

INITIAL STAGES OF ANODIC OXIDATION OF ALUMINIUM IN NEUTRAL FLUORIDE ELECTROLYTES

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Introduction

Nanoporous anodic films on aluminum and other valve metals → increasing attention → applications as *sensors, catalysts, electrodes* for solar cells and batteries with enhanced *photo-catalytic and photovoltaic* activity

Their characteristics → *pore diameter and length* → easily controlled by the anodic oxidation parameters

Incorporation of metals, alloys and other oxides in their pores → new *functional nanomaterials* with unique magnetic, semiconducting and electronic properties

Recently, it has been demonstrated that *neutral fluoride-containing electrolytes* are suitable for formation of self-ordered alumina templates [1] → no consensus over the pore nucleation and growth mechanism

Aim

To investigate the *initial stages* of the oxide template formation, involving *Al dissolution, barrier film growth and nanopore initiation*

Experimental

Working electrodes → pure Al (99.999%) foils (area of 4 cm²), annealed for 1h at 400°C to remove mechanical stress.

Pretreatment → electropolishing, H₃PO₄/ H₂SO₄/ CrO₃, 0.1-0.2 A cm⁻², 82°C, 3 min., brightening in 1.8% CrO₃ and 7% H₃PO₄ at 75°C, 3 min., rinsing with bi-distilled water. **Cell** - Pt mesh counter electrode, situated symmetrically around the working electrode, and an Ag/AgCl/3 M KCl reference electrode.

Electrolytes - 0.5 M (NH₄)₂SO₄ + x M NH₄F (x = 0.050, 0.075 and 0.100)

Electrochemical measurements → Autolab PGSTAT 30/FRA2 using GPES and FRA software (Eco Chemie, The Netherlands) → current vs. time curves registered in the range of potentials from -1.2 to 0 V → after a constant value of the current reached, electrochemical impedance spectra measured at a given potential (frequency range 10 mHz - 10 kHz, ac amplitude 10 mV rms).

Measurement of the quantity of dissolved Al → ICP-OES (Prodigy)

Results and Discussion

Current vs. potential curves (Fig. 1) - several process stages:

Quasi-exponential increase of the current (-1.2..-1.0 V) → mainly dissolution of Al

Current plateau (-1.0..-0.7 V) → passivation, barrier layer formation

Plateau current → linear increase with fluoride concentration

At higher potentials → dissolution of the oxide, pore nucleation?

The dependence of current density on fluoride concentration in this region more complex

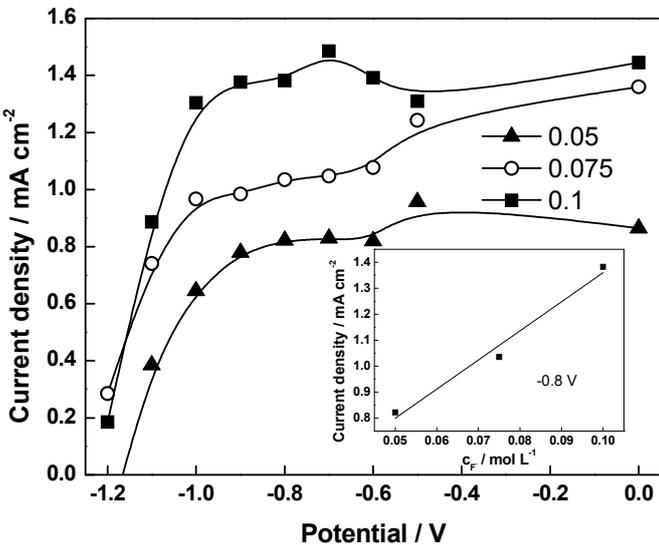


Fig. 1 Current density / potential curves in all investigated electrolytes in the potential range -1.2 - 0 V. Insert - dependence of current density at -0.8 V on fluoride concentration

Impedance spectra (Fig. 2)

In the *active region* (-1.2..-1.0 V) - three to four time constants, multistep dissolution process

In the *passivation region* - two time constants - high-frequency capacitive and low-frequency pseudo-inductive → migration of current carriers and their recombination [2], faradaic pseudo-capacitance at the lowest frequencies

Passivation region - diameters of both high and low-frequency semicircles increase with potential while the current stays almost constant → barrier film growth coupled to dissolution

Diameters of both high- and low-frequency semicircles → decrease with increasing fluoride concentration at constant potential (agreement with current vs. potential curves)

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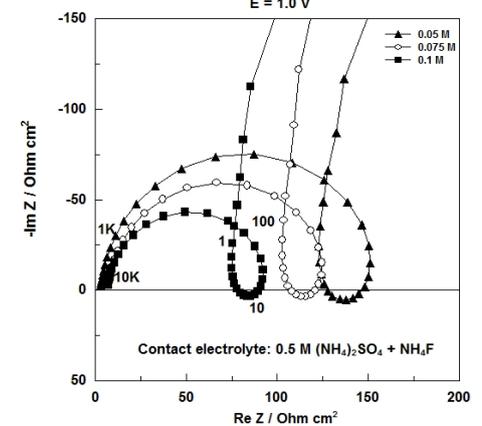
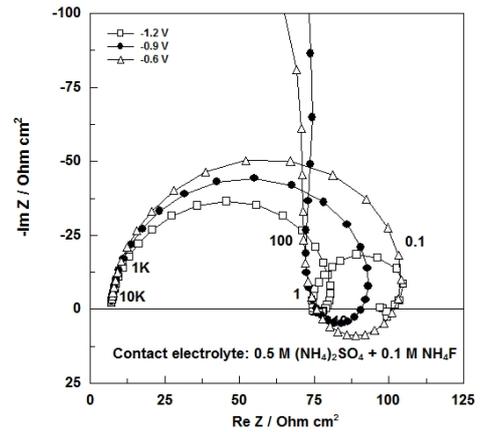


Fig. 2 Electrochemical impedance spectra obtained: a) in 0.5 M (NH₄)₂SO₄ + 0.1 M NH₄F at different potentials; b) at -1.0 V in all three investigated electrolytes

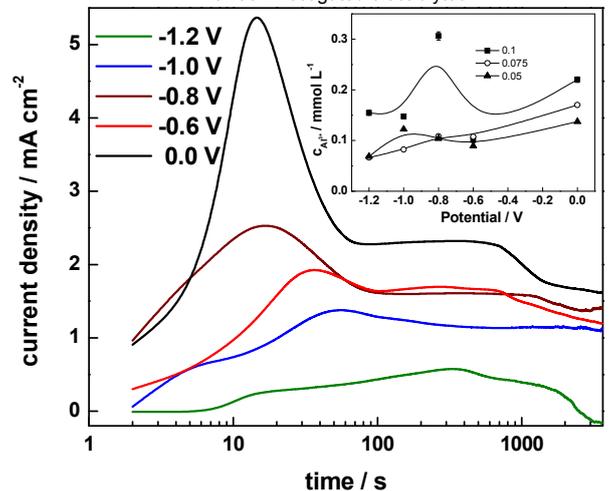


Fig. 3 Current density vs. time curves at different potentials in 0.5 M (NH₄)₂SO₄ + 0.1 M NH₄F electrolyte; Insert - concentration of dissolved Al as depending on potential and fluoride concentration

Current vs. time curves and analysis of dissolved products (Fig.3)

Evidence of *three time constants* in the active region and at least two in the passivation region → agreement with the impedance spectra

Current peak in the passivation region - peak time decreases with increasing potential → pore nucleation?

Dependence of *dissolved Al concentration* on potential and fluoride content complex - at least two parallel paths of dissolution involved

Future steps

- Characterization of the oxides with surface analytical techniques
- Elaboration of a kinetic model of the process based on the surface charge approach combined with a multistep Al dissolution scheme
- Estimation of kinetic and transport parameters

References

1. H. Tsuchiya, S. Berger, J. M. Macak, A. G. Munoz, P. Schmuki, *Electrochem. Commun.* 9 (2007) 545.
2. M. Bojinov, Nanoporous anodic oxides, Ch. 14 in *Handbook of Nanophysics, Vol.5, Functional Nanomaterials*, Kl. Sattler, Ed., Taylor & Francis, 2010, 14-1 - 14-21.