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MEETING POINT OF THE SCIENCE AND PRACTICE IN THE FIELDS OF CORROSION, MATERIALS AND ENVIRONMENTAL PROTECTION

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CONTENTS | *SADRŽAJ*

Galvanostatic electrodeposition of aluminium onto aluminium from $AlCl_3$+NaCl melt

Galvanostatsko elektrohemijsko taloženje aluminijuma na aluminijumu iz rastopa $AlCl_3$+NaCl

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Abstract

The processes of galvanostatic electrochemical deposition of aluminium onto aluminium from chloroaluminate melt made of equimolar $AlCl_3$+NaCl mixture at 200°C have been investigated. The obtained deposits were characterized using scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS).
Galvanostatic Al deposition from the used melt onto aluminium substrate with smaller current densities (2-5 mA cm^{-2}) gave relatively close-packed and well adhering deposits. Aluminium deposits obtained galvanostatically with current densities larger than 5 mA cm^{-2} are less compact, more crystalline and less adhering to the aluminium substrate. Al deposits obtained with 10 and 12.5 mA cm^{-2} were voluminous, very crystalline and poorly adhering to the working electrode substrate. These deposits were made of very small crystallites grouped randomly into more or less separate agglomerates.

Keywords: *galvanostatic deposition, aluminium, chloroaluminate melt*

Izvod

Ispitivani su procesi galvanostatskog elektrotaloženja aluminijuma na aluminijumu iz hloroaluminatnog rastopa napravljenog od ekvimolarne smeše, $AlCl_3$+NaCl, na temperaturi od 200°C. Dobijeni talozi su analizirani skenirajućom elektronskom mikroskopijom (SEM) i energetsko disperzivnom spektroskopijom (EDS).
Galvanostatsko elektrohemijsko taloženje aluminijuma iz upotrebljenog rastopa na aluminijumu pri nižim gustinama struje (2-5 mA cm^{-2}) daje relativno kompaktne i adherentne taloge. Hronopotenciometrijskim taloženjem aluminijuma gustinama struje većim od 5 mA cm^{-2} dobijeni su više kristalični, manje adherentni i kompaktni talozi na podlozi od aluminijuma. Talozi aluminijuma dobijeni gustinama struje od 10 i 12.5 mA cm^{-2} bili su veoma kristalični, nekompaktni i veoma slabo su prijanjali uz podlogu-radnu elektrodu. Ovi talozi bili su sačinjeni od veoma malih kristala grupisanih nasumično u manje-više odvojene aglomerate.

Ključne reči: *galvanostatsko taloženje, aluminijum, hloroaluminatni rastop*

Introduction

In order to be efficiently powered new generation of micro-devices requires integrated batteries. Most of the work in batteries technology, until recently, has been focused on the development of next generation of lithium-ion or metal air batteries [1,2]. The next generation of lithium-ion or metal-air batteries is expected to use new electrode nanomaterials as efficient and cost-effective electrocatalysts [1].
In recent years several studies have shown that three-dimensional electrodes with improved capacity and cycling behaviour compared to corresponding thin film electrodes in Li-ion batteries could be obtained by electrodeposition [3,4]. Although the current battery technology is focused on lithium electrodes there are several alternatives, and aluminium is one worth considering [5] because of its high specific electric capacity. However, aluminium delivers less voltage and repetitive deposition of this metal is difficult in most electrolytes. Oltean at all. manufactured three-dimensional Al rod electrodes [2] which should be suitable for use as a current collectors in three-dimensional Li-ion micro-batteries. These nano-rods were deposited under pulsed galvanostatic conditions with an initial nucleation potential step from an ionic liquid electrolyte (1-ethyl-3methylimidazolium chloride/aluminium chloride). The morphology and homogeneity of the obtained aluminium nano-rods depended on the methods of deposition. It seems necessary to research aluminium deposition from low temperature electrolytes in order to master procedures needed for aluminium deposits of needed morphology on different suitable substrates.
To the best of our knowledge, there are not very many publications dealing with electrochemical deposition of aluminium onto aluminium substrate from low temperature chloroaluminate molten salts. In the present work we report on aluminium galvanostatic electrodeposition onto planar aluminium substrate from low temperature chloroaluminate melt.

Experimental

Electrochemical measurements were performed in three electrode electrochemical cell under an argon atmosphere. All the electrodes were made of high purity aluminium (99.999% pure, Alfa Products, Thiokol/Ventron division, USA). Aluminium wire 3mm in diameter in a Luggin capillary was used as a reference electrode and aluminium plate of 7 cm^2 surface area as a counter electrode. Surface area of 0.8 cm^2 of aluminium working electorde was exposed to the electrolyte used (melt made of equimolar $AlCl_3$+NaCl mixture). Prior to an experiment the electrodes were prepared in the way presented elsewhere [6,7], Fig.1.

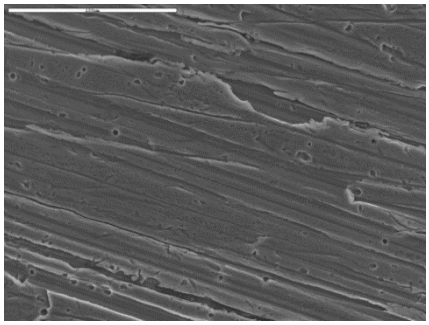


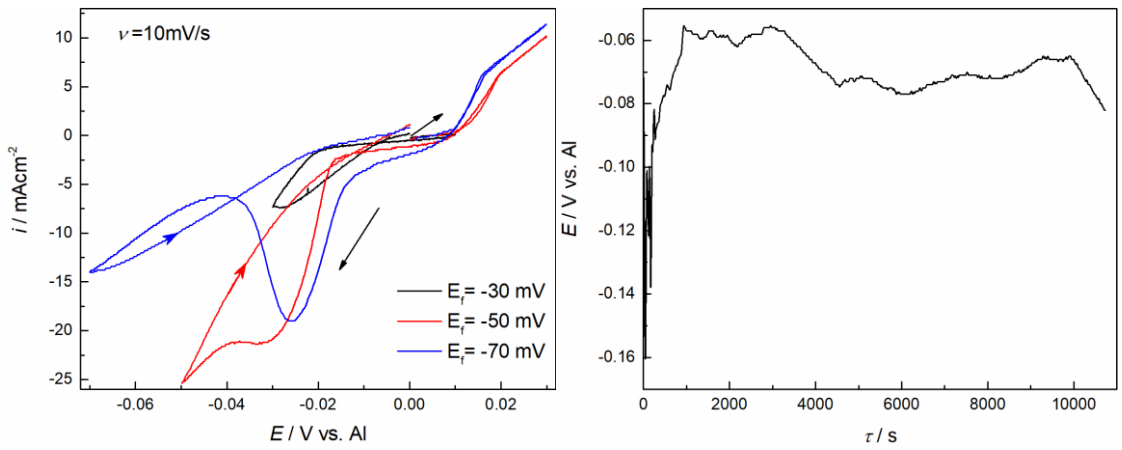
Figure 1. Surface of an Al (99.999%) pure working electrode mechanically polished and chemically etched.

The process of the chloroaluminate molten salt preparation has been described in details elsewhere [7]. Prior to the electrochemical measurements the melt was subjected to preelectrolysis between two aluminium (99.999% pure) plates with large surface area at 200°C with constant current density i =

1.5x10-2 A cm-2 for 10 hours. Aluminium electrodes were cleaned before use, in the same way as described [7].
Cyclic voltammetry (CV) experiments were conducted at different scan rates from starting potential value Es (usually slightly negative to the working electrode open circuit potential) into negative direction (final potential value Ff was 15-100 mV negative to the reversible aluminium potential) and back. Galvanostatic electrodeposition of aluminium was performed with different current densities and after each deposition, the deposits were thoroughly rinsed with deionized water, absolute alcohol and dried at room temperature.
Electrochemical measurements were made using EG&G Potentiostat/Galvanostat Model 273A and accompaning softwere (Princeton Applied Research, Oak Ridge, TN, USA). The morphologies of Al deposits were examined using a scanning electron microscopy (SEM - "JEOL", model JSM-5800, Tokyo, Japan) and surface analysis was performed by energy dispersive spectrometry (EDS - "Oxford INCA 3.2", Abingdon, U.K.).

Results and discussion

A typical voltammograms and a chronopotentiogram of aluminium deposition/dissolution from chloroaluminate melt used onto aluminium electrode are presented in Fig.2.a) and b), respectively. Visible increase of cathodic current starts at potentials very close to -20 mV vs. Al, which would suggest that aluminium deposition overpotential in the system used is two or more times smaller than on glassy carbon substrate under almost the same conditions [8]. Very similar values were reported for Al deposition on Al from some ionic liquids [2, 9]. The same values of Al deposition potential on Al from the used electrolyte was recorded earlier [10].

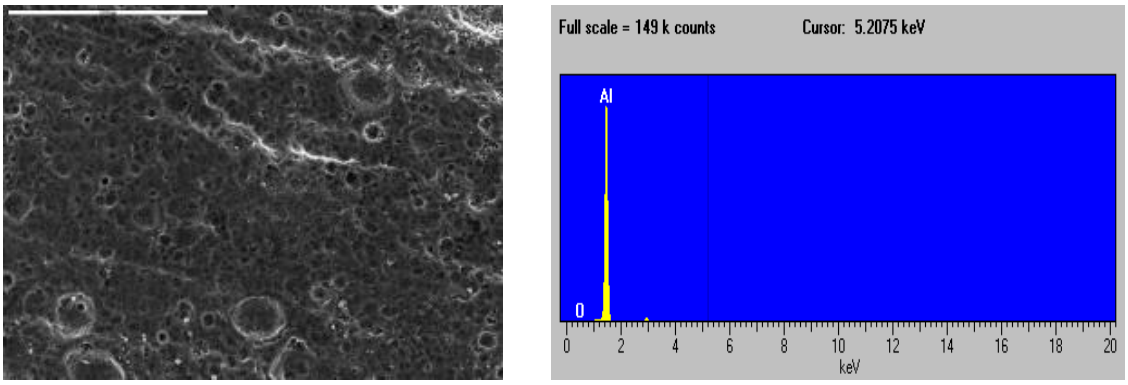


a) *b)*

Figure 2. a) Cycling voltammograms recorded on aluminium electrode; b) Chronopotentiogram depicting Al deposition onto aluminium (current density 2 mA cm-2), from equimolar AlCl3+NaCl melt at 200°C.

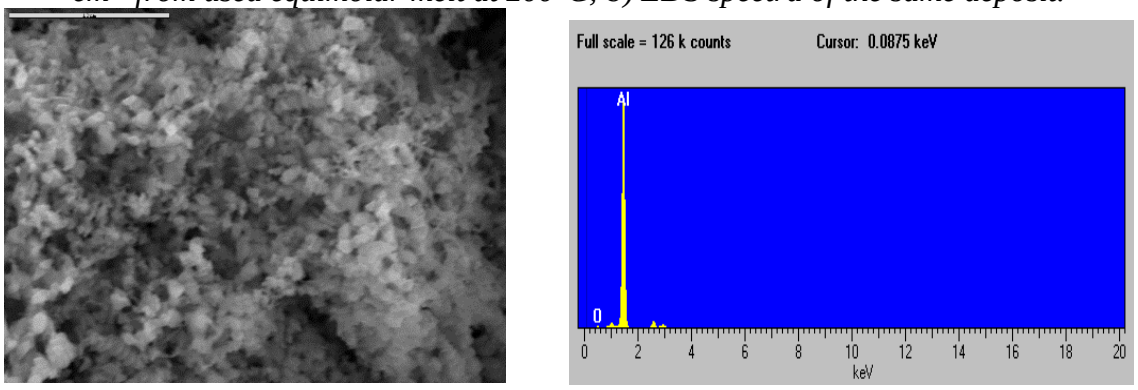
Fig.2.b) shows a typical chronopotentiogram of aluminium deposition onto aluminium from the melt used. Initial electrode potential (around -120 mV vs. Al) relatively quickly fell to values around -60 mV vs. Al. After an hour reached to a plateau of around -75 mV vs. Al where it remained to the end of the experiment.
SEM micrographs and EDS analysis of the aluminium electrodeposited at different current densities are shown in Figs.3, 4 and 5. Morphology of the deposits recorded were considerably different. The deposit made with low current density (2 mA cm-2, Fig.3) seems to be made of relatively continuous layers with certain number of holes and individual grains with diameter of a few nanometres in size. The deposit was adhering well to the substrate. Increasing the deposition current density (10 mA cm-

2, Fig.4 and 12.5 mA cm-2, Fig.5) resulted with deposits of appreciable increasing thickness and granular nature. Grains had sharp edges and very crystal like appearance. Evident were voids in a form of labyrinth like channels in the aluminium deposit formed. The deposit was not compact and it easily fell of during rinsing with absolute alcohol. The adherence of the deposit to the substrate obtained with higher current densities was worse than those obtained with smaller current densities.
The problem of aluminium deposits adherence to the aluminium substrate when electrodeposited from chloroaluminate melts, ionic liquids or deep eutectic solvents is well known.
The adherence of the deposited layers obtained by Al electrodeposition with low current densities, compared with the one obtained by electrodeposited Al at lower overpotential from the same melt is in good agreement.



a) ***b)***

Figure 3. a) SEM photographs of aluminium electrodeposited for 3 h with current density of 2 mA cm^{-2} from used equimolar melt at 200°C; b) EDS spectra of the same deposit.



a) ***b)***

Figure 4. a) SEM photographs of aluminium electrodeposited for 3 h with current density of 10 mA cm^{-2} from used melt at 200°C; b) EDS spectra of the same deposit.

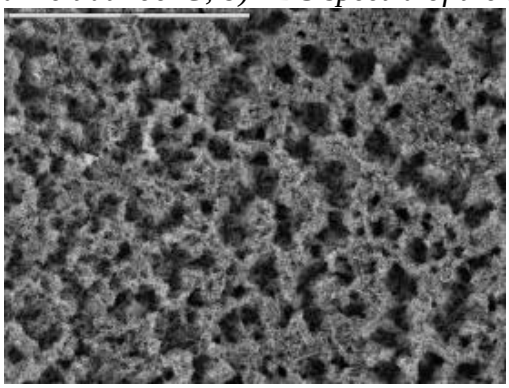


Figure 5. SEM photographs of aluminium electrodeposited for 2 h with current density of 12.5 mA cm-2 from the melt used, temperature 200°C.

Therefore the results that we obtained from equimolar AlCl3+NaCl melt by potentiostatic electrodeposition at very low overpotentials [10] and by galvanostatic electrodeposition with small current densities look promising.

Conclusion

It was confirmed, that aluminium onto aluminium substrate from the melt made of equimolar $AlCl_3$+NaCl mixture can be successfully deposited galvanostatically.
Surface morphology of Al deposits depends on applied current densities. At smaller current densities aluminium deposited was compact and well adhering to the substrate, while at higher current densities the deposit was less compact and less adhering.
Al deposited with current densities of 10 and 12.5 mA cm^{-2} show voluminous, very crystalline deposits made of small crystallites grouped randomly into more or less separate agglomerates with very poor adherence to the working electrode.

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