

***Final Draft***  
**of the original manuscript:**

Sarykevich, M.; Salak, A.N.; Ivanou, D.K.; Yasakau, K.A.; Andre, P.S.;  
Ferreira, R.A.S.; Zheludkevich, M.L.; Ferreira, M.G.S.:

**Effect of the Anodic Titania Layer Thickness on Electrodeposition  
of Zinc on Ti/TiO<sub>2</sub> from Deep Eutectic Solvent**

In: Journal of the Electrochemical Society (2017) Electrochemical Society

DOI: 10.1149/2.1351702jes

# The effect of anodic titania layer thickness on electrodeposition of zinc from deep eutectic solvent

M. Strykevich<sup>1</sup>, A.N. Salak<sup>1</sup>, D.K. Ivanou<sup>2</sup> S. F. H. Correia<sup>3,4</sup>, R. A. S. Ferreira<sup>3,4</sup>,  
M.L. Zheludkevich<sup>1,5</sup>, M.G.S. Ferreira<sup>1,\*</sup>

<sup>1</sup>*Department of Materials and Ceramic Engineering, CICECO-Aveiro Institute of Materials, University of Aveiro, 3810-193 Aveiro, Portugal*

<sup>2</sup>*LEPABE, Faculty of Engineering, University of Porto, 4200-465 Porto, Portugal*

<sup>3</sup>*Physics Department, CICECO-Aveiro Institute of Materials, University of Aveiro, 3810-193 Aveiro, Portugal*

<sup>4</sup>*Instituto de Telecomunicações, Campus Universitário de Santiago, 3810-193 Aveiro, Portugal*

<sup>5</sup>*Institute of Materials Research, Helmholtz-Zentrum Geesthacht, 21502 Geesthacht, Germany*

## Abstract

Zinc electrodeposition from a deep eutectic mixture of ZnCl<sub>2</sub> and choline chloride/ethylene glycol on titanium covered by an anodic titania film of different thicknesses was studied. It has been shown that thin titanium dioxide layers work as insulator and the rate of zinc deposition decreases with film thickness. Thicker titania layers (23 nm and higher) have opposite properties and the zinc reduction rate starts gradually increasing with thickness. This happens because at the higher voltage necessary to grow thicker anodic films they become more crystalline and consequently more conductive.

There is also evidence that in DES no dense organic layer forms on the titanium/titania electrodes. The application of an AC signal superimposed on a DC potential only marginally increases the amount of zinc deposited and FTIR measurements did not reveal the formation of any chemical bonds between the film and DES.

Zn deposition onto titanium/titania is characterised by instantaneous three-dimensional nucleation mechanism, which is independent of titania thickness.

---

\* Corresponding author. Tel.: +351 234370354  
E-mail address: [mgferreira@ua.pt](mailto:mgferreira@ua.pt) (M.G.S. Ferreira)

**Keywords:** Titanium oxide, deep eutectic solvent, zinc electrodeposition.

## Introduction

Electrochemical deposition is a conventional and cheap technique to form 1-D nanostructures. In most of the cases, porous anodic templates on the valve metals are used. Filling of the matrixes by other materials is applied to produce solid state solar cells, photodetectors, magnetic sensors, metal–insulator–metal capacitors [1] etc. The major drawback of the porous template systems is a barrier layer on the bottom, which usually acts as a high resistive medium impairing the flow of current.

Direct investigation of deposition and nucleation processes in porous templates is hindered because the interface is hidden. Electrodeposition on flat samples allows to avoid these limitations and can serve as an appropriate model process for such study. However extrapolation of results found on a bare metal electrode to the processes on the bottom of pores is incorrect because of critical differences between metal/electrolyte and barrier oxide/electrolyte interfaces. Consequently the use of a metallic electrode covered by the anodic oxide layer is mandatory to study the bottom processes. In our previous work [2] zinc electrodeposition from a solution of  $ZnCl_2$  in a choline chloride / ethylene glycol eutectic mixture on dense alumina layers of different thicknesses was studied. It was shown that the potentiostatic deposition of zinc on an alumina barrier layer at  $-1.6V$  and room temperature is impossible even if the layer thickness does not exceed  $\sim 2$  nm (a native alumina film). As a comparison, zinc is easily deposited at  $-1.4$  V from the same solution on a FTO glass electrode. The formation of a dense organic layer due to interaction between OH groups of the organic species with the alumina film was demonstrated. Moreover deposition has been shown to be possible by superimposing an alternating sinusoidal voltage on DC potential ( $-1.6V$ ) or alternatively increasing the solution temperature [2].

The current paper is devoted to studying of electrodeposition of zinc from choline based eutectic on anodic titanium oxide film. Bulk anodic titania has been investigated for more than 50 years. Several properties such as growths factor [3-8], crystallinity [1, 9-12], conductivity, influence of anodization solution and regime [13] were widely studied by different authors. Despite all these studies deposition over anodic titania is still hardly understood. Only works about deposition of copper on titanium oxide films from water solution were described in literature [14, 15]. Electrodeposition of metals from DES on titania covered electrodes has not yet been analysed.

Titanium dioxide films both in pure state and after electrochemical modification have distinguished properties in which concerns certain properties, for instance, catalytic and

photocatalytic [16, 17], self-cleaning and wetting [18], use as solar cell [19] and optical devices [20]. Furthermore, anodic titania is a promising porous matrix to be filled by different materials. Some works have been already done in this area [21-23].

Zinc was chosen as a material to be deposited due to its capability to transform afterwards into semiconductor materials such as zinc oxide and zinc sulphide [24] and for comparison of the results with previous work [2] on deposition of zinc on aluminium/alumina.

Deep eutectic solvent (DES) based on choline chloride was selected as electrolyte for deposition due to its properties, such as negligible vapour pressure, wide electrochemical window and high thermal stability [25]. Choline eutectic is often described in literature as quasi ionic liquid because of the properties similarity. However, in contrast to conventional ionic liquids, DESs are very cheap, not-toxic and have good potential for industrial usage [26]. Abbott et al. have widely studied properties of DESs based on choline chloride, namely viscosity and conductivity [27, 28]. Electrodeposition of metals [29, 30] and particularly zinc [31-37] and Zn-containing alloys [38] from these solvents was explored as well. Moreover the use of DES as electrolyte gives an opportunity to dissolve compounds which are insoluble in water (for example ZnO) and to make deposition from these solutions [36, 39].

## 2. Experimental

Coupons of titanium foil (100×5×1 mm, 99.2%, Alfa Aesar) were used as electrode material for sample preparation. The coupons were rinsed with acetone, ethanol and distilled water and then were dried in air. Before anodization, the electrodes were chemically polished in a HF:HNO<sub>3</sub> mixture (1:3 by volume) to mirror finish and finally were rinsed with deionized water. A part of their surface was isolated with chemically resistant varnish, giving an electrode working area of about 0.5 cm<sup>2</sup>.

A Keithley 237 High Voltage Source-Measure Unit was used as a current source for the sample anodizing. A 1M sulphuric acid aqueous solution was used as electrolyte [12]. The anodization was performed in a galvanostatic mode with a current density of 10 mA/cm<sup>2</sup>. The counter electrode was a platinum foil. The process was terminated after the desired voltage (3, 7, 10, 20, 40 V) was achieved. The thinnest anodic film used in this work (12 nm) was formed at 3V. Preparation of thinner anodic titania layers is hindered because of low reproducibility of the experiments and inhomogeneity of the films. After anodization the electrodes were stored in a desiccator for stabilization of the compact titania layer during 24 hours.

Thickness of the layers was measured by Ellipsometry and Glow Discharge Optical Emission Spectroscopy (GDOES). The spectroscopic ellipsometry measurements were made using an AutoSE ellipsometer (HORIBA Scientific) with a total of 250 points in the wavelength interval 450-850 nm, an incidence angle ( $\theta_0$ ) of 70° and a signal quality of 30. An area of 250×250 μm was measured. GDOES depth profile analysis of the coatings was done using a HORIBA GD-Profilier 2 with a copper anode of 4 mm in diameter. Argon sputtering of the sample surface occurred at a pressure of 900 Pa and power of 10 W.

Preparation of DES electrolytes and the electrodeposition experiments have been done in contact with air. 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 0.3 M solution which was heated and kept at 60 °C under vacuum during 24 h. The as-prepared solution (hereafter DES:Zn) was either used for electrodeposition or was stored in desiccator over P<sub>2</sub>O<sub>5</sub>.

Voltammograms 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 voltammetric curves were recorded starting in the cathodic direction. In all potentiodynamic experiments, the potential scan rate was 20 mV/s.

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

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

### 3. Results and discussion

#### *Titanium anodization*

Figure 1a shows the dependence of the signal intensity of the elements composing the titanium anodized layer (40 V) on its depth obtained by GDOES. It demonstrates homogeneity of the oxide film and uniformity of sulphur distribution. Sulphur is present in the titania film because sulphuric acid solution was used as electrolyte. Deviation of the profiles at the beginning of sputtering can be explained by the presence of an adsorbed layer on the surface containing sulphur and oxygen, probably from the sulphuric acid. The oxygen concentration slightly decreases throughout the film because oxygen migration occurs during the anodization process, from the electrolyte to the electrode leading to higher concentration of oxygen on the free titania surface than on titania/titanium interface. A well-defined interface between anodic titania film and titanium substrate was obtained. The plateau on the titanium and oxygen signals' intensity curves during the etching process corresponds to the oxide layer. Further growth of the titanium signal indicates that the metal sputtering started. The plateau does not appear in the results obtained on the samples prepared at low voltage (less than 10V) (Fig. 1b) because of the very small thickness of the film and microroughness of the interface; nevertheless estimation of the thickness is still possible taking into consideration the change in slope of the depth profile curves.

Ellipsometry measurements were done in parallel with GDOES and data fitting was performed using the Lorentz model. Both of the techniques showed similar results in terms of thickness/voltage ratio.

Fig. 2 shows that the thickness-voltage ratio estimated for the galvanostatic growth of anodic TiO<sub>2</sub> corresponds to the values (2–3 nm/V) that are commonly reported in literature for titania anodic films grown in sulphuric acid solutions [3-8].

#### *Zinc electrodeposition on Ti/TiO<sub>2</sub> electrodes with different film thicknesses*

Typical voltammograms that were obtained on zinc and the titanium electrode covered with compact titania film in DES:Zn are presented in Figure 3. The potential for reduction of zinc on zinc electrode is -1.1V (Fig. 3). Nevertheless, the negative current was only detected at -1.2V on the titanium/titania electrode after pre-treatment (activation) in hydrofluoric acid, which evidences the existence of an overpotential for zinc reduction on the titania surface. The activation in HF results in decrease of the native layer thickness. Fast current increase followed by plateau was observed for these electrodes. Strong cathodic current appears at -1.65V and corresponds to reduction of the organic species. Decomposition occurs according to the

mechanism described in literature [40, 41]. Small current which appears on the titania covered electrodes probably corresponds to reduction of titania ( $\text{Ti}^{4+} + \text{e}^- + \text{H}^+ \rightarrow \text{Ti}^{3+} + \text{H}^+$ ) [23] since zinc was not detected on the surface by SEM studies in this potential region. Electroreduction of zinc was performed in the range from -1.2V to -1.7V with 100mV step to find the best physical properties of the deposit. The quality of the coating was evaluated visually. In the current work deposition was carried out at -1.6V because it gives solid zinc coating with the best adhesive properties.

Initial increase in the barrier thickness from native (HF activated electrode with a barrier thickness of 3-5 nm [42]) till 12 nm by anodic film formation leads to a strong decrease of the reduction current (Fig. 3). It is typical for valve metals because of low conductivity of the oxide film. Normally, the resistance of the film rises with its growth, which makes the deposition difficult. This situation was demonstrated for the likened aluminium/alumina system in our previous work [2]. Increasing the alumina barrier thickness provides significant increase of the resistance and consequently of the zinc reduction current. Nevertheless, in this specific case, the negative current on the titanium/titania electrode with 18 nm titania film stays on the same level as with 12 nm thickness (Fig. 3). Moreover, with further increment of thickness to 23 nm and thicker, the current rises, contrary to the case of alumina where the current decreases dramatically with growth of the film. The maximum current on titanium/titania electrode was obtained at maximal film thickness of 84 nm, and is similar to the current on the activated electrode (Fig. 3). The phenomenon of current increase on thicker anodic titania films was demonstrated in Hyun Chang's work for copper deposition from water solution [15]. The authors modified the Ti cathode surface by temperature oxidation and anodization process. Both cases show enhanced deposition rate because the film is more conductive in spite of the oxide layer is thicker. They explain this fact by better crystallinity of the anodic film at higher anodization voltage and correspondingly at higher film thickness. Similar conclusion was achieved in Shibata's work [9]. The structure of the anodic oxide film on titanium was found to be dependent on the formation potential. Film crystallization occurs at potentials more positive than 7.0 V. We can suggest in the present work an analogous explanation for the current increment according to Hyun Chang's and Shibata's works. The oxide layer remains amorphous on the initial stage of the growth and the conductivity decreases with film thickness (12 and 18 nm films). After reaching a critical anodization voltage, the anodic layer starts crystallizing, which results in higher current for the 23 nm barrier film (that corresponds to 10V) compared to the 12 and 18 nm films (3 and 7V correspondingly). The film crystallinity and conductivity progressively increase with additional accretion of the barrier, which reflects



on the voltammetry curves as increase of current (Fig. 3). These results are in accordance with Shibata's work [9] where it was demonstrated that the crystallization starts after the anodization potential of 7 V.

Fig. 4a depicts the current-time transients resulting from chronopotentiometric experiments on titanium electrode covered with titania of different thicknesses at -1.6 V. Deposition on the activated electrode is much faster than on thin barrier layer (12, 18 nm). The total electric charge starts to increase for the 23 nm layer and rises as the layer thickness grows. As it was mentioned before [2], electrodeposition of zinc on native alumina layer (around 2 nm) was impossible in standard potentiostatic regime. Even after shifting the potential into the deep cathodic region (-5V) intense gas evolution was observed but there was no deposit of zinc on the electrode surface.

The amount of zinc that was deposited during 30 seconds was calculated from Faraday's law for electrolysis:

$$n = \frac{Q}{zF}$$

where  $n$  is the chemical amount of zinc deposited,  $Q$  is the total electric charge passed, which is calculated from the above current-time curves,  $z = 2$  is the number of electrons transferred per ion and  $F$  is the Faraday constant. The results are shown in figure 5 (red line).

Analysis of SEM images of the samples was performed to confirm that the current increase corresponds to the growth of the zinc deposition rate and not to additional competitive reactions (as in the case of aluminium/alumina). The typical image obtained for deposited zinc on titania film 23nm thick, at  $E = -1.6V$ , is shown in Fig. 6a and in the inset after processing by ImageJ. At the early stages of Zn deposition (30 seconds) individual spherical particles with size  $d = 40$  nm were formed. EDS analysis (Fig. 6c) shows the presence of Zn. The number and average size of the particles were determined in the same way for all the samples. It was assumed that the particles are spherical. Then the zinc volume was calculated and the chemical amount of the deposit obtained. The results demonstrate that the quantity of zinc deposited on the surface increases with the barrier thickness growth (Fig. 5, black line). The difference between the black and red line could be due to the fact that the deposition process efficiency is not 100% (around 60%).

As it has been mentioned in the introduction a strong interaction between the solution eutectic components and alumina interface was observed during deposition on anodic alumina in our previous work [2]. Additional AC component superimposed on constant DC potential makes the organic layer on the alumina/electrolyte interface less compact and more permeable to zinc chloride anions. The positive influence of this regime, such as growth of zinc reduction

rate, for electrodeposition on the aluminium/alumina system was demonstrated. Identical study in this work was performed using a sinusoidal potential of 50 mV amplitude superimposed on the DC potential of -1.6 V at the 1 kHz frequency. Specimens with titania layers of 12, 18, 23, 43 and 84 nm were used. Typical SEM images of the electrode surface after 30 seconds of zinc deposition on the titanium electrode covered with 23 nm titania film is presented in Figure 6b.

The particles size on the electrode after AC-PS mode deposition is bigger than on DC (PS) mode, but the number of the particles is less. Estimating the quantity of the deposited zinc in both modes it is 1.5 times less in potentiostatic mode than in the AC-PS regime. Thus it can be concluded that there is a small influence of the AC component on the deposition process. Increase of the zinc amount was much smaller in comparison with the aluminium/alumina system where it was found an increase of 10 times in the same conditions [2]. The small difference observed can be explained by additional “electro stirring” on the AC-PS mode, i.e., migration of charged species in the alternating electric field. The dense organic layer formed in the case of alumina/aluminium system might not exist in the case of titanium/titania.

FTIR measurements have been done to confirm that the organic layer does not form. FTIR-ATR spectra of DES:Zn in contact with titanium electrodes covered by titania are presented in Figure 7. The respective spectrum of blank DES:Zn is shown for comparison. The observed bands in the DES:Zn spectra correlate well with the reference spectroscopic data for ethylene glycol and choline chloride. One can see that contact of DES:Zn with the electrode surface results in no shift of the characteristic bands. It differs from the case of alumina/DES interface where O-H stretching shift around  $135\text{ cm}^{-1}$  was found. Thereby we anticipate that no chemical bonds were formed between the organic species and the titanium/titania electrode. Titanium/titania and aluminium/alumina systems despite chemical similarity demonstrated absolutely different properties in terms of interaction with DES.

#### *Zinc nucleation mechanism*

Electrodeposition of metals on an electrode with low chemical affinity to electrodeposited metal usually occurs with overvoltage and involves three-dimensional nucleation with hemispherical growth of the nuclei [43]. There are two main types of three-dimensional nucleation: instantaneous and progressive. In the instantaneous model all nucleation sites are activated right after potential application. Progressive model is the situation when the nucleation sites become activated during the experiment.

Deep understanding of the nucleation process and other processes, which occur in the beginning of the deposition, is extremely important because the start of the process is crucial to

the properties and structure of the deposited materials. For example, in the same titania matrix inside and over the tubes is possible to obtain either nanowires, nanotubes, sandwich and coaxial multilayer structures.

The mechanism of nucleation and growth can be determined by graphical analysis of the current transients from chronoamperometric measurements. Such an approach is commonly used in studies for metal nucleation on different substrates (Ge, Si, W, vitreous carbon, etc.) [37, 43-46]. Figure 4a shows series of current transients for Zn electrodeposition at -1.6V, on the titanium electrode covered with titania films of different thicknesses. The transients are characterized by an initial increase of current followed by a drop at longer time. Due to the high deposition overpotential (about 100mV) and the transient shape we believe that the nucleation process matches to 3D mechanism followed by diffusion-limited growth [43]. The deposition transients acquired for different thicknesses of titania were plotted in dimensionless form by normalizing the current ( $i$ ) and time ( $t$ ) respectively to the maximum current ( $i_{max}$ ) and time ( $t_{max}$ ) where the maximum current is reached, Fig. 4b.

According to literature [43, 44] for instantaneous nucleation the theoretical normalized rate law is given by:

$$\left(\frac{i}{i_{max}}\right)^2 = 1.9542 \frac{t_{max} - t_0}{t - t_0} \left[1 - \exp\left(-1.2564 \frac{t - t_0}{t_{max} - t_0}\right)\right]^2$$

and for progressive nucleation the theoretical normalized rate law is:

$$\left(\frac{i}{i_{max}}\right)^2 = 1.2254 \frac{t_{max} - t_0}{t - t_0} \left[1 - \exp\left(-2.3367 \frac{(t - t_0)^2}{(t_{max} - t_0)^2}\right)\right]^2$$

where  $t_0$  is the induction time, i.e. the time needed to form a nucleus larger than the critical nucleus size. The theoretical plots are shown in the same Fig. 4b. Comparing the theoretical plots for progressive and instantaneous nucleation and the experimental plots for zinc reduction, it is seen that Zn deposition onto titanium/titania electrode proceeds by instantaneous three-dimensional nucleation. The mechanism is independent of the titania thickness and denotes that practically all Zn nuclei on the electrode surface are formed at once and have the same size. Deviation from the theoretical curves are probably related to accessory processes [40, 41, 47].

#### 4. Conclusions

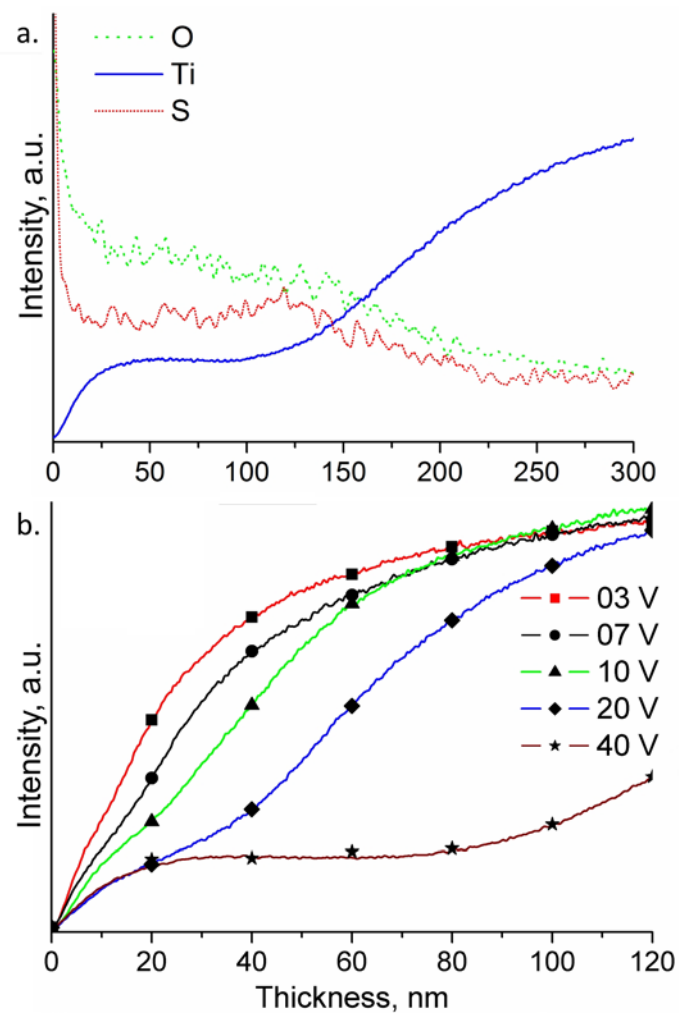
Electrodeposition of zinc from 0.3M ZnCl<sub>2</sub> solution in choline chloride/ethylene glycol eutectic solvent on titania barrier layer was successfully performed. Reduction of zinc

species occurs much faster on thicker anodic films than on thinner ones. The chemical amount of reduced metallic zinc at -1.6V during 30 seconds is 4 times higher on 84 nm thick films than on 12 nm ones. It happens because both film thickness and crystallinity grow with the anodization potential, the latter leading to higher oxide conductivity. Application of -1.6V DC potential, superimposed by an alternating sinusoidal component of 50mV, leads to negligible increase of the amount of zinc reduced. Regarding this fact and additional FTIR results it is assumed that there is no formation of a **dense organic** layer on titanium/titania electrode contrary to the aluminium/alumina system. Thus zinc deposition becomes easier.

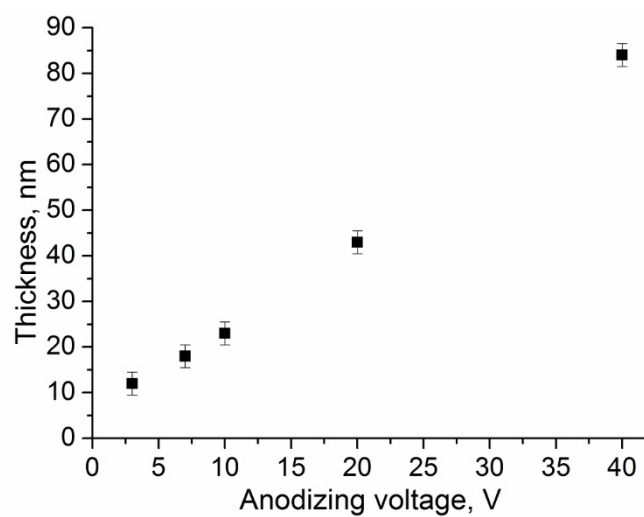
Electrodeposition of zinc at -1.6V from DES occurs by instantaneous three-dimensional nucleation mechanism and it is uninfluenced by the titania layer thickness.

### **Acknowledgements**

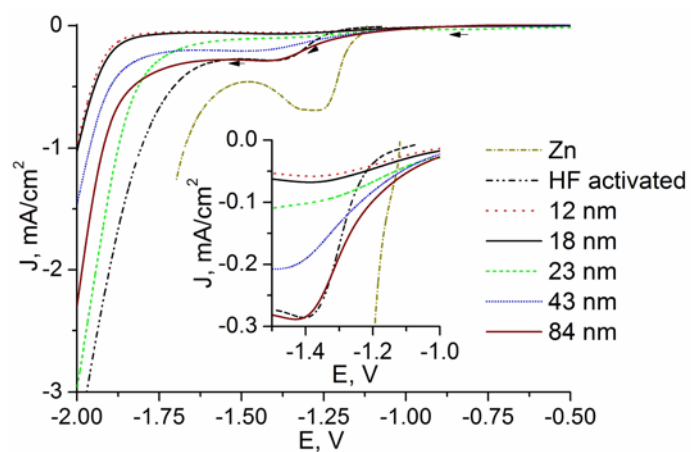
The financial support of the European Commission and Portuguese Foundation for Science and Technology (FCT) in frame of the projects PIRSES-GA-2011-295273 – NANEL and PTDC/CTM-NAN/113570/2009, respectively, is gratefully acknowledged.

**Figures.**

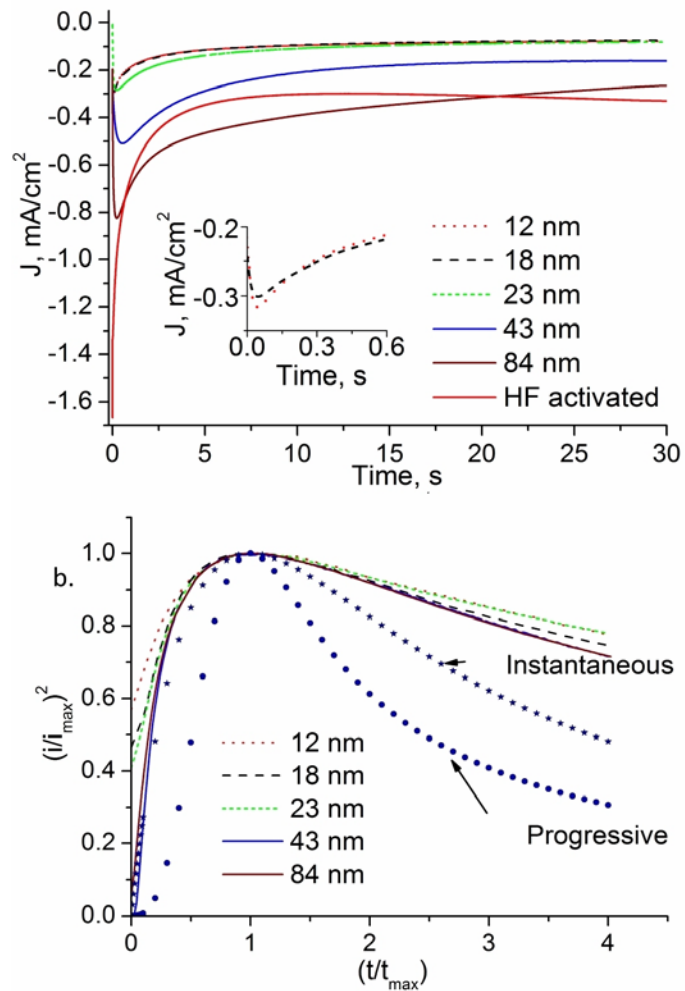
**Figure 1.** Qualitative depth profile of an anodic titanium oxide measured by GDOES. Typical depth profiles of an electrode after anodization at 40 V (a), and titanium signal profile obtained from the electrodes after anodization at different voltages (b).



**Figure 2.** Film thickness as a function of potential for the anodic oxide film formed on titanium by electrooxidation in 1M sulphuric acid solutions.

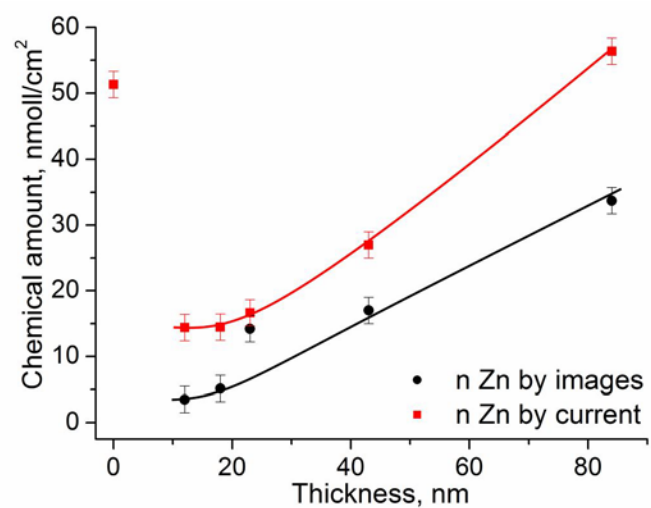


**Figure 3.** Voltammograms measured on zinc electrode and titanium electrode covered anodic titania of different thicknesses (inset: magnification of -1.5 to -1.0 V zone)

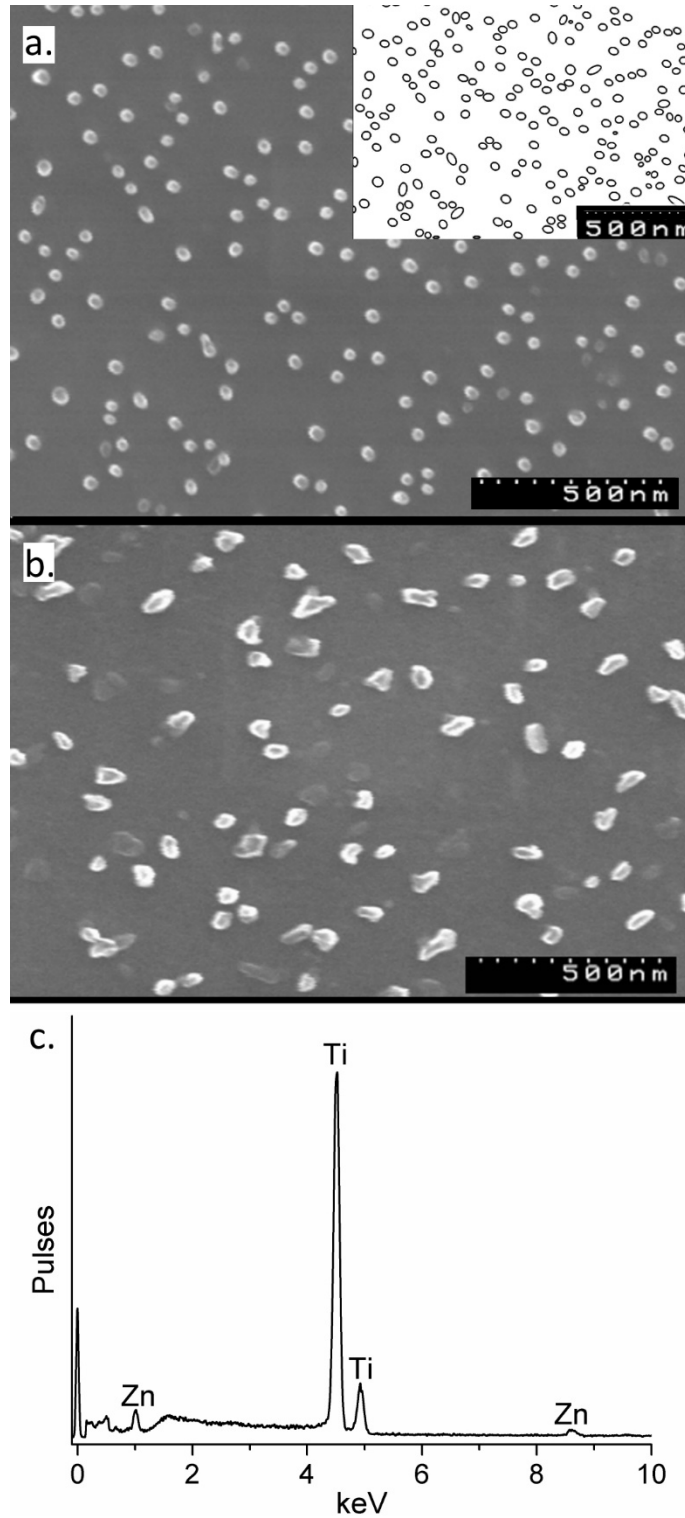


**Figure 4.** Current-time transients resulting from chronoamperometric experiments that were performed at a titanium electrode with different titania layer thickness in DES:Zn at -1.6V applied potential (a). Comparison of experimental data obtained from chronocurrent transients with instantaneous and progressive nucleation models (b).

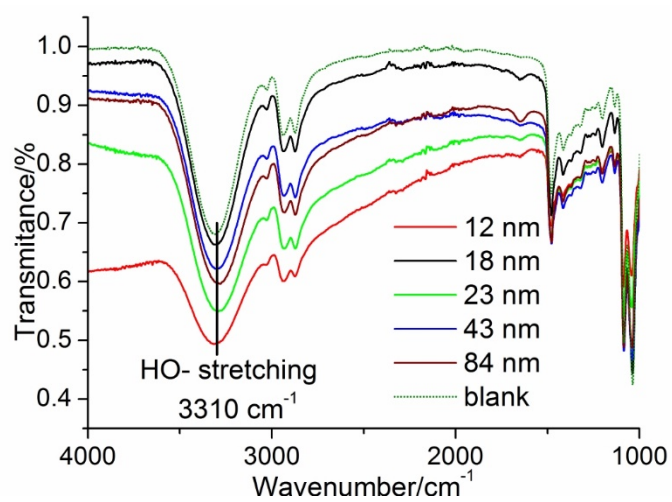




**Figure 5.** Chemical amount of zinc deposited on titanium electrode with titania calculated by ImageJ software (black line) and by Faraday's law (red line). Deposition dwell was 30 seconds. Solid lines are used to guide eyes.



**Figure 6.** SEM images of titanium electrode surface with 23 nm titania film after zinc deposition from DES:Zn in a PS mode (a) and in AC-PS mode (b) inset is a typical image obtained after processing by ImageJ. The EDS spectrum recorded from the sample surface after zinc deposition in a DC mode (23 nm anodic film) (c). Deposition dwell was 30 seconds.



**Figure 7.** FTIR-ATR spectra of blank DES:Zn, and different thicknesses anodic titania films in contact with DES:Zn.

## References

- [1] D. Kannadassan, R. Karthik, M. Shojaei Baghini, P.S. Mallick, Nanostructured metal–insulator–metal capacitor with anodic titania, *Materials Science in Semiconductor Processing*, 16 (2013) 274-281.
- [2] M. Sarykevich, A.N. Salak, D.K. Ivanou, A.D. Lisenkov, M.L. Zheludkevich, M.G.S. Ferreira, Electrochemical deposition of zinc from deep eutectic solvent on barrier alumina layers, *Electrochimica Acta*, 170 (2015) 284-291.
- [3] J.L. Delplancke, R. Winand, Galvanostatic anodization of titanium—I. Structures and compositions of the anodic films, *Electrochimica Acta*, 33 (1988) 1539-1549.
- [4] M. Kozłowski, W.H. Smyrl, L. Atanasoska, R. Atanasoski, Local film thickness and photoresponse of thin anodic TiO<sub>2</sub> films on polycrystalline titanium, *Electrochimica Acta*, 34 (1989) 1763-1768.
- [5] T. Ohtsuka, M. Masuda, N. Sato, Ellipsometric Study of Anodic Oxide Films on Titanium in Hydrochloric Acid, Sulfuric Acid, and Phosphate Solution, *Journal of The Electrochemical Society*, 132 (1985) 787-792.
- [6] S.K. Poznyak, A.D. Lisenkov, M.G.S. Ferreira, A.I. Kulak, M.L. Zheludkevich, Impedance behaviour of anodic TiO<sub>2</sub> films prepared by galvanostatic anodisation and powerful pulsed discharge in electrolyte, *Electrochimica Acta*, 76 (2012) 453-461.
- [7] M. Schneider, S. Schroth, J. Schilm, A. Michaelis, Micro-EIS of anodic thin oxide films on titanium for capacitor applications, *Electrochimica Acta*, 54 (2009) 2663-2671.
- [8] J.W. Schultze, M.M. Lohrengel, Stability, reactivity and breakdown of passive films. Problems of recent and future research, *Electrochimica Acta*, 45 (2000) 2499-2513.
- [9] T. Shibata, Y.C. Zhu, The effect of film formation conditions on the structure and composition of anodic oxide films on titanium, *Corrosion Science*, 37 (1995) 253-270.
- [10] A.G. Mantzila, M.I. Prodromidis, Development and study of anodic Ti/TiO<sub>2</sub> electrodes and their potential use as impedimetric immunosensors, *Electrochimica Acta*, 51 (2006) 3537-3542.
- [11] H. Habazaki, M. Uozumi, H. Konno, K. Shimizu, P. Skeldon, G.E. Thompson, Crystallization of anodic titania on titanium and its alloys, *Corrosion Science*, 45 (2003) 2063-2073.
- [12] C. Jaeggi, P. Kern, J. Michler, T. Zehnder, H. Siegenthaler, Anodic thin films on titanium used as masks for surface micropatterning of biomedical devices, *Surface and Coatings Technology*, 200 (2005) 1913-1919.
- [13] M.V. Diamanti, M.P. Pedferri, Effect of anodic oxidation parameters on the titanium oxides formation, *Corrosion Science*, 49 (2007) 939-948.
- [14] J.L. Delplancke, M. Sun, T.J. O'Keefe, R. Winand, Nucleation of electrodeposited copper on anodized titanium, *Hydrometallurgy*, 23 (1989) 47-66.
- [15] H.K. Chang, B.-H. Choe, J.K. Lee, Influence of titanium oxide films on copper nucleation during electrodeposition, *Materials Science and Engineering: A*, 409 (2005) 317-328.
- [16] M.V. Diamanti, M. Ormellese, E. Marin, A. Lanzutti, A. Mele, M.P. Pedferri, Anodic titanium oxide as immobilized photocatalyst in UV or visible light devices, *Journal of Hazardous Materials*, 186 (2011) 2103-2109.
- [17] M. Valden, X. Lai, D.W. Goodman, Onset of catalytic activity of gold clusters on titania with the appearance of nonmetallic properties, *Science*, 281 (1998) 1647-1650.
- [18] R. Wang, K. Hashimoto, A. Fujishima, M. Chikuni, E. Kojima, A. Kitamura, M. Shimohigoshi, T. Watanabe, Light-induced amphiphilic surfaces, *Nature*, 388 (1997) 431-432.
- [19] M. Gratzel, Photoelectrochemical cells, *Nature*, 414 (2001) 338-344.
- [20] A.K. Sharma, Anodizing titanium for space applications, *Thin Solid Films*, 208 (1992) 48-54.
- [21] T. Gandhi, K.S. Raja, M. Misra, Synthesis of ZnTe nanowires onto TiO<sub>2</sub> nanotubular arrays by pulse-reverse electrodeposition, *Thin Solid Films*, 517 (2009) 4527-4533.

- [22] Y. Kang, J. Zhao, J. Tao, X. Wang, Y. Li, Electrochemical deposition of Co nanowire arrays into self-organized titania nanotubes, *Applied Surface Science*, 254 (2008) 3935-3938.
- [23] J.M. Macak, B.G. Gong, M. Hueppe, P. Schmuki, Filling of TiO<sub>2</sub> Nanotubes by Self-Doping and Electrodeposition, *Advanced Materials*, 19 (2007) 3027-3031.
- [24] P.J. Dale, A.P. Samantilleke, D.D. Shivagan, L.M. Peter, Synthesis of cadmium and zinc semiconductor compounds from an ionic liquid containing choline chloride and urea, *Thin Solid Films*, 515 (2007) 5751-5754.
- [25] D.M. F. Endres, A. Abbott, *Electrodeposition from Ionic Liquids*, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim, 2008.
- [26] E.L. Smith, A.P. Abbott, K.S. Ryder, Deep Eutectic Solvents (DESs) and Their Applications, *Chemical Reviews*, 114 (2014) 11060-11082.
- [27] A.P. Abbott, Model for the Conductivity of Ionic Liquids Based on an Infinite Dilution of Holes, *ChemPhysChem*, 6 (2005) 2502-2505.
- [28] A.P. Abbott, R.C. Harris, K.S. Ryder, Application of Hole Theory to Define Ionic Liquids by their Transport Properties<sup>†</sup>, *The Journal of Physical Chemistry B*, 111 (2007) 4910-4913.
- [29] A.P. Abbott, K.E. Ttaib, G. Frisch, K.S. Ryder, D. Weston, The electrodeposition of silver composites using deep eutectic solvents, *Physical Chemistry Chemical Physics*, 14 (2012) 2443-2449.
- [30] S. Salomé, N.M. Pereira, E.S. Ferreira, C.M. Pereira, A.F. Silva, Tin electrodeposition from choline chloride based solvent: Influence of the hydrogen bond donors, *Journal of Electroanalytical Chemistry*, 703 (2013) 80-87.
- [31] A.P. Abbott, J.C. Barron, G. Frisch, S. Gurman, K.S. Ryder, A. Fernando Silva, Double layer effects on metal nucleation in deep eutectic solvents, *Physical Chemistry Chemical Physics*, 13 (2011) 10224-10231.
- [32] A.P. Abbott, J.C. Barron, G. Frisch, K.S. Ryder, A.F. Silva, The effect of additives on zinc electrodeposition from deep eutectic solvents, *Electrochimica Acta*, 56 (2011) 5272-5279.
- [33] A. Bakkar, V. Neubert, Electrodeposition onto magnesium in air and water stable ionic liquids: From corrosion to successful plating, *Electrochemistry Communications*, 9 (2007) 2428-2435.
- [34] N.M. Pereira, P.M.V. Fernandes, C.M. Pereira, A. Fernando Silva, Electrodeposition of Zinc from Choline Chloride-Ethylene Glycol Deep Eutectic Solvent: Effect of the Tartrate Ion, *Journal of The Electrochemical Society*, 159 (2012) D501-D506.
- [35] A.H. Whitehead, M. Pözl, B. Gollas, Zinc Electrodeposition from a Deep Eutectic System Containing Choline Chloride and Ethylene Glycol, *Journal of The Electrochemical Society*, 157 (2010) D328-D334.
- [36] H. Yang, R.G. Reddy, Electrochemical deposition of zinc from zinc oxide in 2:1 urea/choline chloride ionic liquid, *Electrochimica Acta*, 147 (2014) 513-519.
- [37] L. Vieira, R. Schennach, B. Gollas, The effect of the electrode material on the electrodeposition of zinc from deep eutectic solvents, *Electrochimica Acta*.
- [38] A.P. Abbott, G. Capper, K.J. McKenzie, K.S. Ryder, Electrodeposition of zinc-tin alloys from deep eutectic solvents based on choline chloride, *Journal of Electroanalytical Chemistry*, 599 (2007) 288-294.
- [39] H. Yang, R.G. Reddy, Electrochemical Kinetics of Reduction of Zinc Oxide to Zinc Using 2:1 Urea/ChCl Ionic Liquid, *Electrochimica Acta*.
- [40] K. Haerens, E. Matthijs, K. Binnemans, B. Van der Bruggen, Electrochemical decomposition of choline chloride based ionic liquid analogues, *Green Chemistry*, 11 (2009) 1357-1365.
- [41] D. Yue, Y. Jia, Y. Yao, J. Sun, Y. Jing, Structure and electrochemical behavior of ionic liquid analogue based on choline chloride and urea, *Electrochimica Acta*, 65 (2012) 30-36.
- [42] G. Pacchioni, S. Valeri, *Oxide Ultrathin Films: Science and Technology*, Wiley, 2012.

- [43] E. Budevski, G. Staikov, W.J. Lorenz, Frontmatter, in: *Electrochemical Phase Formation and Growth*, Wiley-VCH Verlag GmbH, 2007.
- [44] G. Gunawardena, G. Hills, I. Montenegro, B. Scharifker, Electrochemical nucleation: Part I. General considerations, *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry*, 138 (1982) 225-239.
- [45] M.-J. Deng, P.-C. Lin, J.-K. Chang, J.-M. Chen, K.-T. Lu, Electrochemistry of Zn(II)/Zn on Mg alloy from the N-butyl-N-methylpyrrolidinium dicyanamide ionic liquid, *Electrochimica Acta*, 56 (2011) 6071-6077.
- [46] C. Ehlers, U. König, G. Staikov, J.W. Schultze, Role of surface states in electrodeposition of Pb on n-Ge(111), *Electrochimica Acta*, 47 (2001) 379-385.
- [47] M.Y. Abyaneh, M. Fleischmann, General Models for Surface Nucleation and Three-Dimensional Growth: the Effects of Concurrent Redox Reactions and of Diffusion, *Journal of The Electrochemical Society*, 138 (1991) 2491-2496.