

Electroplating of Aluminium Using AlCl₃-urea Deep Eutectic Solvent (DES) with Protective Layer in Air

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1. Introduction

Aluminium (Al), renowned for being lightweight, durable, and remarkably corrosion-resistant, holds promise in various fields, especially for nuclear applications. One of its notable properties is its resistance to corrosion, making it an attractive material choice to use in conjunction with materials usually used in the nuclear industry such as Fe, Cr, and Ni.

One prevalent method of Al deposition is electroplating. Unlike other methods that demand high temperatures, electroplating offers numerous benefits. It allows for a high-quality, uniform coating, exhibits excellent adhesion to substrates, and can cover intricate shapes. Moreover, the coating thickness can be controlled.

However, Al presents a unique challenge due to its extremely negative standard reduction potential. When electrodeposition is carried out in an aqueous electrolyte, hydrogen evolution occurs, leading to a decrease in electrodeposition efficiency. As a result, the electroplating process needs to be conducted using non-aqueous electrolytes rather than aqueous ones. Further complicating matters, most electrolytes used for Al electroplating react severely with oxygen and moisture. Hence, Al electroplating typically takes place under nitrogen or argon atmospheres. While this method is effective, maintaining such conditions is not cost-efficient.

Given this backdrop, our research endeavours to explore the possibility of electrodepositing Al in ambient air conditions. Central to this exploration is the choice of the electrolyte, a conductive medium essential for the current flow during electroplating. We have selected Deep Eutectic Solvents (DES) as our preferred electrolyte. DES exhibits a lower melting point than its individual components, making it predominantly liquid at room temperature. Furthermore, DES not only has a broad electrochemical window, but is also economical, environmentally friendlier, more biodegradable, and exhibits greater stability compared to conventional solvents used for electroplating. [1]. Specifically, we

chose AlCl₃-urea DES, classified as a type 4 DES, for Al electroplating considering its cost-effectiveness.

To enhance the feasibility of electrodeposition in the open air, we introduce decane as a protective layer. Decane is recognized for its stable molecular structure, and its inclusion aims to safeguard the electroplating process against potential atmospheric disruptions. [2]

If successful, this innovative approach not only offers a more cost-effective solution for Al electroplating but also holds potential for co-electrodeposition with other metals that typically pair with Al, making it applicable for materials used in nuclear industry.

2. Method and Results

In this section, we detail the chemicals, materials, experimental methods, and characterization techniques employed in our research.

2.1 Chemical and materials

The anhydrous Al chloride (99.985%), decane (99%) and Al granules 8-12 mm (99.9%, metal basis) were purchased by Alfa Aesar (USA). urea (99%) and Al wire (99.999%) were supplied from Sigma-Aldrich Co. (USA). Disk-type copper specimens ($\geq 99\%$) were custom-designed (Φ : 14mm, thickness: 2.1 mm) to fit an electrode holder. The electrode holder ensures that 1cm² of copper is exposed to the electrolyte.

2.2 Synthesis of AlCl₃-urea DES

An AlCl₃-urea DES was synthesized inside an argon-filled glovebox (oxygen and moisture levels below 5 ppm) by carefully blending anhydrous Al chloride with urea. Subsequently, pretreated Al granules were immersed in the DES for 48 hours to purify it by removing residual Hydrochloric Acid (HCl) (Fig. 1) [3].



Fig. 1. Purification of AlCl_3 -urea DES (molar ratio: 1.4:1) after synthesis

2.3 Electrochemical behaviour

To understand how changes in the speciation of ions in the electrolyte influences the electrochemical behaviour, we conducted Raman spectroscopy and cyclic voltammetry studies.

To monitor the change in the speciation of AlCl_4^- , Al_2Cl_7^- (electro-active anion) in the electrolyte with the presence of decane as a function of time, we employed Raman spectroscopy for each sample extracted from the bottom part of the electrolyte. Each sample was drawn at three-day intervals over a period of two weeks (Fig. 2).

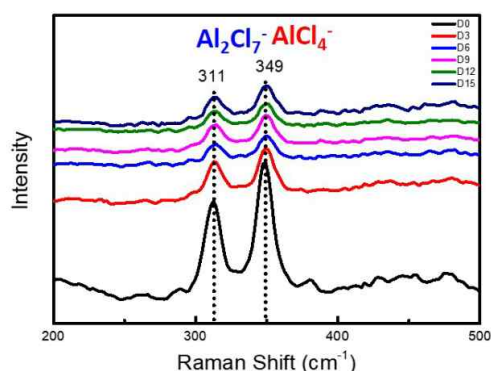


Fig. 2. Variation in the anion composition of AlCl_3 -urea with respect to the time left in the presence of decane via Raman spectroscopy.

Cyclic voltammetry was performed every single day for one week with a scan range of -1.5 V to 1.5 V and a scan rate of 10 mV / s. For working electrodes, the Cu disk electrode and a Pt rod were utilized.

Additionally, the variations in conductivity of AlCl_3 -urea electrolyte with decane were measured over a one-week period.

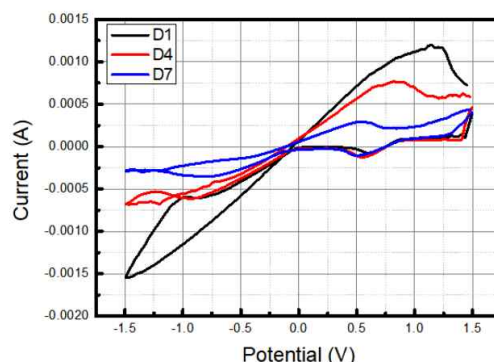


Fig. 3. Cyclic voltammetry plot using copper-disk electrode as working (Φ : 2 mm) with a scan range of -1.5 V to 1.5V and a scan rate of 10 mV/s

Based on the results, it is evident that decane influences the speciation of ions in the electrolyte, leading to a decrease in current flow over time (Fig. 3).

2.4 Electrodeposition

Electrodeposition was performed with two kinds of methods, which are galvanostatic polarization (GP) and bipolar current pulse polarization (BCP) as can be seen in the following figures (Fig. 4).

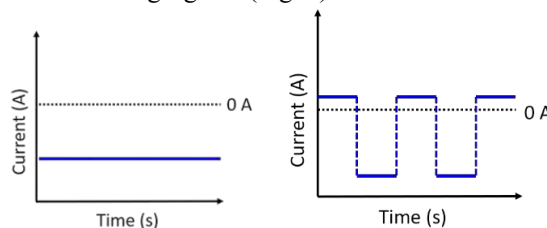


Fig. 4. Galvanostatic polarization method (left), bipolar current pulse polarization method (right) [4].

The electrochemical cell was designed for Al electrodeposition as follows (Fig. 5).

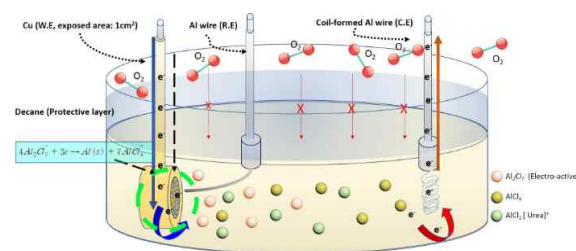


Fig. 5. Electrochemical cell setting.

Electrodeposition was conducted at specific intervals: immediately after taking it out from the glovebox, three days, and seven days later. At each interval, the electrodeposition was executed using both methods.

For GP, a current density of -10 mA / cm^2 was maintained for 3,600s with agitation of 500 rpm at 60 C. In contrast, for BCP, while the cathodic current was the

same as GP, an anodic current density of 1 mA/cm^2 was employed. Both the cathodic and anodic current densities were applied for durations of 0.25 s per cycle. The total current-applied time was 7,200 s (Fig. 6).

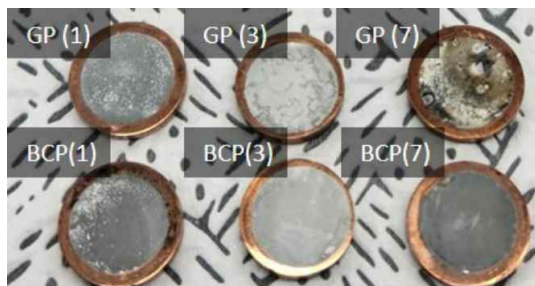


Fig. 6. Images of Al deposits on the copper substrates

2.5 Characterization of deposit

To analyze the structure of these deposits such as crystal structure and phase conformations on the surface, X-ray diffraction (XRD) was performed with a 2-theta value range of 10 to 100 [5].

To confirm the morphology and microstructural formation of the deposits Field scanning electron microscopy (FESEM) (Fig. 7) and Electron dispersive spectroscopy (EDS) was conducted (Fig. 8).

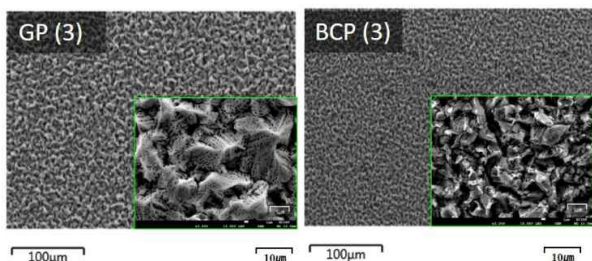


Fig. 7. SEM images of GP (3) and BCP (3)

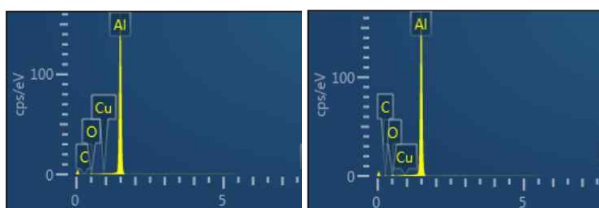


Fig. 8. EDS composition analysis of GP (3) and BCP (3)

2.5 Electrodeposition efficiency

For deposits obtained from electrodeposition, Faraday's efficiency was calculated by comparing the variation of before and after mass with theoretical mass.

3. Conclusions

We sought to develop a method of Al electrodeposition from AlCl_3 -urea DES in air. To achieve this purpose, we studied the influence of decane as a protective layer to allow the electrodeposition to occur without additional

atmospheric controls. Contrary to our initial expectation, decane gradually reacted with DES, impacting the speciation of the electrolyte. Nevertheless, it was observed that the electrochemical system remained operational for a relatively short period, approximately three days.

Regarding electrodeposition techniques, the Bipolar current pulse polarization (BCP) method worked more effectively compared to the Galvanostatic polarization method (GP).

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