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## An impedance study of complex Al/Cu-Al<sub>2</sub>O<sub>3</sub> electrode

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**Abstract.** Electrochemical impedance spectroscopy (EIS) was used to investigate different Cu deposition regimes on Al surface obtained by internal electrolysis and to characterize properties of fabricated electrodes. EIS experimental data confirmed that Cu deposition by internal electrolysis is realized and the complex electrode system is obtained. The main difficulty in preparation of Al/Cu electrodes is to prevent aluminium oxidation before and during electrochemical deposition of Cu particles. In this work NaCl, CH<sub>3</sub>COONa, K<sub>2</sub>SO<sub>4</sub>, mono- and diammonium citrate electrolytes were examined to determine their suitability for impedance measurements. Al/Cu-Al<sub>2</sub>O<sub>3</sub> electrode composition was approved by equivalent circuit analysis, optical and scanning electron microscope methods. The most optimal Cu deposition mode using internal electrolysis was determined. The obtained results are promising for future electrochemical fabrication of nanostructures directly on Al surfaces by internal electrolysis.

### 1. Introduction

Electrochemical deposition is a promising technique for fabrication of particles arrays on the surfaces due to its easy-to-use procedure and low cost of implementation [1]. Al surfaces are often used as substrate for fabrication of particle arrays [2]. However, surface pre-treatment should be done to remove oxide layer grown on electrode surfaces before and during element deposition. In the case of aluminium oxidation problems can be overcome by using H<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>/H<sub>3</sub>PO<sub>4</sub> solution mixture [3, 4]. H<sub>3</sub>PO<sub>4</sub> as an electrolyte component are often used during the element deposition process on bare Al surface with a view of not allowing Al<sub>2</sub>O<sub>3</sub> barrier layer formation on refined Al surface [5]. Presence of oxide on Al surface can be detected and characterized by EIS.

Potentiostatic [6] and galvanostatic [7] electrochemical deposition methods are described for the fabrication of particles on different surfaces, but internal electrolysis is not yet applied. The electrochemical deposition of Cu particles on the electrode surface was performed by internal electrolysis method. Properties of Al surface after Cu deposition were controlled by electrochemical impedance spectroscopy.

### 2. Experimental

0.10 mm thick Al plates with 99.9 % purity were used in experiments. Al plates were treated with acetone, annealed at 600 °C and etched 2-3 hours at room temperature in 0.2 M H<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>/0.4 M H<sub>3</sub>PO<sub>4</sub>

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solution mixture to remove organic material and oxide layer. Cu was deposited on Al surface from electrolyte containing 0.4 M CuSO<sub>4</sub> solution in 10 % H<sub>3</sub>PO<sub>4</sub> in temperature interval 20-50°C. The deposition time was varied from 3 to 14 minutes.

Al/Cu-Al<sub>2</sub>O<sub>3</sub> electrodes were investigated by EIS, optical and scanning electron microscope methods. A computer controlled frequency response analyzer FRA with module (Autolab PGSTA-30 for Windows version 4.9) was used in experiments. Impedance spectra were obtained in frequency range from 65 kHz to 0.1 Hz and from 10 kHz to 0.1 Hz, using 40 points per spectrum, with AC potential amplitude of 10 mV and conditioning time 5 seconds. Pt plate was used as an anode and an Ag/AgCl as reference electrode respectively. Parameter fitting for equivalent circuit elements for electrodes in electrolytes was performed by simulation program "RCNTRANS and EQUIVCRT", which is based on non-linear least squares method. R<sub>1</sub>R<sub>2</sub>Q equivalent circuit was used for Al-Al<sub>2</sub>O<sub>3</sub> electrode characterization, where R<sub>1</sub> – electrolyte resistance, R<sub>2</sub> – Al<sub>2</sub>O<sub>3</sub> layer resistance (impedance), Q – Constant Phase Element (CPE) of Al<sub>2</sub>O<sub>3</sub> layer. R<sub>1</sub>(C[R<sub>4</sub>(R<sub>3</sub>Q)]) equivalent circuit was used for Al/Cu-Al<sub>2</sub>O<sub>3</sub> electrode characterization. In this circuit C is the capacitance of Cu globules, R<sub>4</sub> is resistance (impedance) of Cu globules, R<sub>3</sub> is Al<sub>2</sub>O<sub>3</sub> layer resistance (impedance). CPE, capacity and complex impedance values were estimated.

For impedance measurements a non-cyclic algorithm was used: holding times 15, 30, 45 and 60 min without polarization potential, 5 s of electrode conditioning (polarization potential - 10 mV) – 5 min of measuring (polarization potential -10 mV).

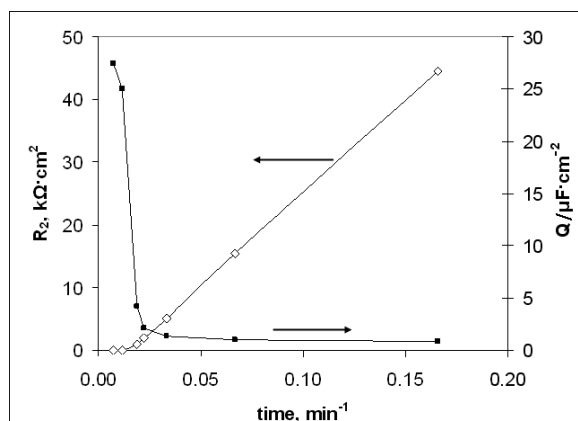
### 3. Results and discussion

In the beginning detailed investigations of Al<sub>2</sub>O<sub>3</sub> dissolution from oxidized Al electrode in H<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>/H<sub>3</sub>PO<sub>4</sub> water solution at room temperature aiming forming clean Al surface was performed by EIS. From analysis of functions R<sub>2</sub> = f(1/t) and Q = f(1/t) (Figure 1) was concluded that oxide layer dissolves almost completely in 50 min. After this time polarization resistance R<sub>2</sub> corresponds to resistance of Al layer and remains practically constant, which means that oxide free Al surface is obtained. Hence preparation of oxide free Al surfaces can be considerably decreased in time scale even at room temperature compare to literature data (60°C, 3 h [3]; 70°C, 15 h [4]). These Al surface preparation conditions were used for Cu deposition by internal electrolysis on the surface.

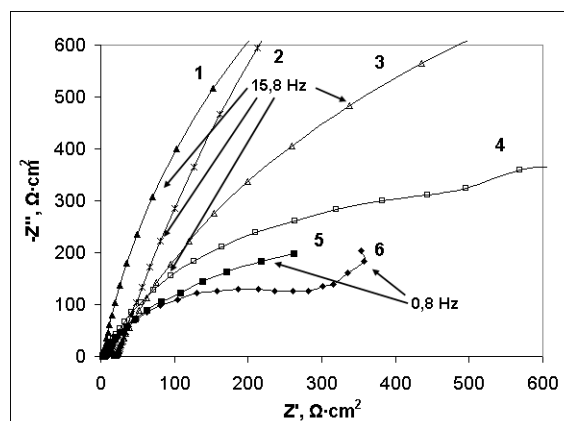
Development of EIS methodology for Al/Cu-Al<sub>2</sub>O<sub>3</sub> electrode characterization was started with electrolyte choice. Optimal electrolyte exhibiting low impedance and low corrosion rate was found. The most commonly used electrolytes in EIS measurements of the oxidized Al electrodes are NaCl [8], K<sub>2</sub>SO<sub>4</sub> [9, 10] and CH<sub>3</sub>COONa [11, 12] water solutions. Additionally to most used electrolytes application of mono- and diammonium citrate solutions for EIS measurements were also investigated due to expected lower corrosion rate. It was established that complex impedance values grow up noticeably in following direction (for 0.1 M solutions): NaCl, CH<sub>3</sub>COONa, K<sub>2</sub>SO<sub>4</sub>, monoammonium citrate, diammonium citrate. That matches to electrolyte aggressiveness, i.e. the decrease of electrode corrosion rate [13]. As in NaCl solution Al corrosion process dominates [6] it was stated that the optimal electrolyte is 0.1 M CH<sub>3</sub>COONa. High resistance values (R<sub>2</sub>) were obtained in citrate solutions; therefore these electrolytes are not appropriate for the characterisation of electrodes by EIS. Although in the case of K<sub>2</sub>SO<sub>4</sub> electrolyte R<sub>2</sub> value is lower in comparison to citrate solutions resistance value is 10 times higher than resistance than of 0.1 M CH<sub>3</sub>COONa.

Impedance spectra in 0.1 M CH<sub>3</sub>COONa electrolyte of oxidized Al and bare Al surfaces with deposited Cu are presented in Figure 2. Cu particles were fabricated on Al surfaces at all deposition conditions as it was observed in SEM images after internal electrolysis (see, for example, Figure 3). For all electrodes obtained at different internal electrolysis conditions the complete loop in measured frequency range is not observed. Such results for oxidized Al electrode are in good agreement with literature data for aluminium [9, 10]. Impedance spectrum of Al electrode after 14 min Cu deposition at 50 °C (Figure 2, curve 2) are close to the oxidized Al impedance spectrum (curve 1) which means that oxide layer is formed between Al surface and Cu particles. Therefore this regime should not be used for Cu deposition on Al surface when good electrical contact has to be ensured. The impedance

curve can be shifted in direction to Cu impedance spectrum meaning good electrical contact between Al and Cu when oxygen is removed from the solution by nitrogen during internal electrolysis of Cu (Figure 2, curve 3). In oxygen containing solution better electrical contact between Al surface and Cu particles is established for samples when either deposition time or temperature was decreased in comparison to conditions applied for curve 2 in Figure 2 (see curves 4 and 6 in Figure 2). 14 min deposition at 40°C in oxygen containing electrolyte (Figure 2, curve 6) were stated as optimal conditions for Cu deposition on Al surface by internal electrolysis as it follows after impedance, SEM and light microscopy data comparison.

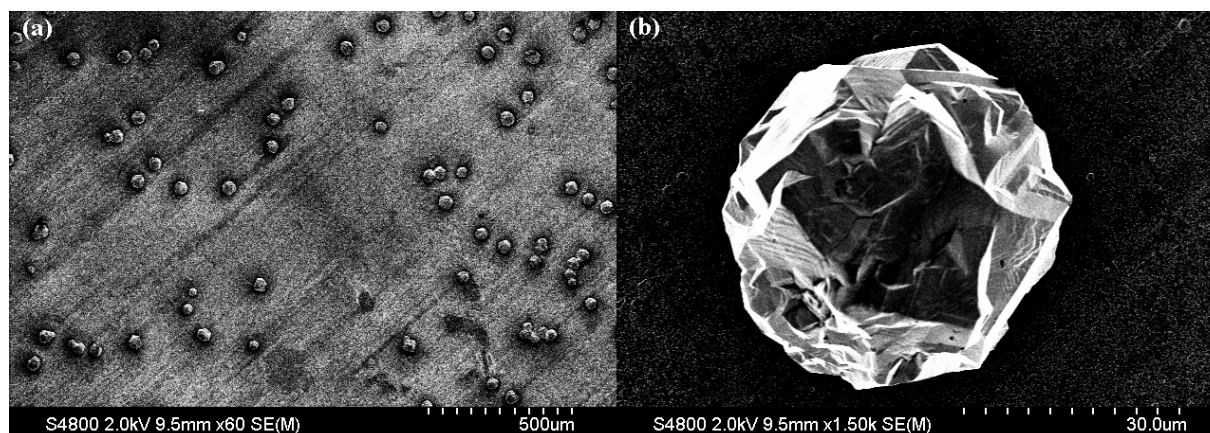


**Figure 1.** Functional relationship of polarization resistance ( $R_2 = f(1/t)$ ) and constant phase element ( $Q = f(1/t)$ ) for Al-Al<sub>2</sub>O<sub>3</sub> electrode treatment in 0.2 M H<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>/0.4 M H<sub>3</sub>PO<sub>4</sub> water solution from on dissolution time.



**Figure 2.** Electrochemical impedance spectra of Al cathode with native Al<sub>2</sub>O<sub>3</sub> layer (1), Al/Cu-Al<sub>2</sub>O<sub>3</sub> electrodes (2, 3, 4, 6) and Cu electrode (5). Deposition conditions of Cu by internal electrolysis: 14 min 50°C (2); 14 min 50°C, deaerated with N<sub>2</sub> (3); 7 min 50°C (4); 14 min 40°C (6).

For internal electrolysis highest density of Cu particles on Al surface correspond to optimal deposition conditions presented for curve 4 in Figure 2. Distribution of Cu globules on the electrode surface is presented on Figure 3a. Investigation of X-ray diffraction of Al/Cu-Al<sub>2</sub>O<sub>3</sub> electrodes reveals crystalline structure of Cu particles (see also SEM image of the Cu particle in Figure 3b). Average particle size was 10-50 μm. SEM image of single Cu crystal with the diameter of 37 μm on the Al/Cu-Al<sub>2</sub>O<sub>3</sub> electrode surface is presented in Figure 3b.



**Figure 3.** Scanning electron microscope images of Al/Cu-Al<sub>2</sub>O<sub>3</sub> electrodes. a - Cu particles distribution on the oxidized Al electrode surface (14 min 40°C, Cu globules average size of 30 μm), b – the crystalline shape of Cu particle (14 min 40°C, size of 37 μm).

#### 4. Conclusions

Before Cu deposition by internal electrolysis Al surface has to be treated with  $\text{H}_2\text{Cr}_2\text{O}_7/\text{H}_3\text{PO}_4$  solution for at least 50 min. 0.1 M  $\text{CH}_3\text{COONa}$  was used as electrolyte for characterization of electrochemical impedance of Al/Cu- $\text{Al}_2\text{O}_3$  electrode.  $R_1(C_1[R_2(R_3Q_2)])$  equivalent circuit well describes Al/Cu- $\text{Al}_2\text{O}_3$  electrode electrochemical parameters. The most optimal conditions of internal electrolysis in oxygen containing solution are: 14 min of Cu deposition in 0.4 M  $\text{CuSO}_4$  and 10 %  $\text{H}_3\text{PO}_4$  electrolyte at 40°C temperature. Removing of oxygen from the solutions during Cu internal electrolysis prevents formation of oxide layer between Al surface and Cu particles. The current experiments of Al/Cu- $\text{Al}_2\text{O}_3$  electrode model with Cu microglobes on the surface shows that internal electrolysis is promising technique for formation of Cu nanoparticles on Al surface. Further investigations are in progress.

#### 5. Reference Section

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