



# Electrochemical deposition of zinc from deep eutectic solvent on barrier alumina layers



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## ABSTRACT

The direct use of high-ordered porous templates of anodic aluminium oxide for formation of nanostructures via electrochemical deposition is difficult because the presence of the barrier alumina layer in the bottom of pores. In this paper, zinc electrodeposition from a solution of ZnCl<sub>2</sub> in a choline chloride/ethylene glycol eutectic mixture on dense alumina layers of different thicknesses was studied. In a potentiostatic regime, the deposition on a barrier layer was found to be hardly possible even when the layer is a native alumina film (about 2 nm thick). Choline and ethylene glycol form an adsorbed stable layer at the alumina/electrolyte interface and thereby block the access of zinc chloride anions to the electrode.

It has been shown that zinc can be directly deposited on a barrier layer by means of application of a combined potential mode in which an AC component of 50 mV superimposed on the DC potential of −1.6 V. Increasing the temperature of the eutectic solution allows zinc electrodeposition in a potentiostatic regime already at 50 °C. By application of any of these conditions, zinc can be deposited on a barrier alumina layer up to about 60 nm thick. The range of frequencies of the AC component and the temperature range where the deposition is optimal were considered. The mechanism of unblocking of the electrode by the alternating potential and by the temperature rise has been suggested.

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## 1. Introduction

In the last decade the high-ordered porous templates of anodic aluminium oxide (AAO) have widely been used for preparation of 1-D nanostructures [1]. Nanorods and other nanostructures are produced using electrochemical deposition that is the most conventional and cheap method. However, there is a limitation for application of AAO templates that arises from the presence of a barrier layer at the bottom of pores. The alumina film formed as a result of anodization or immediate oxidation of aluminium acts as a high resistive medium impairing the flow of current.

Generally, a detached AAO membrane (free AAO) with sputtered metallic contact is used for electrofilling of the pores [2–4]. A multi-stage process of removal of both substrate and the barrier layer followed by contact deposition is typically applied [5].

Both stages are time-consuming, require expensive equipment and have a poor scalability. In this respect, preparation of 1-D nanostructures by means of direct deposition in pores AAO template has a good practical potential. The method is much cheaper and faster than a deposition using a detached membrane. A number of ways to thin the barrier layer have been reported. The decrease of potential at the end of anodizing process [6–8] and dissolution of the oxide layer are the most promising of them. Unfortunately, the layer cannot be completely removed by any of these methods, and results in difficulties in electrochemical deposition into pores. The direct growth of nanostructured materials on barrier alumina layers opens new possibilities, as to create different metal-insulator-metal and metal-insulator-semiconductor devices, which can be used as sub-wavelength plasmonic waveguides [9,10] and supercapacitors [11,12].

It is well-known that ionic liquids (ILs) demonstrate a number of important properties such as negligible vapour pressure, wide electrochemical window and high thermal stability [13]. Deep eutectic solvents (DESS) have similar properties but, in contrast to

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the conventional ILs, DESs are much cheaper, non-toxic, water-/air-stable, and therefore have a good potential for use in industrial scale [14]. Abbott et al. have widely studied properties of DESs based on choline chloride namely viscosity and conductivity [15,16]. Electrodeposition of metals [17,18] and particularly zinc [19–24] and Zn-containing alloys [25] from these solvents was explored as well.

In our previous work [26], we formed zinc nanorods in an AAO template through zinc electrodeposition from DES based on choline chloride. Zinc was chosen as a model metal for deposition due to possibility of subsequent transformation into semiconductor materials such as zinc oxide and zinc sulphide [27]. It is known that the use of DES prevents a chemical destruction of the barrier which is typical for acidic/basic aqueous electrolytes. An ordered porous template was prepared by anodization of aluminium substrate without complete removal of the barrier layer. Different pulse plating and pulse reverse plating techniques for electrodeposition have been suggested and a summarization can be found in [28]. In this work a two-step process was used; pulse nucleation of zinc nanoparticles on the bottom of the pores followed by a growth of the rods in a potentiostatic mode. Application of the alternating current (AC) stage in the beginning of the process allowed us to deposit zinc in presence of the barrier [26]. It has been demonstrated that electrofilling of an AAO template without removal of the barrier layer is also feasible as well in aqueous electrolytes [29,30]. An AC mode method or a pulse deposition [31] were shown to be the most promising methods in this respect. However, no systematic study of electrodeposition over an aluminium oxide layer has been reported. The mechanisms of nucleation at the bottom of pores are also not fully understood.

The study of nucleation processes in porous templates is not easy because of the fact that the interface is buried. Besides, the diffusion limitations in the pores can create interfering effects. In this respect, electrodeposition on flat samples allows to avoid these limitations and can serve as an appropriate model process for such study. This work aims at investigating ways of zinc electrodeposition from DES based on choline chloride over barrier alumina layers in terms of temperature, oxide layer thickness, and potential profile applied. Effects of Zn deposition using a potentiostatic (PS) regime and a PS regime modified with a small alternating potential (AC-PS) were considered.

## 2. Experimental

Coupons of aluminium foil (10×5×0.2 mm, 99.990%, Good-fellow) and Fluorine doped Tin Oxide (FTO) glass (Sigma-Aldrich) were used for template preparation. Part of their surface was isolated with varnish, giving an electrode working area of about 0.5 cm<sup>2</sup>. Before anodization, the metallic electrodes were chemically polished in a mixture of phosphoric acid, nitric acid and acetic acid at 70–90 °C. Finally, the samples were rinsed with acetone, ethanol and distilled water, and then dried in air.

### 2.1. Preparation of anodized samples

A Keithley 237High Voltage Source-Measure Unit was used as a current source for sample oxidation. A 0.1 M ammonium pentaborate aqueous solution served as electrolyte. A two-step anodization procedure was applied at room temperature. The first anodization step was performed in a galvanostatic mode with a current density of 1 mA/cm<sup>2</sup>. Platinum foil was used as counter electrode. The process was terminated after the desired voltage (10, 20, 40 V) was achieved. The second anodization step was done in a potentiostatic regime at the same voltages during 10 min. After the two steps of anodization the electrodes were stored in a desiccator for stabilization of the compact alumina layer.

### 2.2. Oxide layer thickness measurements

Thickness of the layers was measured by Electrochemical Impedance Spectroscopy (EIS) and Glow Discharge Optical Emission Spectroscopy (GDOES).

The EIS measurements were performed using a Gamry FAS2 Femtostat with a PCI4Controller over a 10<sup>5</sup>–10<sup>–2</sup> Hz frequency range with a step of 7 points per decade. Impedance spectra were recorded applying a 10 mV (rms) sinusoidal perturbation at open circuit potential. The measurements were carried out in a three-electrode cell (consisting of a Mercury/Mercury sulphate reference electrode, a platinum foil as the counter electrode and the working electrode with an area of 0.5 cm<sup>2</sup>). All measurements were performed in the Faraday cage to avoid interferences with external electromagnetic fields. A 0.1 M ammonium pentaborate aqueous solution was the working electrolyte. The impedance plots were fitted using the Echem Analyst software from Gamry Inc. All spectra were successfully fitted using a parallel R-C network.

GDOES depth profile analysis of the coatings was completed using a HORIBA GD-Profilier 2 with an anode of 4 mm in diameter and operating at a pressure of 650 Pa and a power of 10 W.

Both EIS and GDOES methods gave the same thickness values (Table 1).

### 2.3. Electrodeposition study

Preparation of DES electrolytes and the electrodeposition experiments were done in air atmosphere. The eutectic system was prepared by mixing choline chloride (ChCl, 98%) and ethylene glycol (EG, 99+%) in the molar ratio of 1:2. Anhydrous zinc chloride (99.99%) was added to the DES to obtain a 0.1 M solution which was then heated and kept at 60 °C under vacuum during 24 h. As-prepared solution (hereafter DES:Zn) was either used for electrodeposition or stored in desiccator over P<sub>2</sub>O<sub>5</sub>.

Cyclic voltammograms (CVs) were obtained using a Bio-Logic SAS SP-300 potentiostat. Measurements were performed in a Faraday cage. A three-electrode cell consisting of a platinum wire as reference electrode, graphite rod as counter electrode and the working electrode was used. All cyclic voltammetric curves were recorded starting in the cathodic direction. The potential scan rate was 0.1 V/s in all potentiodynamic experiments.

Investigations of electrode surface morphology and elemental analysis were performed using a Hitachi S-4100 scanning electron microscope (SEM) coupled with energy dispersive spectroscopy (EDS). An ImageJ 1.48 v image processing software was applied for calculation of the electrode areas covered by the deposited zinc.

Fourier transform infrared (FTIR) spectra were recorded using a Bruker IFS55 spectrometer equipped with a single horizontal Golden Gate attenuated total reflectance (ATR) cell.

## 3. Results and discussion

### 3.1. Electrodeposition of zinc in potentiostatic (PS) regime

Initially, zinc electrodeposition from DES:Zn on an electrode with a good conductivity for characterization of electrochemical

**Table 1**  
Thickness of the barrier alumina layers.

Voltage	Thickness
0 V	2 nm
10 V	15 nm
20 V	27 nm
40 V	54 nm

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