

**PROCEEDINGS,
49th INTERNATIONAL OCTOBER CONFERENCE
on Mining and Metallurgy**

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University of Belgrade, Technical Faculty in Bor

Publisher: University of Belgrade, Technical Faculty in Bor

For the publisher: Dean Prof. dr Nada Štrbac

Circulation: 200 copies

Printed by "Happy trend DOO", Zaječar, 2017

ISBN 978-86-6305-066-2

CIP - Каталогизacija у публикацији - Народна библиотека Србије, Београд

622(082)

669(082)

INTERNATIONAL October Conference on Mining and Metallurgy (49 ; 2017 ; Bor Lake)

Proceedings / 49th International October Conference on Mining and Metallurgy - IOC 2017,

Bor Lake, Serbia, October 18-21, 2017;

[organized by] University of Belgrade, Technical Faculty Bor and Mining and Metallurgy Institute Bor;

editors Nada Štrbac, Ivana Marković, Ljubiša Balanović. - Bor : University of Belgrade, Technical Faculty,

2017 (Zaječar : Happy trend). - XXIII, 664 str. : ilustr. ; 25 cm

Tiraž 200. - Bibliografija uz svaki rad. - Registar.

ISBN 978-86-6305-066-2

a) Рударство - Зборници b) Металургија - Зборници

COBISS.SR-ID 246349324

Bor Lake, Serbia, October 18-21, 2017

ALUMINIUM ELECTRODEPOSITION FROM CHLOROALUMINATE MELTS

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Abstract

Electrodepositing aluminium from a low temperature equimolar chloroaluminate melt onto a planar aluminium cathode was investigated. Experimental techniques used were linear sweep voltammetry, potential step and analytical techniques were SEM and EDS. Results show that a relatively adherent and compact aluminium deposit featuring high surface area can be successfully electrodeposited from melts at 200°C. Electrodeposition done under potentiostatic control indicates that aluminium deposits are made up of extremely small particles of irregular shape and that a moderate increase in applied overpotential leads to decrease in crystallite down to nanoparticle size. Surface morphology of the Al deposit can be optimized by adjusting electrodeposition parameters.

Keywords: batteries, aluminium electrodes, aluminium deposition, chloroaluminate melt

1. INTRODUCTION

Development of renewable energy production and storage technology represents one of the major scientific challenges of this century. Contemporary batteries do not provide satisfactory levels of energy and power density for sensors, in vivo medical devices, micro-electromechanical systems (MEMS), etc. [1]. Efforts to manufacture cost-effective electrodes with improved kinetics and energy efficiency for use in electrochemical energy conversion process continue to be intensively studied [2,3]. Although current battery technology is focused on lithium ion technologies, there are several electrode material alternatives that show potential, and one of them certainly worth considering is aluminium [2].

Novel development of three-dimensional Al electrodes, a new promising material with high surface area, was reported by Perre at all [4,5]. Authors electrodeposited aluminium nano-rods within ordered alumina templates under pulsed-potential conditions, using 1-ethyl-3-methylimidazolium chloride/aluminium chloride ionic liquids electrolyte [4,5]. According to their work, the length of the aluminium nano-rods is dependent on the charge passed during the electrodeposition process while the shape of the obtained deposit is entirely dependent on the alumina template used.

To the best of our knowledge, there is a handful of contemporary publications dealing with the subject of electrochemical deposition of aluminium onto an aluminium substrate from low temperature chloroaluminate melts. In the present work, Al was electrodeposited onto planar aluminium metal substrate using potential pulse techniques from low temperature chloroaluminate melt in order to obtain optimum deposition conditions for compact adherent deposit layer.

2. EXPERIMENTAL

All the electrochemical measurements were performed in a three electrode electrochemical Pyrex cell under a purified argon atmosphere. Aluminium wire (3mm diameter) placed in a Luggin capillary was used as a reference electrode, while an aluminium plate (15 cm² surface area) served as a counter electrode. Surface area of 0.8 cm² of a planar Al working electrode was

exposed to the melt used. All the electrodes were of high purity aluminium (99.999% pure, Alfa Products, Thiokol/Ventron division, USA). After mechanical polishing procedure [6,7], all the electrodes were etched in the solutions made of: a) 50 vol% HF + 15 vol% H₂O, and b) conc. NH₄OH + 5 vol% H₂O₂, then rinsed with deionized water, absolute ethyl alcohol, dried in air and mounted into the cell.

The process of the chloroaluminate molten salts preparation has been described in details elsewhere [7]. Prior to the electrochemical measurements, the melt was subjected to pre-electrolysis between two aluminium (99.999% pure) plates with large surface area at 220-250 °C with constant current density $i = 1.5 \times 10^{-3} \text{ Acm}^{-2}$ for 10 hours. Both aluminium plates were prepared as described above.

Cyclic voltammetry (CV) experiments were conducted at various scan rates from a starting potential value E_i (usually slightly positive to the aluminium open circuit potential) toward the negative final potential value E_f (usually 15-100 mV negative to the reversible aluminium potential) and back. Potentiostatic current transients ($J-t$) curves within the same potential window were also recorded. After each deposition experiment, working electrodes were thoroughly rinsed with deionized water, alcohol and dried at room temperature in air.

All electrochemical experiments were performed using EG&G Potentiostat/Galvanostat Model 273A and accompanying software (Princeton Applied Research, Oak Ridge, TN, USA). The morphologies of Al deposits were recorded by Scanning Electron Microscopy (SEM - "JEOL", model JSM-5800, Tokyo, Japan) and surface was analyzed by Energy Dispersive Spectrometry (EDS - "Oxford INCA 3.2", Abingdon, U.K.).

3. RESULTS AND DISCUSSION

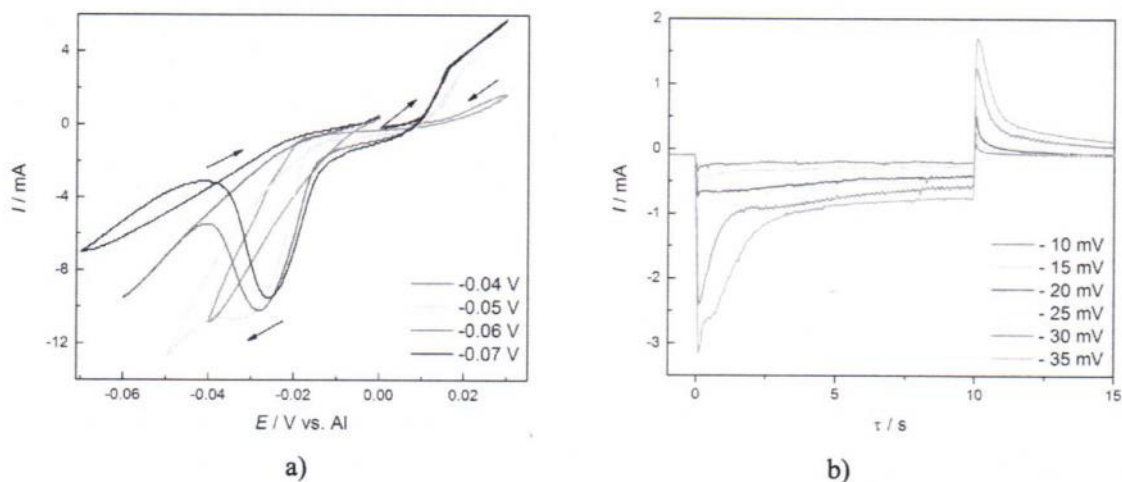


Figure 1 - a) Cyclic voltammograms on an Al electrode recorded from $E_i=0.3\text{V}$ to different vertex potential values for each scan E_f at 20 mV/s ; b) current-time transients obtained on the Al electrode by Al electrodeposition at different overpotentials, from chloroaluminate molten salts at 200°C for all curves

Figure 1.a) presents cycling voltammograms of an Al substrate obtained with changing cathodic end potentials in equimolar chloroaluminate melt. Aluminium deposition process and its corresponding peaks in the cathodic part of the scan are clearly visible. Appearance of a large reduction current peak and subsequent increase of cathodic current at overpotentials higher than -20 mV vs. Al reflect aluminium electrodeposition from two aluminium ions (AlCl_4^- and Al_2Cl_7^-) that are present in the equimolar $\text{AlCl}_3+\text{NaCl}$ melt electrolyte.

Current-time transients on the Al substrate resulting from potential step experiments are shown in Fig. 1.b). At overpotentials more positive than -15 mV, the current density reaches steady-

state values already 2s after the application of the potential step. However, when more negative overpotentials were applied, corresponding initial as well as subsequent steady state current densities increased proportionally. Initial falling portion of the transients suggests diffusion controlled aluminium deposition from AlCl_4^- ions followed by additional deposition from Al_2Cl_7^- ions.

The results obtained with aluminium planar electrode at constant overpotentials of -25 and -20 mV vs. Al held for 1.5 and 2 hours are presented in Figures 2 and 3 respectively. EDS analysis (Fig. 2.b) and 3.b)) recognizes aluminium as the only deposit on the aluminium planar electrodes used. SEM photographs (Fig. 2.a) and 3.a) and c)) reveal some differences in the surface morphology of the deposits.

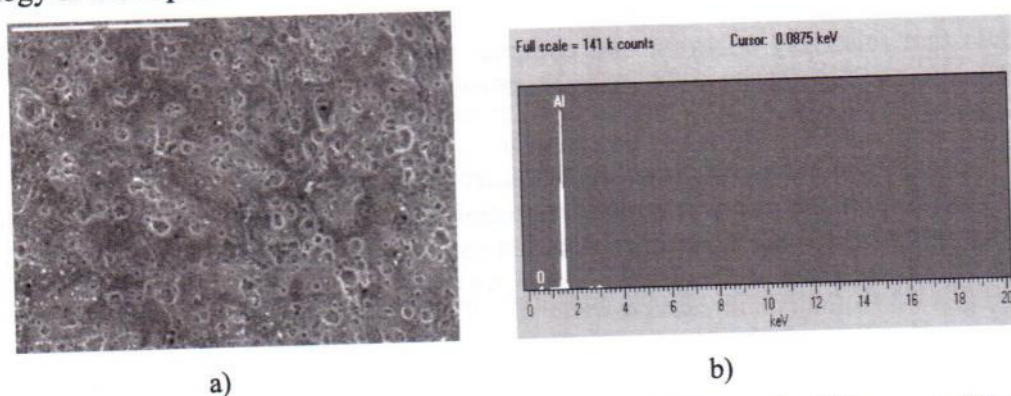


Figure 2 - a) SEM image; b) EDS spectra of aluminium electrodeposited for 1.5 hours at -25 mV vs. Al from chloroaluminate molten salts, temperature 200°C

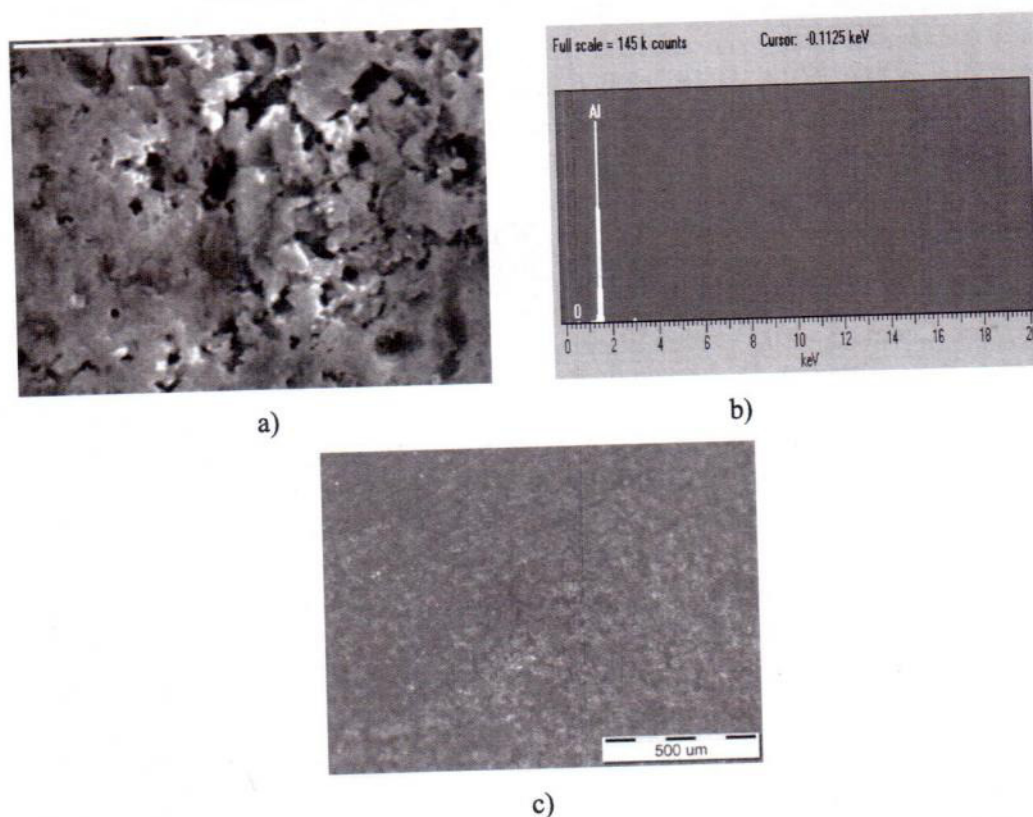


Figure 3 - a) SEM image; b) EDS spectra and c) optical micrograph, of Al electrodeposited at -20 mV for 2 h from chloroaluminate molten salt, temperature 200°C

The deposits, although not very homogenous, appear to cover the entire substrate. However, it seems that the deposit obtained at - 25 mV was somewhat more compact, and grains appear to be smaller and morphologically more complex. It seems that the thickness of this deposit is smaller than the one in Fig. 2.a) and it exhibits fewer cavities. SEM photographs revealed significant roughness, coarse morphology and high surface area of the obtained deposits. In addition, it appears from the photographs, that deposit is well adhered to the substrate. However, when washed with relatively intense water or alcohol beam the deposit can be partially removed from the electrode surface. This suggests a cautious approach to washing of the highly developed surface area of aluminium deposit in order to get rid of remaining chloroaluminate electrolyte.

4. CONCLUSION

It was shown that relatively adherent and compact aluminium deposit with high surface area from low temperature equimolar chloroaluminate melt (200°C) onto planar aluminium surface can be successfully electrodeposited.

The electrodepositions done under potentiostatic control indicate that aluminium deposits consist of extremely small particles with irregular shape and that a moderate increase in overpotential applied leads to decrease in crystallite size down to nanoparticles.

Surface morphology of Al deposit can be optimized by adjusting electrodeposition parameters.

ACKNOWLEDGEMENTS

This work was supported by the Ministry of Education, Science and Technology of the Republic of Serbia (Grant OI 172060).

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