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Comparison of Electrochemical Polishing Treatments between Phosphoric Acid and a Deep Eutectic Solvent for High-Purity Copper

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Abstract: This study investigated and compared the acid-free electropolishing of copper with the state-of-the-art acidic electropolishing process. The acid-free medium used in this study is based on a deep eutectic solvent comprised of 2:1 ethylene glycol and choline chloride. The electrochemical study included voltammetry and chronoamperometry tests during the electropolishing process. The characterization techniques used were atomic force microscopy (AFM) and digital microscopy, and surface morphology comparisons summarized the electropolishing efficiency of phosphoric acid and acid-free deep eutectic solvent treatments for high-purity copper. Electropolishing copper with a deep eutectic solvent resulted in a mirror finish and a post-treatment surface that was 8× smoother than the original metal surface prior to electropolishing treatments with a smoothing efficiency of 91.1 ± 1.5%. This eco-friendly solution produced polished surfaces superior to those surfaces treated with industry standard acid electrochemistry treatments of 1 M H_3PO_4.

Keywords: electropolishing; Cu; deep eutectic solvent

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1. Introduction

Electrochemical polishing or electropolishing is the controlled corrosion of metal surfaces [1]. The concept behind this mechanism of liquids corroding metals is to reduce the surface roughness of the polished metals [2,3]. Unlike surface buffing alternatives, electropolishing can reduce surface roughness and impurities to nearly negligible quantities on polished surfaces. Currently, large quantities of surface-polished products are being treated with hazardous chemical solutions, such as phosphoric and sulfuric acids that are used to electropolish stainless steel [4].

Recently, the benefits of electrochemical polishing are gaining more recognition as an ideal method for improving a metal's optimum roughness that can also greatly improve electrical conductivity [5]. Many acid treatments currently utilized for electropolishing metal surfaces provide an ideal mirror finish by removing the exposed surface layer of the sheet metal. However, acid solutions provide this clean, electropolished finish to the metal at the expense of hydrogen contamination [2,5]. The removal of hydrogen contamination generally entails the use of high temperature treatments in excess of 800 °C for several hours in vacuo [6].

Deep eutectic solvents have shown a great promise for many electrochemical applications [1–8]. The main advantages for deep eutectic solvents over state-of-the-art acidic electropolishing are the wide potential windows and high conductivity compared to other non-aqueous solvents [1–8].

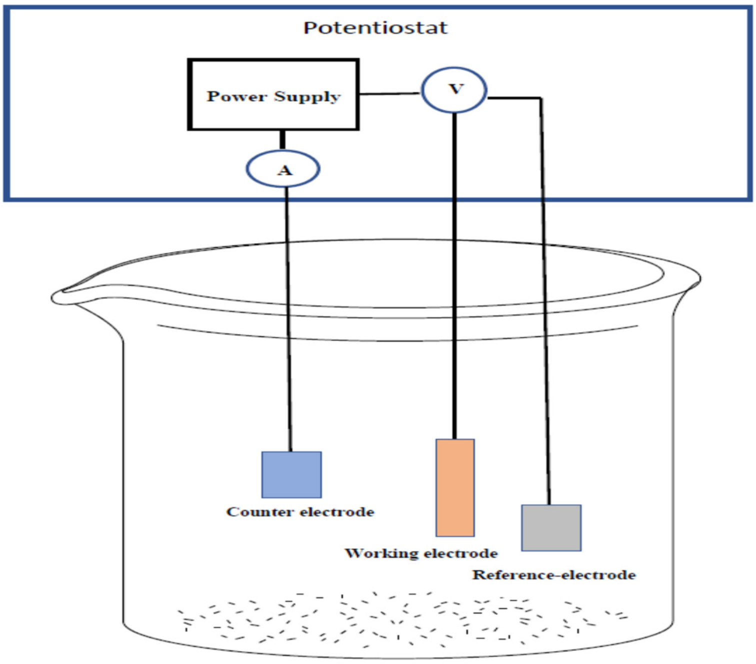
In the current study, high-purity metal samples of copper will be tested to determine the effectiveness of both an industry standard acid solution (1 M phosphoric acid), and a deep eutectic solvent medium comprised of ethylene glycol and choline chloride mixed in a 2:1 molar ratio, respectively [7,8]. Several scientists have demonstrated the effectiveness of various conformities of this deep eutectic solvent with various metals and alloys [1,3,9,10]. It is the aim of this investigation to optimize the electrochemistry tests to produce a superior polish for copper metals, and to weigh the benefits of this deep eutectic solvent against an industry standard 1M phosphoric acid electropolishing treatment.

2. Materials and Methods

Materials: A 1 M phosphoric acid mixture was used for the acid treatments (Sigma-Aldrich, St. Louis, MO, USA, 85%). Acid-free treatments were carried out using a deep eutectic solvent comprised of choline chloride (Acros Organics, Fair Lawn, NJ, USA, 99%) and ethylene glycol (Sigma-Aldrich, St. Louis, MO, USA, 99.8%); both chemicals were used as received. The deep eutectic solvent mixture was created by stirring the two components together at a component ratio of 2 ethylene glycol: 1 choline chloride at 70 °C until a homogeneous colorless liquid emerged.

Samples Preparation: Samples of high-purity copper (>99.95%) were bored from supplied sheets (3 mm thickness) and labeled for use. In each test, five samples of each respective sample were taped with polyimide film tape to restrict electrochemical activity, but leaving (not covering with the tape) a 1 cm^2 region on both the front and back faces of each metal to polish. This resulted in a 2 cm^2 region of polishing for each sample when calculating current density. Metal samples were then immersed in the electropolishing solution of choice, such that the regions for polishing were completely immersed. Each metal was submitted to a cursory linear sweep voltammetry test to determine optimum voltage conditions to set for running chronoamperometry over a 900 s polishing sequence.

Electrochemical Setup and Measurements: The deep eutectic solvent's effects on electropolishing the metal surfaces of interest were analyzed using the necessary machines. Voltammetry and chronoamperometry tests were conducted using a three electrodes system (Scheme 1) connected to a Gamry PCI4-G750 potentiostat and controlled using the accompanying framework and *e-chem Analyst* (v. 5.5) software.



Scheme 1. Schematic diagram presenting the three-electrode system used in this study.

The electropolishing procedure made use of a flat platinum counter electrode plate with a silver wire reference with a spacing of 2.5 cm between each electrode for the experimental setup. The temperature was maintained at 70 °C and flow control inside the beaker was induced by a slow rotation at 60 rpm using a 1-inch magnetic stir rod via a hotplate. Both electrodes were degreased using deionized water and acetone to preserve the purity of samples during testing. The working electrode was abraded with 150 grit glass paper, rinsed and dried prior to each recorded measurement to ensure reproducible voltammetric effects. Electrochemical measurements were performed at 70 °C with a constant scan rate of 20 mV/s used in voltammetric experiments.

Characterizations: An AFM surface analysis was carried out using a Dimension 3100 Nanoscope IV scanning probe microscope, manufactured by Digital Instruments, with software version 6.12 in tapping mode. Step height measurements were recorded in µm via the Alpha Step 200 by Tencor Instruments. A KH-1300 HIROX digital microscope was utilized for optical comparison to produce representative images scaled to 1600 × 1200 pixels. After completion of each experiment, samples were dried and weight was recorded using a high precision digital scale for calculations of mass loss due to electrochemical etching.

3. Results

The mechanism for electropolishing copper metal surfaces using the deep eutectic solvent electrolyte is represented in Figure 1. Upon comparison of voltammograms generated for both the deep eutectic solvent and phosphoric acid treatments of copper samples when stepped from 0 to 3 V at a constant scan rate of 20 mVs^{-1}, the ideal scenario for chronoamperometry settings for both electrolytes revealed to be 1.5 V (Figure 2A). With a fixed voltage of 1.5 V, both chronoamperograms revealed electropolishing rates consistent with the currents reported from the I-V curve from linear sweep voltammetry with expressed means of 0.38 A/cm^2 and 0.06 A/cm^2 for the phosphoric acid and acid-free electrolytes, respectively (Figure 2B). Having selected a fixed voltage of 1.5 V for electropolishing copper with the deep eutectic solvent, a reported current range of 0.04 to 0.08 A/cm^2 for the majority of chronoamperometry displayed a very slow rate of current decline (Figure 2B). A comparison of mass before (7.382 ± 0.03 g) and mass post-electropolishing (7.329 ± 0.04 g) revealed a difference of 0.053 g with an electropolishing rate of 59.44 µg/s (Table 1).

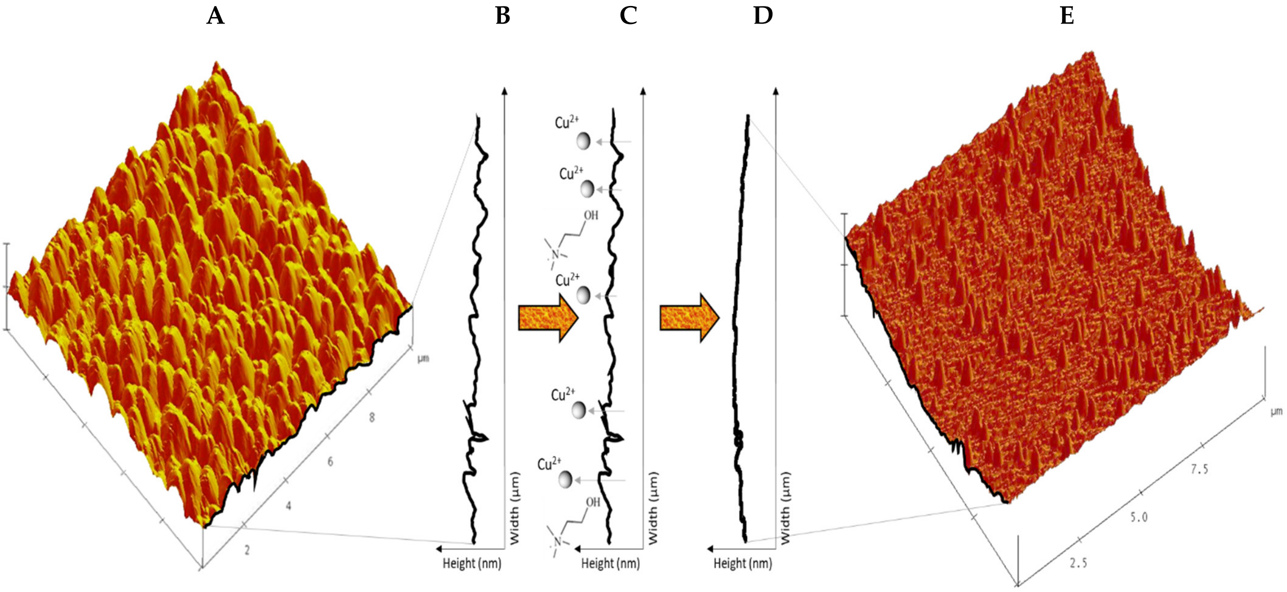
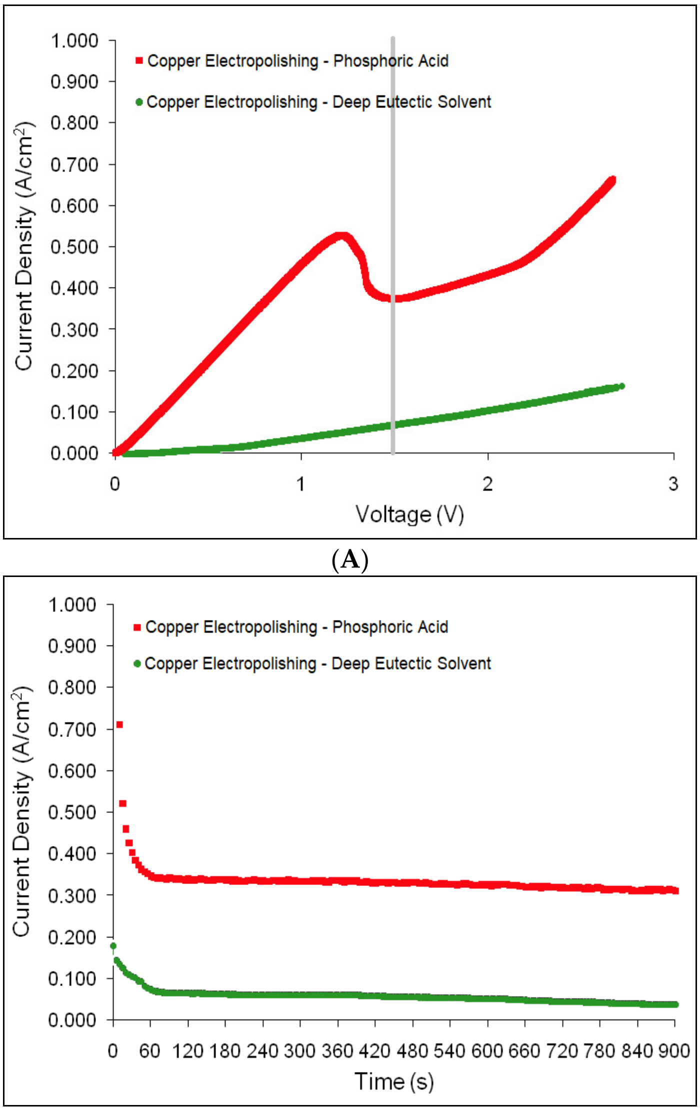


Figure 1. Schematic diagram of anodic leveling of high-purity copper surfaces via AFM at different phases of the study: (**A**) before electropolishing, and (**E**) after electropolishing treatments with the deep eutectic solvent, with representative 2D surface profiles depicted (**B**) before, (**C**) during and (**D**) after experiments. Presence of $(CH_3)_3NCH_2CH_2OH$, the choline chloride radical, and Cu^{2+} are abbreviated in (**C**). AFM *Z*-axis = 100 nm/div.



(**A**)

(**B**)

Figure 2. Linear sweep voltammograms (**A**) for both electropolishing mediums with copper samples stepped from 0 to 3 V at a constant scan rate of 20 mV/s at 70 °C. The dashed line indicates the ideal voltage utilized for (**B**) chronoamperometry for phosphoric acid (0.33 A/cm^2) and the deep eutectic solvent eutectic (0.06 A/cm^2) with high-purity copper samples. Both figures feature samples collected every 5 s, and the working potential of 1.5 V was selected based upon the stabilized local minima, noted as the gray line in A.

Table 1. Average copper electropolishing rate (µg/s) calculations for five samples with a potential of 1.5 V in each medium at 70 °C over a 900 s treatment.

Electrolyte	Mass Before (g)	Mass After (g)	Mass Diff. (g)	Surface Degradation Rate (µg/s)
Deep Eutectic Solvent	7.382 ± 0.03	7.329 ± 0.04	0.053 ± 0.03	59.44 ± 2.83
Phosphoric Acid	7.340 ± 0.03	7.274 ± 0.08	0.066 ± 0.05	73.44 ± 4.03

As-received copper samples returned an average roughness of 167 ± 9 nm upon scanning with AFM in tapping mode (Table 2). When compared with a 14.7 ± 2 nm roughness average for post-treatment with the deep eutectic solvent medium (Figure 3), a roughness comparison calculated a difference of 152.4 ± 3 nm (Table 2). This resulted in a post-treatment surface 8× smoother than the original metal surface prior to electropolishing treatments (Table 2). This differentiation in roughness accounts for a high percentage of smoothing efficiency, 91.1 ± 1.5% (Table 2). This efficiency calculation provides the average roughness difference divided by the roughness prior to treatment (expressed as a percentage) permitted for the exposed 2 cm^2 region of the working electrode. Since this percentage cannot ever truly be zero, given that a smoothness of zero would inevitably be a frictionless surface, a value of 91.1 ± 1.5% is extremely high (Table 2). The step height recorded for the deep eutectic solvent electropolishing treatment was 20.2 μm (Table 3).

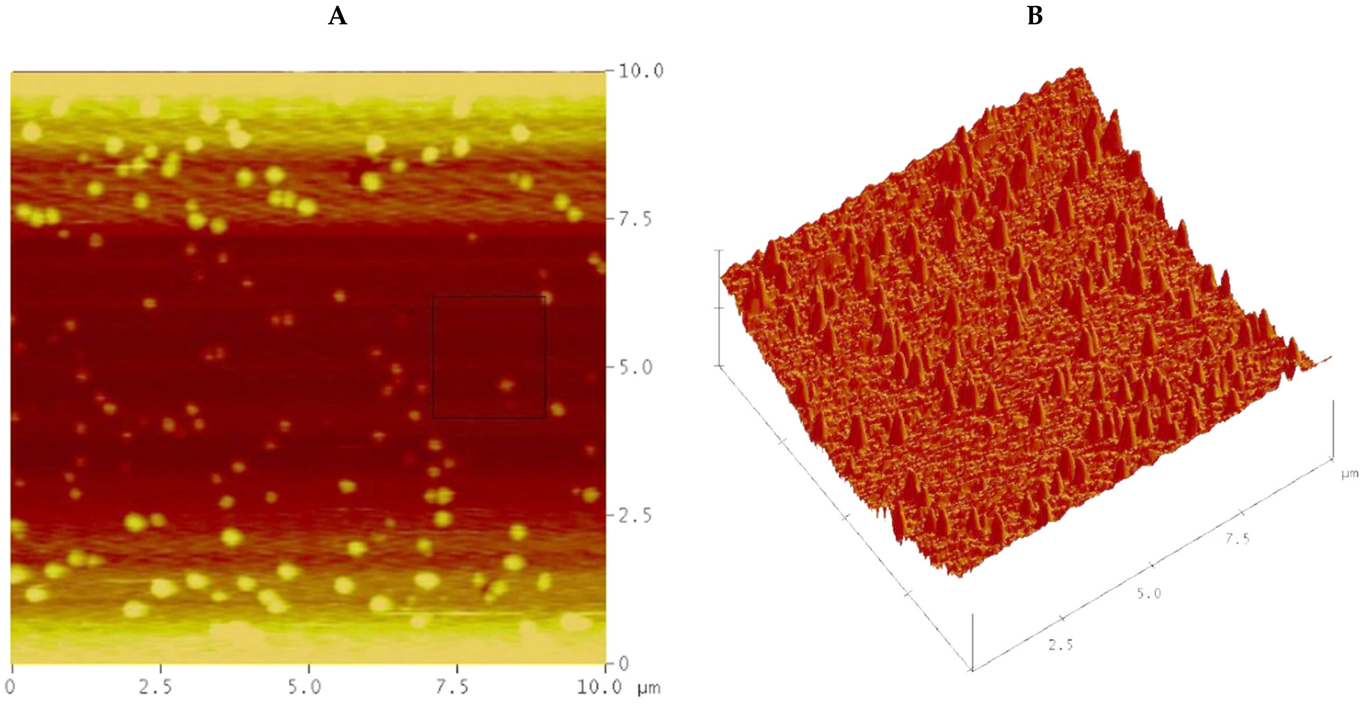


Figure 3. AFM of a copper sample in 2D (**A**) and 3D (**B**) after electropolishing treatments with a deep eutectic solvent, recording an average roughness of 14.7 ± 2 nm via the roughness average method. AFM Z-axis = 100 nm/div.

Table 2. Roughness average (Ra) in nm for five copper specimens post and prior to treatments with the respective solutions noted at 70 °C for 900 s. Calculated differences determined % smoothing efficiency (SE) for each sample. Compiled data from external references also noted for comparison.

Electrolyte	Metal	Ra Before (nm)	Ra After (nm)	Ra Diff. (nm)	% Ra SE *	Reference
Deep Eutectic Solvent	Cu	167.1 ± 4	14.7 ± 2	152.4 ± 3	91.1 ± 1.5	This Study
Phosphoric Acid	Cu	167.6 ± 4	82.6 ± 6	85.0 ± 5	50.7 ± 4.8	This Study
Deep Eutectic Solvent	Al	159.3 ± 4	26.6 ± 2	132.6 ± 3	83.2 ± 3.9	[3]
Phosphoric Acid	Al	159.1 ± 4	97.7 ± 7	61.3 ± 6	38.5 ± 1.2	[3]
Deep Eutectic Solvent	Ni	112.6 ± 3	18.6 ± 2	93.9 ± 2	79.3 ± 4.1	[2]
Deep Eutectic Solvent	Ag	151.4 ± 4	18.4 ± 2	132.9 ± 3	82.9 ± 2.2	[4]

* All smoothing efficiency measurements reported as a % out of 100.

Table 3. Average recorded step heights in μm for five copper samples after treatment with the respective electrolytes listed at 70 °C for 900 s.

Electrolyte	Step Height (μm)
Deep Eutectic Solvent	20.2 ± 0.2
Phosphoric Acid	24.0 ± 0.4

Electropolishing copper specimens with phosphoric acid revealed a steady incline from 0 to 1.25 V with an initial peak at 0.54 A/cm^2 and with an immediate decline to a local minimum of 0.37 A/cm^2 at 1.5 V. After this local minimum, the incline rate increased at 2.25 V and remained constant until nearly 3 V where, much like the deep eutectic solvent curve for copper electropolishing, it reached a point of irreproducibility (Figure 2A).

After surveying the local maxima and minima present in the linear sweep voltammogram, 1.5 V was selected to run chronoamperometry (Figure 2B). With the voltage fixed at 1.5 V, the current would not only be checked to authenticate the linear sweep voltammogram for relative accuracy, but the optimum voltage could be confirmed while revealing a resulting current density across the exposed surface used for polishing. The current range from chronoamperometry was 0.34 to 0.30 A/cm^2 in the form of a very gradual decline nearly identical to the chronoamperogram produced by the deep eutectic solvent, with the exception of a significantly higher current (Figure 2B). When compared to the copper sample weight prior to electropolishing treatments, the mass difference was calculated to be 0.053 g for an electropolishing rate of 73.44 µg/s (Table 1). Comparisons with other similar pure metals revealed that the smoothing efficiency of the deep eutectic solvent in this paper was greater than those observed in the external literature using the same deep eutectic solvent under similar electropolishing conditions (Table 2).

A recorded roughness average of 82.6 ± 6 nm for phosphoric acid electropolishing revealed that a roughness difference of 85.0 ± 5 nm exists between the original as-received sample roughness and the subsequent electrochemical testing reported (Table 3). It can be noted that, although pitting affected the phosphoric acid representative polish of the total region, there were extreme peaks and troughs left due to pitting at low current densities. Hydrogen contamination can be observed to affect the overall roughness average of the region, with an average roughness of 16 ± 2 nm in a 4.5 × 4.5 µm recording region (Figure 4A). A step height analysis revealed a vertical step distance of 24.0 µm etched away from the original copper metal surface during electropolishing (Table 3).

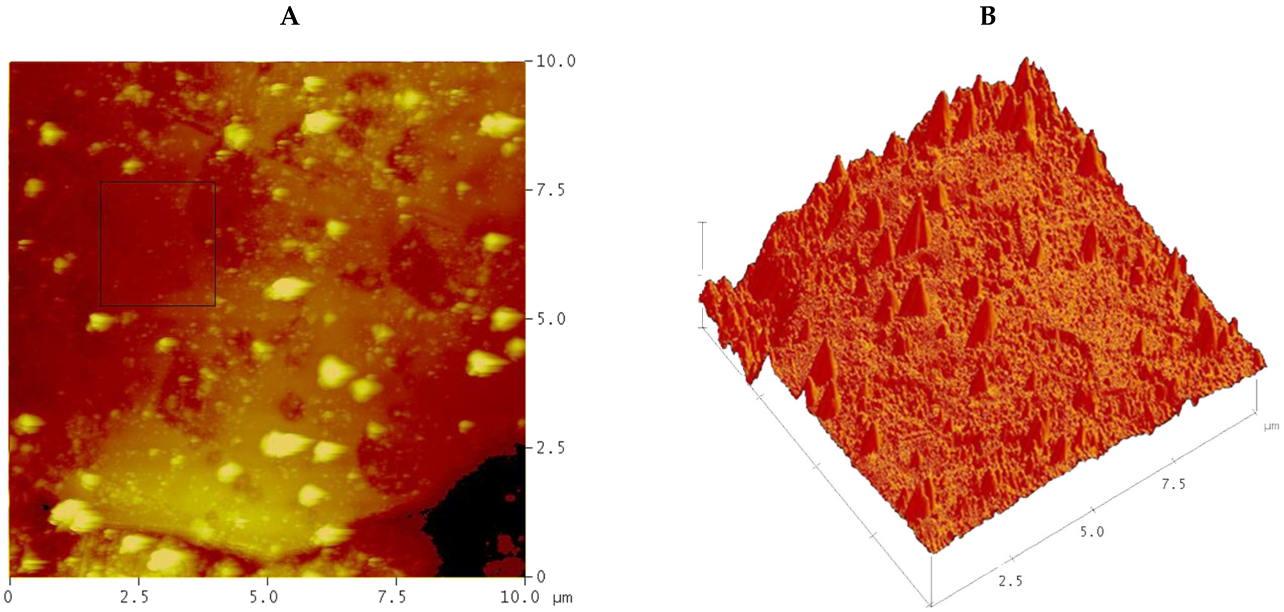


Figure 4. AFM of copper post-electropolishing with phosphoric acid in 2D (**A**) and 3D (**B**), recording an average roughness of 82.6 ± 6 nm by utilizing the roughness average method for calculation. A 10 × 10 µm recording region was utilized. AFM Z-axis = 100 nm/div. The yellow pattern shown in the bottom center of A is an example of aberrant hydrogen contamination.

4. Discussion

The electropolishing rate for copper with phosphoric acid was reported as 73.44 µg/s, whereas treatments via the deep eutectic solvent electrolyte yielded a less comprehensive polishing rate of 59.44 µg/s (Table 1). When comparing step height of both samples, it was again confirmed that the etching efficiency was higher for phosphoric acid treatments with copper, measuring at 24.0 μm, compared to a step height of only 20.0 μm reported for deep eutectic solvent electropolishing results (Table 3).

Roughness averages for copper samples using both electrolytes shared little in common (Table 2). The roughness difference for the deep eutectic solvent was reported as 152.4 ± 3 nm, whereas phosphoric acid treatments reported an overall change in roughness from pre-treatment to post-treatment of 85.0 ± 5 nm (Table 2). This difference being nearly double for the deep eutectic solvent mixture, the indication is clearly that the phosphoric acid mixtures are utilized for their superior rate of etching, and not for their overall smoothing efficiency [9]. Providing roughness averages to consider, a post-treatment roughness analysis revealed heavy splotching in the copper samples treated with phosphoric acid, which is only further accentuated by a view of the accompanying 3D microscale terrain map. With a reported roughness average of 82.6 ± 6 nm, the phosphoric acid solution revealed significant peaks and residual splotches likely caused by oxidation at the metal's surface during electropolishing (Figure 4) [10].

Throughout the 900-s electropolishing experiment, a chemical reaction occurred at the anode immersed in the deep eutectic solvent due to the oxidation of Cu and the formation of $CuCl_2$ (Equation (1)). This is notably similar to the literature documenting reactions with high-purity nickel noted in [2]:

$$\mathrm{Cu} \rightarrow 2\mathrm{e}^- + \mathrm{Cu}^{2+} \xrightarrow{2\mathrm{Cl}^-} \mathrm{CuCl_2} \tag{1}$$

We observed the presence of trimethylamine, ethanol, ethylene glycol and other products, with the incidence of trimethylamine being accounted for by the Hofmann elimination of the choline base as choline hydroxide (Equation (2)):

$$\mathrm{(CH_3)_3NCH_2CH_2OH} + {}^-\mathrm{OH} \rightarrow \mathrm{N(CH_3)_3} + \mathrm{H_2O} + \mathrm{HOCH_2} = \mathrm{CH_2} \leftrightarrow \mathrm{O} = \mathrm{CH_2CH_3} \tag{2}$$

The reduction reaction at the cathode (counter electrode) involves the decomposition of choline by the formation of a choline radical via the acceptance of an electron:

$$\mathrm{(CH_3)_3NCH_2CH_2OH} \xrightarrow{+\mathrm{e}^-} [\mathrm{(CH_3)_3NCH_2CH_2OH}]^{\blacksquare} \rightarrow \mathrm{N(CH_3)_3} + {}^{\blacksquare}\mathrm{CH_2CH_2OH} \tag{3}$$

Thus, the transient choline radical, depicted in parentheses (Equation (3)), results from the addition of an electron from the anode at the cathode, and quickly decomposes to trimethylamine [2]. A review of the literature also indicates that the residual pitting on the surface of the metal not only affects surface reflectivity, but also is likely to affect conductivity due to increased surface area [11–13]. The plentiful abrasions and bumps generated during the electropolishing procedure (clearly visible in AFM imagery) are a result of bubbles formed on the metal's surface during electropolishing. With significant proportions of the metal surface being deteriorated per second, the bubbling that occurs at the cathode can often leave these marks as they pop on the metal's surface, sometimes marring the newly treated surface (Figure 5B) [12,14].

Once electropolishing is complete, surface scrapes seem mostly absent from both the phosphoric acid and acid-free treatments. Although some of the surface reflectivity of the metal seems contained in the smoothed outlines of the present scratches, the roughness is relatively unaffected with an average of 14.7 ± 2 nm (Figure 3) [11]. With the aberrant marring of the copper sample during phosphoric acid electropolishing treatments, the roughness average greatly suffers (82.6 ± 6 nm), with intermittent peaks that caused the silicon tip attached to the AFM cantilever to become stuck during the trace and retrace of scattered spots on the copper metal surface. This occurred during two discarded post-electropolishing surveys, which required tip replacement and AFM recalibration (Figure 4) [2,12].

This exchange is heavily recorded in the literature regarding electropolishing and extensive use of hydrogen evolution at the cathode as a driver for this type of pitting. The bubbles tend to form at points in the range when low current densities occur in the electropolishing procedure [15]. This tends to happen towards the end of the trial, when most of the originally protruding surfaces to be polished and deteriorated away have been removed [16,17]. When this occurs, the associated chronoamperogram reports a slow and steady decline, as the remaining surface area available to be electropolished slowly decreases at the rate recorded in Table 1.

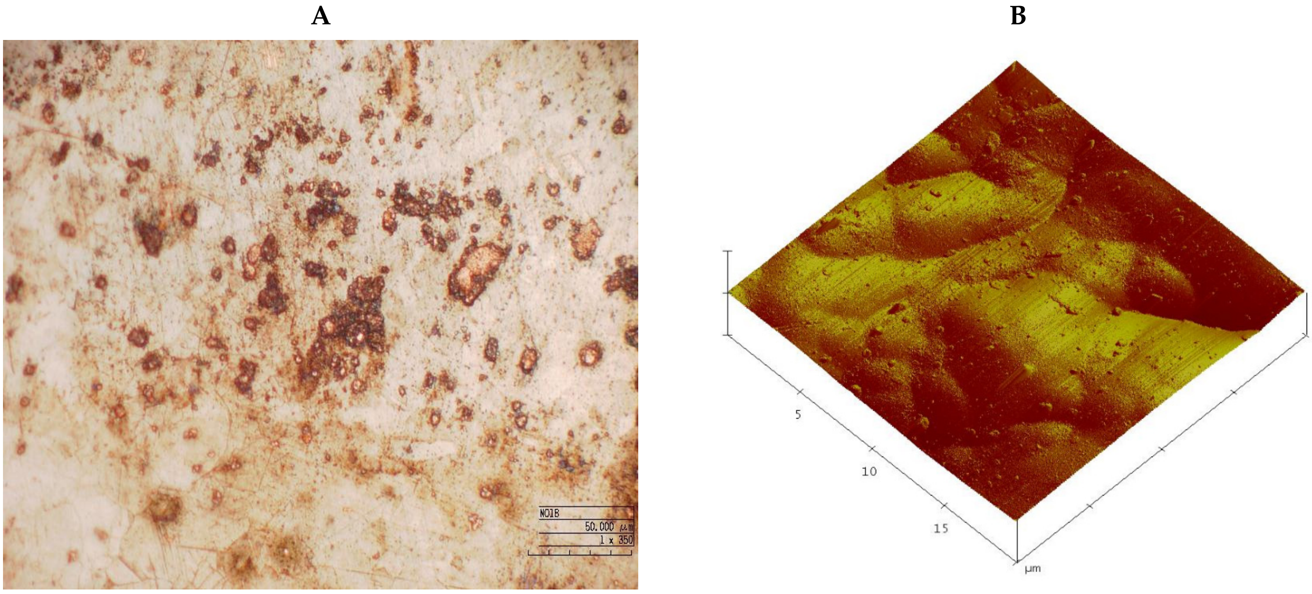


Figure 5. Comparative imagery of a copper sample electropolished with 1 M phosphoric acid. Digital microscopy (**A**) at 1 × 350 μm resolution displays surface marring resulting from pitting at low current densities. (**B**) AFM of a 20 × 20 μm area shows residual pitting on the copper surface. AFM *Z*-axis = 100 nm/div.

Pitting tends to occur at low current densities, or when the current applied through the 2 cm^2 exposed surface of the metal is occurring over less and less surface area as the sample is being polished [1,18]. This pitting is relatively inevitable, since the concept of electropolishing is to always have less surface area than prior to treatment [19]. With good fortune, this decreased surface area will be accompanied by the benefit of an overall smoother surface and heightened electroconductivity properties as electrical impulses will have less distance to dissipate along the microscale surface of the metal over significant distances [13]. For this to occur, the protruding peaks, Figure 1A,B, must somehow be electropolished at a faster rate than the average surface in the working electrode surface. Provided that all of these interactions occur appropriately at the metal's surface and at the proper prescribed rates, an efficient electropolishing treatment can be achieved [11].

5. Conclusions

Electropolishing treatments of high-purity copper metal using a phosphoric acid electrolyte mixture etched at a faster rate than the deep eutectic solvent electropolishing treatments, including those observed in other pure metals surveyed in the literature. This distinction is likely to be the reason why the global industry has made it and other acid solutions the standard for electropolishing. The caveat of this fast rate of polishing is that this acid-based method of electropolishing facilitates extensive hydrogen evolution at the working metal cathode, causing pitting at low current densities or bubbling that ultimately mars the treated surfaces of acid polished samples. This occurrence of overpotentials causes the roughness of copper metals to yield more favorable results for average roughness with the utilization of the deep eutectic solvent medium comprised of ethylene glycol and choline chloride. Electropolishing copper with a deep eutectic solvent comprised of (2:1) ethylene glycol and choline chloride resulted in a mirror finish and a post-treatment surface 8× smoother than the original metal surface prior to electropolishing treatments with a smoothing efficiency of 91.1 ± 1.5%.

Regarding the replacement of the industry standard 1 M phosphoric acid mixture, it is likely that the deep eutectic solvent mixture could replace phosphoric acid as an efficient electrolyte for polishing on the grounds that smoother surfaces are generated. The deep eutectic solvent mixture additionally provides the added benefits of recyclability without loss of electropolishing efficiency to present an ecologically friendly supplement for the electropolishing of high-purity copper metals.

Author Contributions: Conceptualization, validation, formal analysis, investigation, resources, supervision, writing, review and editing, T.M.A.-F.; Data curation, documented the results, and wrote the paper draft, J.D.L. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no conflict of interest.

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