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*The Conference is dedicated to the*

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## *E - Electrochemistry*

## MORPHOLOGY OF ALUMINIUM ELECTRODEPOSITED ON ALUMINIUM FROM $\text{AlCl}_3$ +UREA SOLVATE IONIC LIQUID

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### ABSTRACT

The ionic liquid, made of urea and  $\text{AlCl}_3$ , known as deep eutectic solvent (DESs) has already shown to be low-cost electrolyte suitable for aluminum electrodeposition. By applying appropriate potentiostatic or galvanostatic electrolysis regime, aluminium is successfully electrodeposited from the deep eutectic solvent onto aluminium substrate at nearly room temperatures. Morphologies of the produced deposits were characterized by scanning electron microscopy (SEM) and chemical composition by energy-dispersive X-ray (EDX) analysis. The electrodeposited aluminium displayed different morphology depending on the deposition conditions applied.

### INTRODUCTION

Because of outstanding thermal properties, electric conductivity, light weight, and good corrosion resistance aluminium and its alloys are very significant [1,2,3]. It is now common knowledge that aluminium cannot be electrodeposited from aqueous electrolyte because its standard potential is much more negative than standard potential of hydrogen evolution ( $-1.662$  V vs NHE). Therefore, the majority of the electrolytes investigated for possible Al electrodeposition are inorganic molten salts at elevated temperatures, mostly composed from  $\text{AlCl}_3$  and NaCl, KCl and LiCl [4,5]. Research efforts have also been directed towards finding even more suitable non aqueous electrolytes applicable for Al deposition close to room temperatures. It was found that novel electrolytes, called ionic liquids (ILs), might be suitable for the electrodeposition of reactive metals including Al and Al alloys [2,6]. One of those appeared to be the mixture of aluminium chloride and 1-ethyl-3-methylimidazolium chloride ([EMIm]Cl) [2]. Although able to operate at near room temperatures the ionic liquids are expensive and very hygroscopic, and thus unsuitable for industrial electrolysis.

A new class of low cost ionic liquids with increased stability in air called deep eutectic solvents (DESs) was reported not long ago [7]. DESs are systems produced from an eutectic mixture of Lewis or Brønsted acids and bases, consisting of a different anionic and/or cationic species [7]. DESs have proven to possess several advantages over traditional ILs such as low vapor pressure, high solubility for metal salts, easy preparation. Research done so far showed that DES is very promising electrolyte for electrodeposition and dissolution of a number of metals and alloys including aluminium [7].

Our previous study has shown that aluminium can be successfully electrodeposited from deep eutectic system, based on  $\text{AlCl}_3$ +urea, onto glassy carbon and aluminium at near room temperatures [8]. This paper focuses on the conditions leading to different aluminium morphology electrodeposited onto aluminium substrate. This is very important having in mind possibility that this system is considered suitable for electrochemical renewable energy source [9].

### EXPERIMENTALS

Electrochemical measurements and electrodeposition processes were conducted in three-electrode electrochemical cell made of Pyrex glass, under dry argon atmosphere. High purity aluminium (Al, 99.999%, Alfa Products, Thiokol/Ventron division, USA) was used as electrodes material. Aluminium wire 3 mm in diameter served as the reference electrode, a rectangular shovel of aluminium was used as the counter electrode and  $0.5 \text{ cm}^2$  plate of aluminium was employed as the

working electrode. Previous to each experiment aluminium electrodes were mechanically polished with sand paper and etched as reported earlier [8].

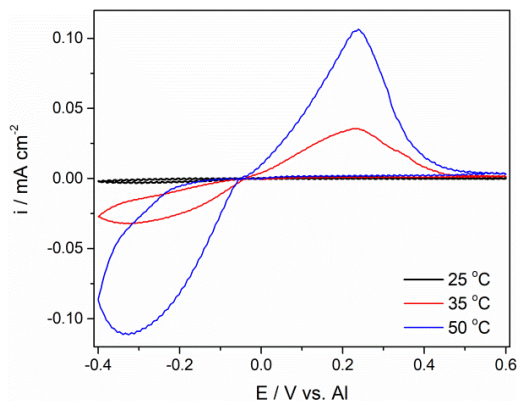
Deep eutectic solvent (DES) used as the electrolyte was made from anhydrous aluminium chloride (used as received, >99%, Aldrich Chemical Company, Inc.) and urea (used as received, p.a. Carlo Erba, France) with molar ratio of 1.6:1. The process of the electrolyte preparation was specified in our previous work [8].

Electrochemical techniques used for examination of aluminium deposition/dissolution processes were cycling voltammetry (CV), potentiodynamic polarization curves, chronoamperometry and chronopotentiometry with an electrochemical workstation (EG&G model PAR 273A) regulated by Power Suite software (Princeton Applied Research, USA). Electrochemical study was carried out at three different temperatures: 25 °C, 35 °C and 50 °C. The galvanostatic and potentiostatic electrodepositions were done at 35 °C. The electrolyte was not stirred. After deposition working electrode was washed with absolute ethanol (C<sub>2</sub>H<sub>5</sub>OH, Zorka-Pharma, Šabac, Serbia) to remove any electrolyte residue and then dried before further deposit analysis. The morphological forms and chemical composition of the deposits obtained were determined by scanning electron microscopy assembled with energy dispersive X-ray spectroscopy (SEM, TESCAN Digital Microscope; model VEGA3, Brno, Czech Republic and EDX-Oxford INCA 3.2, UK).

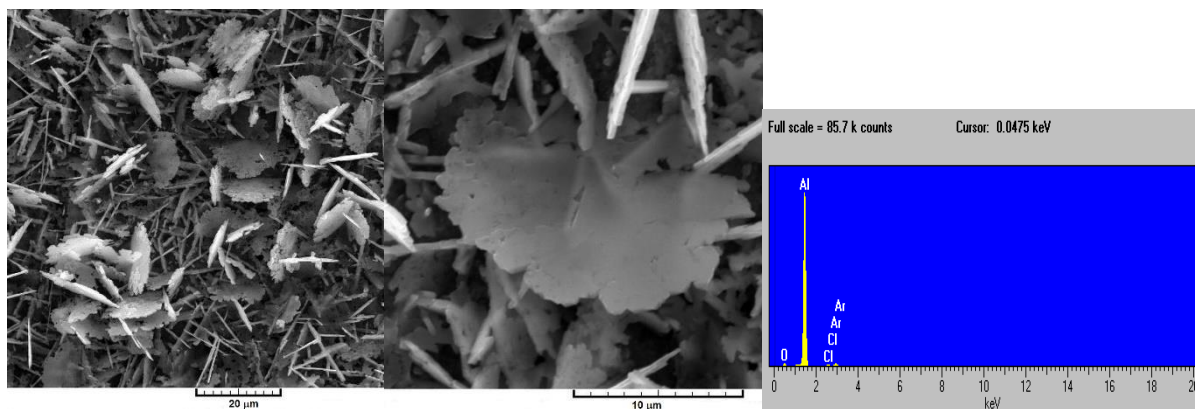
## RESULTS AND DISCUSSION

Examples of cyclic voltammograms recorded on the Al cathode within the same potential range at three different temperatures are presented in Figure 1. It appeared that working temperature significantly influences aluminium electrodeposition process in the electrolyte used (made of 1.6:1 molar ratio AlCl<sub>3</sub>:urea). The maximum peak current densities of both cathodic and anodic peaks recorded increased several times when working temperature was enlarged by ten degrees Celsius. The charge encompassed by the recorded cathodic and anodic currents was also increased considerably as the result of said temperature change. The cathodic charge (reflecting aluminium deposition) was more or less equal to anodic charge (reflecting dissolution of the deposited aluminium) showing reasonable reversibility of the two opposite processes (Al(III) ↔ Al) under applied conditions and the DES chosen. The voltammograms suggest aluminium deposition potential close to – 50 mV vs. Al irrespective of working temperature. From the point of possible use of the system in batteries this can be considered as positive. However, the deposition and dissolution current densities recorded by voltammograms were rather low, less than 100 μA cm<sup>-2</sup>. This should not be surprising, because low conductivity of the electrolyte used at applied temperatures is known.

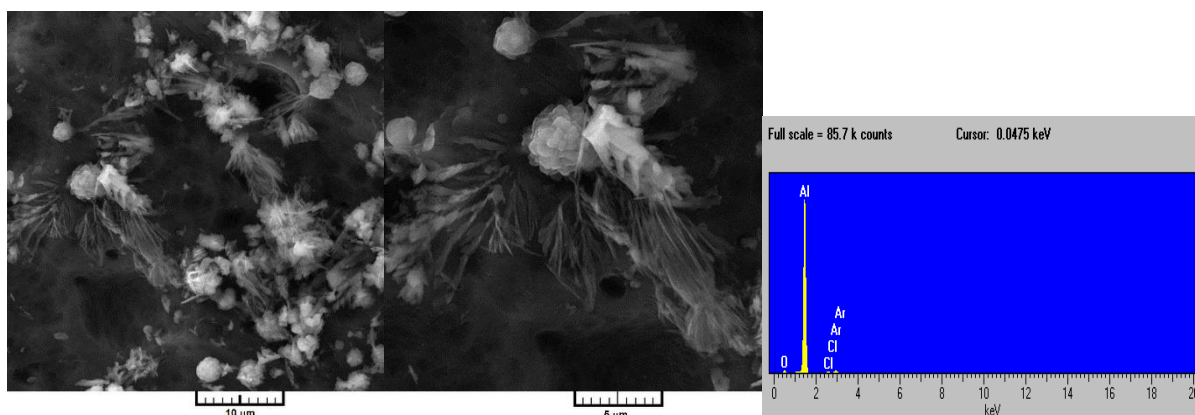
Scanning electron micrographs and chemical composition of the aluminium electrodeposited onto aluminium by applying constant deposition potential of – 250 mV vs. Al at 35 °C are presented in Figure 2. The deposits of very high specific surface area were obtained showing pure aluminium with complex three-dimensional morphology. It was the deposit made of the flake-like dendrites randomly oriented predominantly formed as the upper layer, and positioned over lower layer of densely grown much smaller needle-like crystallites. This implies that, immediately after nucleation, the deposit proceeds to grow under 3D diffusion control. These crystallites could be a problem for some future renewable power source.



**Figure 1.** CV recorded on Al working electrode at different temperatures; potential range:  $E_{INITIAL}=000\text{ mV} \rightarrow E_{CATHODIC}=-400\text{ mV} \rightarrow E_{ANODIC}=600\text{ mV} \rightarrow E_{FINAL}=000\text{ mV}$  vs. Al; sweep rate= $10\text{ mVs}^{-1}$ .



**Figure 2.** a) and b) SEM images (magnification:1500x and 6000x) and c) EDX analysis of aluminium deposits obtained at 35 °C on Al after potentiostatic regime at  $-250\text{ mV}$  vs. Al, during 30 min.



**Figure 3.** a) and b) SEM images (magnification:5000x and 10000x) and c) EDX analysis of the aluminium deposits onto Al substrate obtained at a current density of  $-2\text{ mA cm}^{-2}$  for 30 min at  $T=35\text{ }^{\circ}\text{C}$ .

SEM micrographs and chemical compositions of the aluminium electrodeposited onto aluminium substrate from the chosen electrolyte at 35 °C under constant current density of  $-2\text{ mA cm}^{-2}$  are presented in Figure 3. The obtained aluminium deposit was tree-dimensional consisting of grains in

different sizes and crystal shapes. Apparently, crystal grains as the most dominant form were grouped randomly into more or less separate agglomerates. The shape of the grains seems to be changing from the form of crystalline boulders and nodular grains to a very complex and irregular morphology almost from the beginning of the deposition. The dendrites were formed on the boulders and grains as highly branched crystallites of various shapes that grew oriented towards the bulk of the electrolyte. These highly developed 3D crystallite forms are expected result of the diffusion controlled deposition of the aluminium under applied condition. Applied deposition current density of  $-2 \text{ mA cm}^{-2}$  provoked cathodic overpotential in the range of  $-1000 \text{ mV}$  vs. Al at  $35 \text{ }^\circ\text{C}$ . It was again apparent that a uniform Al deposit layer could not be put down onto the Al substrate under the experimental conditions described.

## CONCLUSION

Aluminum was successfully electrodeposited on Al by applying constant potential or constant current density, from deep eutectic solvent ( $\text{AlCl}_3\text{:urea} = 1.6:1$ ).

Although successfully electrodeposited onto aluminium at a temperature ranging from  $25 \text{ }^\circ\text{C}$  to  $50 \text{ }^\circ\text{C}$  it was apparent that a uniform Al deposit layer could not be put down onto the aluminium substrate under the experimental conditions described. Instead, aluminium deposits consisting of great number of crystallites of various shapes were obtained. These findings should arise caution in the circles considering the used system as promising for rechargeable batteries.

The deposit obtained by applying constant deposition potential makes denser surface population than the deposit made by applying constant deposition current density which consists of randomly distributed groups of individual grains. However, in both cases no compact deposit covering whole substrate is possible but individual flake-like, dendrites of different shapes, needles, boulders and crystalline grains.

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