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Article

Electropolishing of Aluminum at Room Temperature Using a Green DES of Choline Chloride and Propylene Glycol

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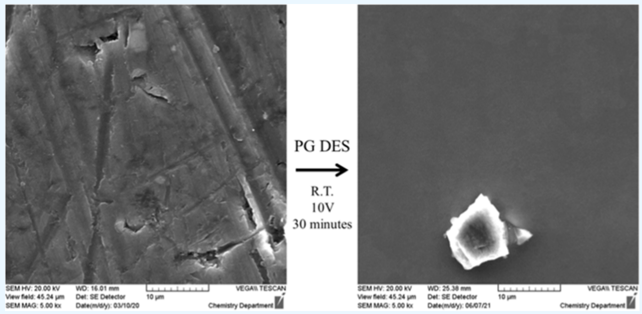

ABSTRACT: For applications of aluminum where the smoothness or reflectivity of the aluminum matters, electropolishing is necessary to polish the aluminum surface sufficiently. This electropolishing is traditionally done with hazardous solutions in non-ideal conditions, such as low-temperature perchloric acid−ethanol mixtures. Here, we describe electropolishing of aluminum using a deep eutectic system composed of propylene glycol and choline chloride, with polishing accomplished at room temperature and using an inexpensive apparatus. This polishing was performed using both 99.5 and 99.99% pure aluminum, and scanning electron microscopy images show substantial improvement with both purities of aluminum. In addition, reflectivity measurements show significant improvement over sanding of aluminum. This method provides a simple, green method for electropolishing aluminum that can be used in any research where careful polishing of aluminum is necessary.

■ INTRODUCTION

Aluminum is a low-density metal used widely in construction and aerospace.[1] It is ductile, malleable, and has a low melting point of 660 °C, all of which allow it to work easily. Aluminum is also a good thermal and electrical conductor, comparable to copper, while being much less dense. It is low cost in comparison to other metals and forms a protective oxide layer that prevents rust and contributes to its corrosion resistance. For applications of aluminum where reflectivity matters, such as reflectors, it is important for the aluminum surface to be as smooth as possible.

For attempts to obtain smooth aluminum at a macro-level, sanding is the traditionally used method (as it is for most metals). Some chemical polishing methods are also employed, including exposure of aluminum briefly to nitric acid or to a hydroxide solution.[2,3] These methods can produce smooth aluminum at a macro-level but are generally unable to obtain a smooth aluminum surface suitable for applications at the micro-level.

For micro-level smooth aluminum surfaces, electropolishing is required. The fundamental principle of electropolishing is the formation of an electrolytic cell, with the aluminum as the anode suspended in the electropolishing solution. The electric current oxidizes the aluminum preferentially on the surface, that is, on the micro-peaks found on the surface.[4,5] This is due to an increased electric field found at the peaks. When the peaks get oxidized, the aluminum eventually becomes completely smooth, and the aluminum is oxidized at an equal rate across the entire sample.

An ideal electropolishing solution has a high viscosity and a high electrical conductivity, as these contribute to mass-transfer control for the polishing process.[6,7] This allows for the rate of aluminum ions leaving to be controlled, improving the polishing and allowing for the micro-peaks to be smoothed out.

Traditionally, electropolishing of aluminum is often performed using a perchloric acid−ethanol solution.[6] Temperatures are generally kept below 10 °C, and the potential used is generally around 20 V. Perchloric acid is not an ideal electropolishing solution, from the perspective of safety as well as environmental concerns. Perchloric acid can form shock-sensitive perchlorate salts in the ductwork of hoods and is often used in designated hoods. It can react violently with organics, similar to nitric acid, and is generally a safety concern. Waste concerns are also evident with perchloric acid, as the explosive perchlorate salts can form in these waste bottles. Perchlorates are a considerable environmental hazard and have negative effects on human health, disrupting the thyroid.[8] Although it can be used to electropolish aluminum and can provide good results, perchloric acid is difficult to use safely and is an environmental concern.

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One major area that is traditionally difficult to make completely safe and environmentally friendly is solvents, as many solvents are volatile and may have negative impacts on both the health of humans and the environment. It is in this area that deep eutectic solvents (DESs) can be used as alternative solvents. DESs are very broadly defined as a mixture of two substances that, when mixed, form a mixture that has a melting point below either of the two substances (a eutectic mixture).[9] Being considered a "deep" eutectic is not universally agreed upon but is generally considered to be when the melting point of the eutectic is substantially lowered; this distinction is often overlooked. These mixtures generally consist of a quaternary ammonium salt with a molecular compound that acts as a hydrogen bond donor; often the quaternary ammonium salt is a halide, the most used being chlorides. Although often compared to ionic liquids, DESs differ in that, unlike ionic liquids, they do not contain only discrete ions. On the contrary, the lowering in the melting point is attributed to the hydrogen bond donation to the chloride anion. Physically, they behave similarly to ionic liquids, but their chemical makeup differs.

These eutectic mixtures, similar to ionic liquids, have some useful characteristics that make them attractive as green alternatives for solvents. They generally have very low vapor pressures and are often environmentally friendly and not a health risk to humans.

Even compared to ionic liquids, they tend to be less hazardous; however, compared to ionic liquids, DESs are sometimes more reactive.[9]

Although the first paper on DESs was published relatively recently in 2001, research into the uses of these solvents has increased significantly since that first publication. Uses of DESs are varied, including but not limited to metal electrodeposition,[10] metal extraction, metal electropolishing, carbon dioxide and other gas adsorption, drug solubilization, polymer synthesis biotransformations, and biodiesel purification.[9,11,12] With respect to electropolishing, DESs have been shown to electropolish stainless steel,[13−15] nickel, and cobalt[16] as well as some nickel superalloys.[17]

Recently, it has been shown that a DES containing choline chloride and ethylene glycol could electropolish aluminum at room temperature.[18] This solution, compared to perchloric acid solutions, is reasonably neutral and reasonably safe for brief contact with human skin. It also has a very low vapor pressure, also benefiting its safety. The drawback to this solution is the incorporation of ethylene glycol, as ethylene glycol poses concerns for both human toxicity and waste disposal. This solution, though, is able to obtain the desired high viscosity and high electrical conductivity desired for electropolishing, without being acidic or basic like other electropolishing methods.

Other DESs can be formed with choline chloride, and DESs made from choline chloride and propylene glycol have been shown to have conductivity and viscosity similar to those made from choline chloride and ethylene glycol, albeit with lower conductivity.[19] Propylene glycol is less of a concern for human toxicity and waste disposal than ethylene glycol and is used as an additive in food and personal care products like deodorants.

Herein, we show that a green DES made from choline chloride and propylene glycol can be used to electropolish aluminum at room temperature, using an inexpensive apparatus.

■ EXPERIMENTAL SECTION

To prepare the propylene glycol DES, choline chloride (99%, Acros Organics) and propylene glycol (MP Biomedicals, LLC) were dried in an oven for 12 h at 90 °C and then stored in a desiccator. The propylene glycol and choline chloride DES was prepared in molar ratios of 2.5−3:1 of propylene glycol and choline chloride. This solution was stirred vigorously and heated to 70 °C. Once a clear, viscous solution was produced, the solution was heated for one additional hour.

99.5% pure aluminum with a thickness of 0.5 mm (Advent Chemicals Ltd) and 99.99% pure aluminum with a thickness of 0.5 mm (Alfa Aesar) were cut into pieces roughly 10 cm by 10 cm and placed into a furnace from Evenheat Kiln Inc. to be annealed at 500 °C for 7 days under ambient atmosphere. The annealed aluminum was then punched into circles with diameters of either 1.27 or 3.125 cm. These circles were sanded by hand using sandpaper with grits of 500, 5000, and 7000 (3M). Following sanding, a small hole was punched into each aluminum circle using a small screwdriver. Through this small hole (roughly 2 mm in diameter), a piece of 99.9% aluminum wire (1 mm diameter, Aldrich) was threaded. This wire was then made equal on either side of the small hole and clamped with pliers to produce a wire lead to the aluminum piece. To insulate the back side and edges of the aluminum circle, including areas where the aluminum wire was threaded, a GB liquid tape was applied and allowed to dry in a fume hood overnight to set.

For electropolishing experiments, approximately 100 mL of the propylene glycol DES was placed in a beaker with stir bar. A stainless steel cathode (Type 304, Jets Inc.) was placed in the beaker as well as the aluminum sample. Both electrodes were connected to a BK Precision 1698 power supply, which was then connected to a Fluke 45 DMM. The Fluke 45 was connected to a computer, and a LabVIEW 8.2 program was used to capture data.

For scanning electron microscopy (SEM) imaging, all imaging was done using the Tescan Vega II W-SEM located at CSU-Pueblo. The accelerating potential was generally 20 kV, with working distances between 15 and 25 mm. Normal scattering detection was used, with no back-scattering detector being involved in any images. As the samples were conductive, no sample coating was performed.

For atomic force microscopy (AFM) imaging, all imaging was done using a PicoSPM from Molecular Imaging using the Picoscan 5.3.3 software, located at CSU-Pueblo. The images were obtained in a contact mode with a silicon nitride tip. Images were leveled with a first-order leveling, and the software VisualSPM from Molecular Imaging was used to calculate RMS roughness.

■ RESULTS AND DISCUSSION

The lowest molar ratio of propylene glycol to choline chloride that was found to maintain a liquid DES in normal atmospheric conditions was 2.5:1, with ratios up to 3:1 being used successfully in electropolishing of aluminum. However, all ratios used from 2.5:1 to 3:1, except 2.7:1, would not maintain a DES in normal atmosphere for an entire electropolishing experiment (for the low values) or would not consistently polish aluminum (and would instead produce a white appearance on the aluminum rather than a mirror-like finish). The best ratio was 2.7:1, which is the ratio used in all results shown. This ratio provided consistency of the polish and was

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able to be used multiple times under normal atmospheric conditions without a loss in polishing capability. This reusability allowed for one solution to produce multiple samples of consistent polish, so the results shown are all using the ratio of 2.7:1.

A potential of 10 V was applied, with a stainless steel plate used as a cathode, which allowed for both 99.5 and 99.99% aluminum to be electropolished with a current density of 8 and 6 mA/cm^2, respectively. No other potentials attempted resulted in polished samples. Previously reported values for electropolishing of aluminum using an ethylene glycol DES[18] were higher at approximately 10 mA/cm^2, as expected from the lower conductivity propylene glycol DES.

SEM was used to determine the effectiveness of the electropolishing at a microscopic level. Figure 1 shows the

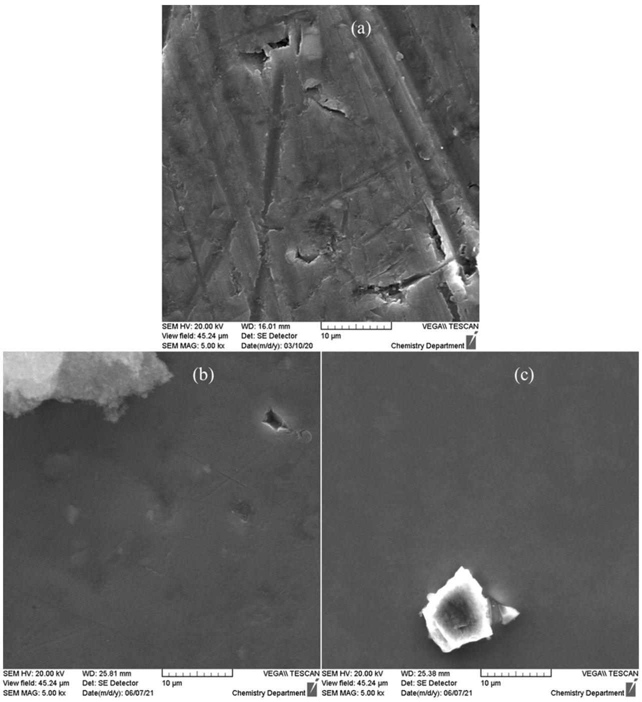

Figure 1. SEM images of aluminum. (a) Sanded aluminum with no electropolishing, (b) 99.5% pure aluminum electropolished in a propylene glycol DES, and (c) 99.99% pure aluminum electropolished in a propylene glycol DES. Artifacts kept to show surface focus.

SEM imaging of (a) a piece of sanded aluminum, showing the aluminum surface before any electropolishing; (b) 99.5% aluminum electropolished in the propylene glycol DES for 20 min; and (c) 99.99% aluminum electropolished in the DES for 25 min. The SEM images show substantial improvement in the smoothness of aluminum for both purities of aluminum, with an expected and more pronounced improvement when using the higher purity aluminum. While the less pure aluminum is less expensive, the SEM image of the less pure aluminum shows that the electropolishing procedure produces a less polished surface when performed on less pure aluminum. The plots of current density for both purities of aluminum are shown in Figure 2. These plots show the current being consistent over long periods of time.

AFM was used to determine the roughness of the surface at a microscopic level, which correlates to the level of polish achieved by the electropolishing. Figure 3 shows the AFM imaging of (a) a sanded piece of aluminum before electro-

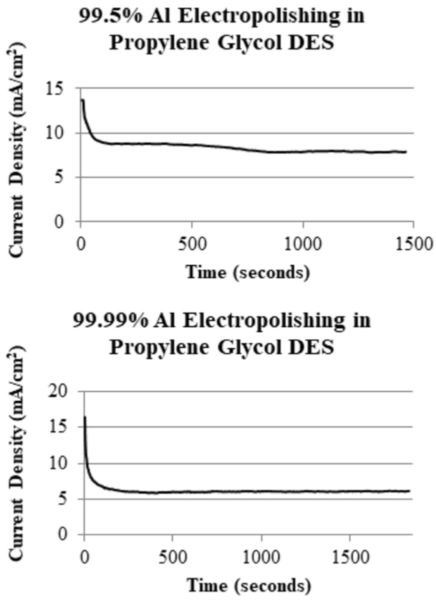

Figure 2. Current density vs time for the electropolishing of 99.5 and 99.99% aluminum in a propylene glycol DES.

polishing and (b) 99.99% aluminum electropolished in the DES for 25 min. The RMS roughness of the sanded aluminum was calculated as 171 nm, whereas the electropolished aluminum had an RMS roughness of 27 nm. This significant improvement in RMS roughness indicates an improvement in the overall smoothness of the aluminum from the electropolishing process. The decrease in RMS roughness (84%) is comparable to the surface roughness decrease as previously reported using an ethylene glycol DES[18] (50%), taking into account the longer electropolishing time used here compared to that report.

In order to determine the improvement of the reflectivity of the aluminum that resulted from the electropolishing, the aluminum was used as a mirror for a 532 nm laser. The power was measured before the mirror and after the mirror, with the ratio being the reflectivity of the aluminum. This reflectivity is a measure of the amount of light from the laser that remained unscattered, and a more reflective and polished surface will scatter the light less. Table 1 shows these results for the sanded aluminum, 99.5% aluminum electropolished in the DES, and 99.99% aluminum electropolished in the DES. Substantial improvement is seen from both purities of aluminum.

To attempt to quantify the improvement of the electropolishing with respect to the principles of green chemistry, a quantitative metric system was required. The DOZN 2.0 system[20] from MilliporeSigma was used to satisfy this requirement. In the DOZN system, a higher score indicates that the system is less environmentally friendly, and each of the categories is based on one of the 12 principles of green chemistry. For example, prevention corresponds to the principle that it is better to prevent the creation of waste than to create a method to clean up waste. The method of electropolishing shown here, using a propylene glycol DES at room temperature, was compared to the traditionally used method of electropolishing in lower temperatures (10 °C) using a mixture of 1 part concentrated perchloric acid to 4 parts ethanol and was also compared to the use of a 2:1 ethylene glycol/choline chloride DES. The results from the DOZN 2.0 system are shown in Table 2.

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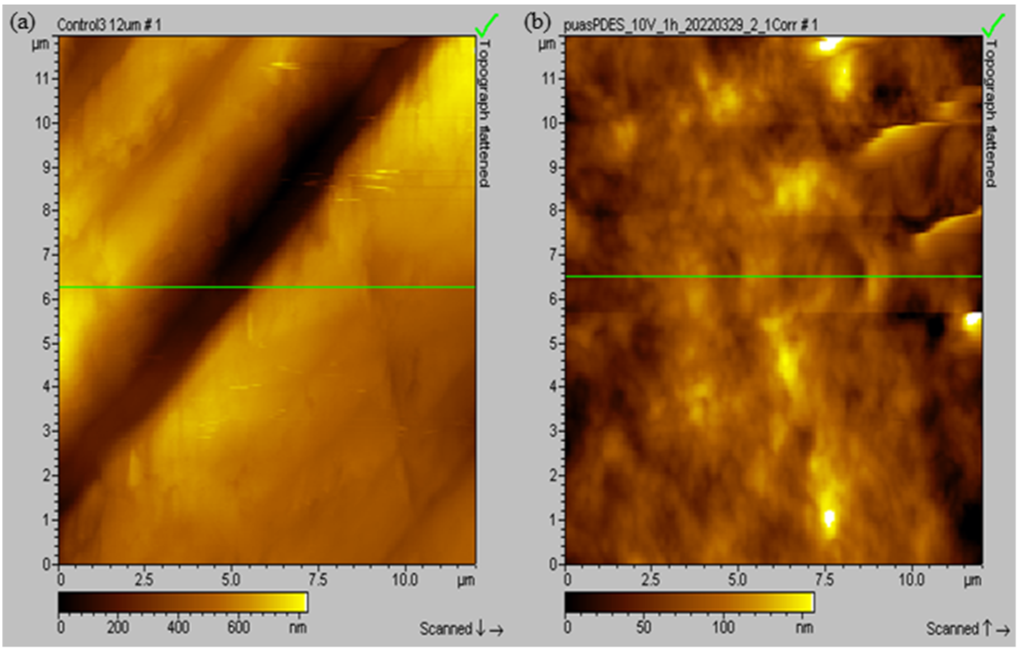

Figure 3. AFM images of aluminum. (a) Sanded aluminum with no electropolishing. (b) 99.99% pure aluminum electropolished in a propylene glycol DES.

Table 1. Comparison of Reflected Power Detected before and after Propylene Glycol DES Electropolishing

sample	before mirror power (mW)	after mirror power (mW)	reflected power
sanded Al	20.12	7.20	0.358
electropolished 99.5% Al	19.63	15.36	0.782
electropolished 99.99% Al	20.16	17.23	0.855

Table 2. DOZN 2.0 Results Comparing Perchloric Acid, Ethylene Glycol DES, and Propylene Glycol DES Electropolishing Methods

principle	PA score	EG DES score	PG DES score
1. prevention	198.4	0.000	0.000
2. atom economy	38.80	56.10	52.00
3. less hazardous chemical synthesis	169.5	228.40	53.00
4. designing safer chemicals	5.260	5.000	2.000
5. safer solvents and auxiliaries	35.67	60.10	0.000
6. design for energy efficiency	12.93	0.000	0.000
7. use of renewable feedstocks	38.80	56.10	52.00
12. inherently safer chemistry for accident prevention	137.0	57.10	53.00
Categories			
improved resource use	92.00	37.40	34.67
increased energy efficiency	12.93	0.000	0.000
reduced human and environmental hazards	86.86	87.65	27.00
overall	191.8	125.05	61.67
aggregate	3.8	2.5	1.2

As Table 2 shows, there is an improvement over perchloric acid in all principles except atom economy and use of renewable feedstocks. The propylene glycol DES uses a solution that contains more mass, and therefore, it has a worse atom economy. Because none of the materials were made from renewable sources (the material produced from a renewable biological system, such as being taken from plant material), the same reasoning applies to the worse use of renewable feedstocks. Effectively, more mass derived from nonrenewable sources is used. For all other principles, there is a significant improvement. Each of the three categories also has significant improvement, and the combined improvement can be considered to be 67.8% using the DOZN 2.0 system. When comparing the propylene glycol DES to an ethylene glycol DES, the propylene glycol DES shows an improvement in every category, but most notably an improvement in less hazardous chemical synthesis and safer solvents and auxillaries.

In summary, a DES consisting of propylene glycol and choline chloride has been shown to be a green, effective material for electropolishing of aluminum. SEM images show substantially fewer defects in the surface of the aluminum after electropolishing, and reflectivity measurements show a marked improvement of the reflectivity of the aluminum following electropolishing. In comparison to electropolishing with perchloric acid, the DES is better with respect to almost every principle of green chemistry. Because of the ability to use the DES at room temperature and with an inexpensive apparatus, this method would be available to any researcher and would improve both the safety and the environmental impact of any such research requiring polished aluminum.

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Notes

The authors declare no competing financial interest.

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■ ABBREVIATIONS

DES, deep eutectic solvent; SEM, scanning electron microscopy; PG, propylene glycol; PA, perchloric acid; EG, ethylene glycol

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