropolishing system designed by Fort Wayne Metals for processing straight wire. During the Phase II program, the system will be retrofitted to allow streamline processing medical device wires. Upon process demonstrations the technology will be transitioned to our industrial partner, Fort Wayne Metals. Additionally, a manufacturing process flow and economic assessment was completed in this task.

5. PRODUCTS DEVELOPED AND TECHNOLOGY TRANSFER ACTIVITIES

5.1 Publications

T.D. Hall, E.J. Taylor, and M. Inman, Electropolishing of Passivating Materials (like Nitinol, Nb, Ti, Ta, and Mo) in HF-Free Low Viscosity Water Based Electrolytes, *MS&T 2013*, Montreal, QC, October 2013.

M. Inman, T.D. Hall, H. Garich and E.J. Taylor, Environmentally Benign Electropolishing of Biomedical Alloys, *MSEC 2014*, Detroit, MI, June 2014.

M. Inman, T.D. Hall, H. Garich and E.J. Taylor, Electropolishing of Nitinol for Biomedical Applications, *ECS 2014 Fall Meeting*, Cancun, MX, October 2014.

5.2 Web site

For general information about the FARADAYIC® ElectroEtching and ElectroPolishing Processes, please refer to Faraday's website: http://www.faradaytechnology.com .

5.3 Networks or Collaborations Fostered

Faraday has continued the development of a relationship a number of medical device companies. Our primary industrial partner is Fort Wayne Metals (Fort Wayne, IN), a major supplier of wire and other product forms fabricated from Nitinol and other materials to the medical device and implant manufacturers.

5.4 Inventions/Patent Applications

While there are no inventions to report yet, the following patent applications are Background Intellectual Property, owned by Faraday:

- C. Zhou, E.J. Taylor, J.J. Sun, L.E. Gebhart, R.P. Renz "Electrochemical Machining using Modulated Electric Fields" U.S. Patent No. 6,402,931 June 11, 2002.
- E.J. Taylor "Sequential Electromachining and Electropolishing of Metals and the Like using Modulated Electric Fields" U.S. Patent No. 6,558,231 May 6, 2003.
- M. Inman, E.J. Taylor, A. Lozano-Morales, T. Hall, H. Garich "Electrochemical System and Method for Machining Strongly Passivating metals" U.S. Patent Appl. No. 13/153,874 June 6, 2011.
- M. Inman, E.J. Taylor, A. Lozano-Morales, T. Hall, H. Garich "Electrochemical System and Method for Machining Strongly Passivating metals" Foreign Patent Appl. No. PCT/US11/39354 June 9, 2011.
- E.J. Taylor, M. Inman, T. Hall "Electrochemical System and Method for Electropolishing Superconducting Radio Frequency Cavities" U.S. Patent Application No. 13/546,072 July 11, 2012.
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