

## Electrodeposition of ZnO from DMSO Solution: Influence of Anion Nature and its Concentration in the Nucleation and Growth Mechanisms

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A influência da natureza aniônica e sua concentração na eletrodeposição de ZnO em um eletrodo de ouro de soluções de dimetilsulfóxido (DMSO) foi estudada. Experimentos voltamétricos mostraram alterações importantes no processo de eletrodeposição de óxido de zinco dependendo do ânion empregado como eletrólito. A partir de experimentos de cronoamperometria, as correspondentes curvas corrente-tempo foram ajustadas com diferentes modelos de mecanismos de nucleação e crescimento. A análise destes resultados mostrou a mudança de um crescimento instantâneo para um progressivo quando a composição da solução foi mudada de ZnCl<sub>2</sub> para ZnCl<sub>2</sub> + LiCl. A modificação do mecanismo está associada à adsorção de íon cloreto nos sítios ativos da superfície do eletrodo quando LiCl está presente na solução.

The influence of the anion nature and its concentration in the electrodeposition of ZnO onto a gold electrode from dimethylsulfoxide (DMSO) solutions was studied. Voltammetric experiments revealed important changes in the zinc oxide electrodeposition process depending on the employed anion as electrolyte. From chronoamperometric experiments, the corresponding current-time curves were fitted with different nucleation and growth mechanism models. The analysis of these results showed changes from an instantaneous to a progressive growth when the solution composition was changed from ZnCl<sub>2</sub> to ZnCl<sub>2</sub> + LiCl. The change of the mechanism is associated to the adsorption of chloride ion on the active sites of the electrode surface when LiCl is present in the solution.

**Keyword:** ZnO, electrodeposition, DMSO, nucleation and growth mechanism

### Introduction

Zinc oxide is a material of great technological interest due to its unique physical and chemical properties, which are ideal for application in optoelectronic, photovoltaic, magnetic and piezoelectric devices.<sup>1-4</sup> A particular characteristic of this material is the possibility of forming films and diverse nanostructures as nanotubes, nanorods, nanowires<sup>5</sup> and hierarchical nanostructures.<sup>6,7</sup>

Different synthetic routes have been employed for the preparation of good quality ZnO films and nanostructures. Due to relatively low temperature and moderate pressure of operation, the deposition from solutions is an attractive and non-expensive method for the formation of a variety of

ZnO structures. Particularly, electrodeposition is a viable alternative to the traditionally preparation methods due to the precise control of the experimental parameters (*i.e.*, potential and current).<sup>8-11</sup> Electrodeposition from aqueous solution traditionally employs three oxygen precursors: molecular oxygen, hydrogen peroxide and nitrate ion. Whatever be the case, the solution composition has showed to be crucial for tailoring zinc oxide morphology and crystalline structure.<sup>12</sup> On the other hand, the electrodeposition from non-aqueous solution opens the possibility of obtaining deposits at operation temperatures higher than in aqueous media, allowing to improve the crystalline character of the material.<sup>5</sup> Dimethylsulfoxide (DMSO) has been employed in the electrodeposition of ZnO films at different temperature intervals (from 30 to 150 °C).<sup>13,14</sup> High crystalline films were obtained,

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but a clear dependence on the film properties with the electrolytic bath composition (especially with the nature of the employed anion) has been detected. In aqueous media, diverse studies reported that the anion and its concentration influence on the film properties and morphology.<sup>15-17</sup> In some cases, the nucleation and growth analyses have helped to study the influence of some experimental parameters (*i.e.*, temperature) on the ZnO film properties.<sup>18</sup> However, so far this effect has not been reported in DMSO solutions. In a previous study related to ZnO nanowires electrodeposition on alumina membrane templates, we observed changes in the nucleation and growth mechanism when the concentration of chloride ions in the electrolytic DMSO solution was changed.<sup>19</sup> To get a deeper insight in this subject, in current paper, we conducted a detailed study regarding the influence of anion nature and its concentration in the nucleation and growth mechanism of ZnO films from DMSO employing molecular oxygen as oxygen precursor.

## Experimental

All the electrochemical experiences were carried out in a CHI potentiostat (CHI 604C) connect to a PC. The electrochemical cell consists in a conventional cell with three electrodes. A Pt wire and Ag/AgCl<sub>(sat)</sub> electrode ( $E = 0.194$  V vs. ENH) were used as counter and reference electrode, respectively. All the potentials in this work are referred to this reference electrode. The working electrode was a gold disk electrode (BAS, 1.6 mm diameter). Previous to each measure, this electrode was polished with alumina of 0.3  $\mu\text{m}$  and, subsequently with alumina of 0.05  $\mu\text{m}$  to obtain a clean and smooth surface. Using this procedure, clear and reproducible results were obtained. All the experiences were performed at 85 °C.

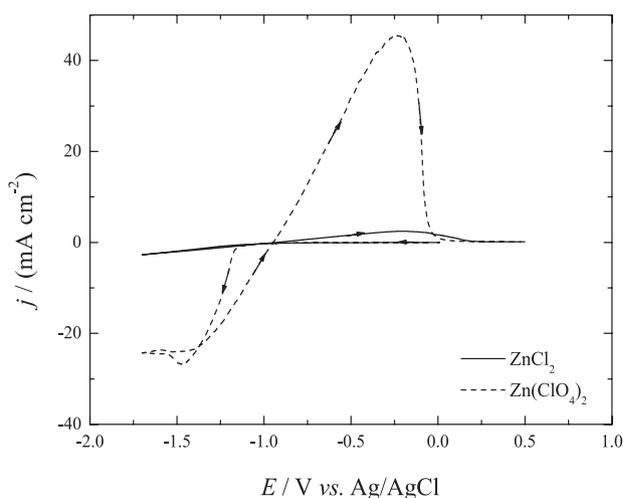
Electrolytic solutions were prepared with dry DMSO (Merck) and analytical grade electrolytes without previous treatment. In the experiences carried out without oxygen, the solutions were bubbled with argon during 20 min before each experiment. To avoid the oxygen incorporation in the electrolytic solution, an argon stream was kept over the solution during the measurements. In experiments in presence of oxygen, the solutions were bubbled with oxygen until saturation (20 min) before each measurement. An oxygen stream was kept over the solution during the measure to assure solution saturation.

The voltammetric study was carried out with chloride or perchlorate Zn(II) solutions both in presence and absence of oxygen. In all the cases, the Zn(II) concentration was 0.05 mol L<sup>-1</sup>. LiCl (Merck) and LiClO<sub>4</sub> (Sigma-Aldrich) were added to study the effect of chloride and perchlorate concentration, respectively.

## Results and Discussion

### Voltammetric studies in absence of oxygen

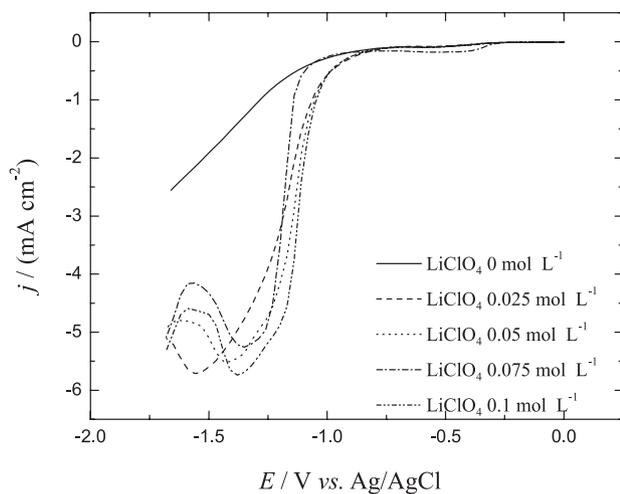
Cathodic and anodic current contributions are present in the cyclic voltammograms recorded for DMSO solutions of ZnCl<sub>2</sub> and Zn(ClO<sub>4</sub>)<sub>2</sub> at 85 °C (Figure 1). In both cases, the cathodic peak is related to the reduction of Zn(II) to metallic Zn, whereas the anodic one corresponds to the stripping of the latter. The differences in the current peak intensities depend on the amount of available free zinc ions in solution which, in turn, depends on the respective coordinating character of both anions. It has been reported that in DMSO and DMSO-water solutions, there are not interactions between perchlorate and Zn(II).<sup>20,21</sup> Instead of this, X-ray absorption spectroscopy (XAS) studies have shown that Zn(II) coordinates to six DMSO molecules in a regular octahedral geometry.<sup>22</sup> Then, the observed resistive response in chloride media suggests that a stable complex is formed between Zn(II) and chloride anions, releasing only small amounts of both ions into solution. Notwithstanding, following the overall stability constant values for Zn(II) and chloride anions that were reported for a perchlorate-DMSO solution of constant ionic strength at 25 °C,<sup>20</sup> the amount of free ionic species, that was calculated for our experimental conditions, should be enough to obtain a relatively more conducting solution (free [Zn(II)] = 6.73 × 10<sup>-3</sup> mol L<sup>-1</sup>, [Cl<sup>-</sup>] = 2.5 × 10<sup>-3</sup> mol L<sup>-1</sup>, [ZnCl<sup>+</sup>] = 1.448 × 10<sup>-3</sup> mol L<sup>-1</sup> and [ZnCl<sub>3</sub><sup>-</sup>] = 0.0124 mol L<sup>-1</sup>).



**Figure 1.** Cyclic voltammograms of Au/ZnCl<sub>2</sub> 0.05 mol L<sup>-1</sup> (continuous line) and Au/Zn(ClO<sub>4</sub>)<sub>2</sub> 0.05 mol L<sup>-1</sup> (dotted line) interfaces in DMSO at 85 °C. Scan rate of 50 mV s<sup>-1</sup>.

A less resistive response is obtained when an inert electrolyte is added to the ZnCl<sub>2</sub> solution (*i.e.*, LiClO<sub>4</sub>). Figure 2 shows the cathodic wave for the Au/ZnCl<sub>2</sub> interface

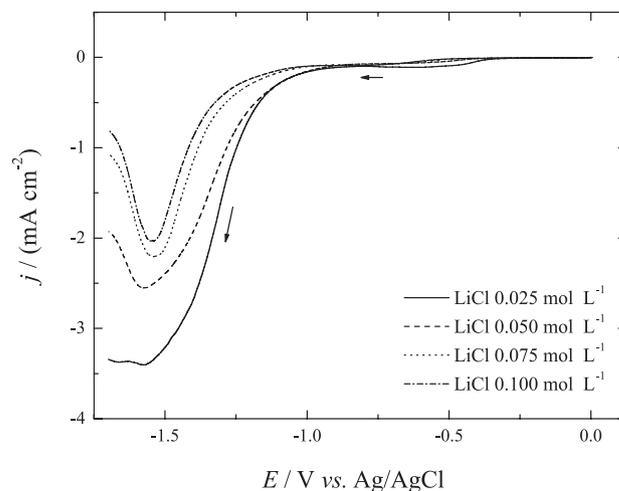
at different  $\text{LiClO}_4$  concentration. Confirming the lack of interactions between  $\text{Zn(II)}$  and perchlorate anions, the electrochemical response is similar in the considered interval of perchlorate concentration. The discrepancy can be attributed to a change in the overall stability constant values for  $\text{Zn-Cl}$  species. It happened a change in the complex coordination number due to the presence and absence of perchlorate anions in solution. This effect has been observed for  $\text{ZnCl}_2$  in DMSO-water solutions (in absence of additional supporting electrolyte), where the coordination number is sensitive to the solution composition.<sup>23</sup> At high DMSO mole fraction, an octahedral complex with two chloride ions is proposed. Besides, at high water mole fraction, a change in the coordination number allows the formation of a tetrahedral complex. Accordingly, in absence of any supporting electrolyte (as in our case), an octahedral complex should be formed between  $\text{Zn(II)}$  with DMSO and chloride ions. A less stable tetrahedral complex is formed in presence of chloride and perchlorate anions, and the reported overall stability constant are referred for this situation and not for the complex between  $\text{Zn(II)}$  and chloride anions alone.<sup>20</sup>



**Figure 2.** Linear sweep voltammety (cathodic wave) of  $\text{Au/ZnCl}_2$   $0.05 \text{ mol L}^{-1}$  interface in DMSO at  $85^\circ\text{C}$  at different  $\text{LiClO}_4$  concentrations. In all cases, scan rate of  $50 \text{ mV s}^{-1}$ .

Solutions containing  $\text{LiClO}_4$  (Figure 2) exhibit the same reduction potential in the cathodic responses when compared to  $\text{Zn(ClO}_4)_2$  solution (Figure 1), *i.e.*, they correspond to free  $\text{Zn(II)}$  reduction. Assuming that the current intensity is proportional to the electroactive specie concentration (and considering that in a  $\text{Zn(ClO}_4)_2$  solution free  $[\text{Zn(II)}] = [\text{Zn(ClO}_4)_2] = 0.05 \text{ mol L}^{-1}$ ), in presence of perchlorate, the zinc concentration in chloride media is close to  $0.0134 \text{ mol L}^{-1}$ . This value is higher than the theoretical value that was calculated from the overall stability constant (free  $[\text{Zn(II)}] = 6.73 \times 10^{-3} \text{ mol L}^{-1}$ ). These differences are

related to the plating bath temperature ( $85^\circ\text{C}$ ), which is higher than that reported by Ahrlund and Björk.<sup>20</sup> Therefore, as the complexes between  $\text{Zn(II)}$  and chloride ions are less stable, at that temperature, the free  $\text{Zn(II)}$  concentration increases. When the chloride concentration is progressively increased, the free  $\text{Zn(II)}$  concentration decreases due to the formation of zinc-chloride complexes explaining the diminution of the current peak intensity (Figure 3).



**Figure 3.** Linear sweep voltammety (cathodic wave) of  $\text{Au/ZnCl}_2$   $0.05 \text{ mol L}^{-1}$  interface in DMSO at  $85^\circ\text{C}$  at different  $\text{LiCl}$  concentrations. In all cases, scan rate of  $50 \text{ mV s}^{-1}$ .

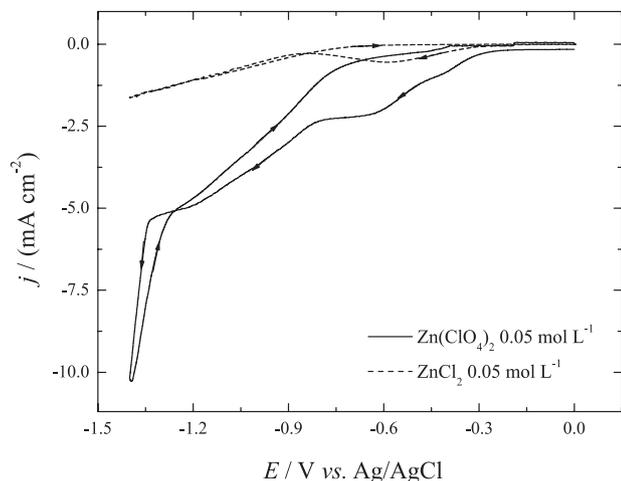
These results show that the electrolyte composition is crucial to determinate the type and concentration of the electroactive species in solution because both play an important role in the nucleation and growth mechanism of zinc oxide films (*vide infra*).

#### Cyclic voltammety in presence of molecular oxygen

Figure 4 shows the cyclic voltammograms corresponding to  $\text{Au/Zn(ClO}_4)_2$   $0.05 \text{ mol L}^{-1}$  and  $\text{Au/ZnCl}_2$   $0.05 \text{ mol L}^{-1}$  interfaces in presence of molecular oxygen.

Both cathodic scans show current contributions corresponding to the electrochemical reduction of oxygen and zinc ions. No current peak is observed in the anodic sweep because a resistive  $\text{ZnO}$  film was formed according to the following sequence:<sup>24,25</sup>





**Figure 4.** Cyclic voltammograms of Au/Zn(ClO<sub>4</sub>)<sub>2</sub> 0.05 mol L<sup>-1</sup> (continuous line) and Au/ZnCl<sub>2</sub> 0.05 mol L<sup>-1</sup> (dotted line) interfaces in DMSO at 85 °C in presence of molecular oxygen in solution. Scan rate of 50 mV s<sup>-1</sup>.

In Zn(ClO<sub>4</sub>)<sub>2</sub> media, the oxygen reduction presents three cathodic waves ranging between -0.260 and -1.30 V. The first two waves (between -0.260 and -0.800 V) are associated to the reduction of oxygen onto different gold crystalline planes.<sup>26</sup> The third wave is attributed to the oxygen reduction onto ZnO film that is formed during the previous cathodic processes on the gold surface.

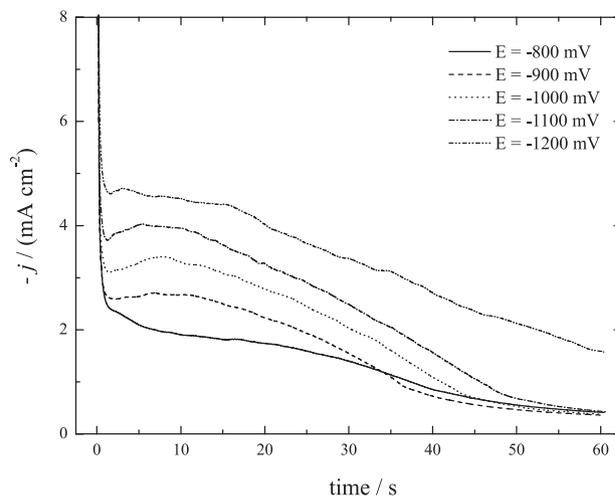
In ZnCl<sub>2</sub> media, only two cathodic processes are observed. The wave centered at -0.580 V clearly corresponds to the oxygen electroreduction. The second cathodic process is not associated to zinc reduction because this reaction occurs at potentials more negative than that presented in Figure 4 (see Figures 1 and 2). Thus, the second cathodic process is also attributed to the oxygen reduction on different crystalline planes. The potential shifting is due to the high solution resistivity because of the low ionic concentration. Furthermore, this situation produces a decreasing in the oxygen rate reduction, and is reflected in a lower cathodic current as compared with perchlorate media. This last effect will be determinant in the analysis of the nucleation and growth mechanism of ZnO from different electrolytic media.

#### Nucleation and growth mechanism

##### Zn(ClO<sub>4</sub>)<sub>2</sub> media

Figure 5 shows the current-time curves for the ZnO electrodeposition from a Zn(ClO<sub>4</sub>)<sub>2</sub>/DMSO solution at different potentials on a gold electrode.

As previously discussed, Zn(II) ions do not form complex with perchlorate, then they can be considered as completely free in DMSO solution. Furthermore, comparing the magnitude of the cathodic currents, the



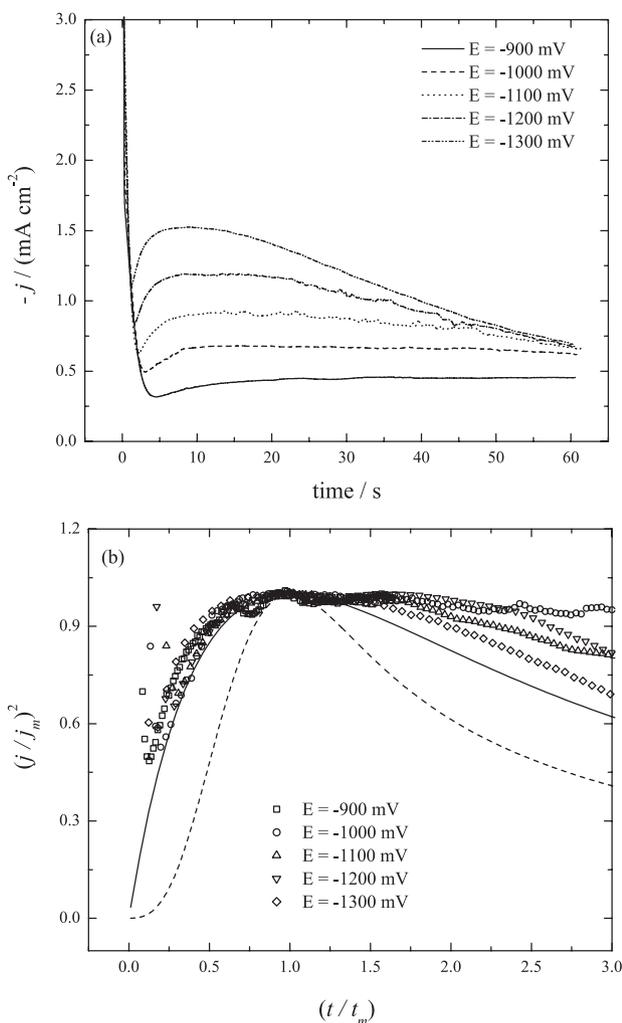
**Figure 5.** Chronoamperometric curves for the ZnO electrodeposition on a gold electrode from a 0.05 mol L<sup>-1</sup> Zn(ClO<sub>4</sub>)<sub>2</sub> solution in DMSO at 85 °C saturated with molecular oxygen at different potentials.

rate of oxygen reduction in perchlorate is higher than in chloride media. In the first stages of the electrodeposition, a high cathodic current is observed, followed by an abrupt decrease in the current density close to 0.4 mA cm<sup>-2</sup> at the end of the curves. An exception is the curve at  $E = -1200$  mV, where metallic zinc electrodeposition takes place. The curves between -800 and -1100 mV do not fit the equations that were formulated by Scharifker and Hills<sup>27</sup> for the analysis of nucleation and growth mechanism of an electrodeposited solid compound. To use this type of analysis, the rate determining step (rds) must be an electrochemical step. However, because of the high reduction current, the rds should be a chemical step (either of the steps 2, 3 or 4 of the mechanism previously shown).

##### ZnCl<sub>2</sub> media

Figure 6 shows the obtained chronoamperometric curves at different potentials for the ZnO electrodeposition from a ZnCl<sub>2</sub> solution in DMSO.

Now, the oxygen reduction rate is lower than in perchlorate media and this process will be the rds of the overall process. The chronoamperometric curves show the classical behavior of nucleation and growth of three dimensional centers, allowing for this case to apply the developed equations by Scharifker and Hills.<sup>27</sup> The non-dimensional plots show that at short times, all the curves can be adjusted using instantaneous nucleation model. This is attributed to the nucleuses formation on the active sites of the substrate. However, as a second process is coupled at longer time, a more detailed study by the independent analysis of each curve is required. Figure 7 shows the obtained results at four different potentials, the



**Figure 6.** (a) Chronoamperometric curves for the ZnO electrodeposition on a gold electrode from a  $0.05 \text{ mol L}^{-1} \text{ ZnCl}_2$  solution in DMSO at  $85^\circ \text{C}$  saturated with molecular oxygen at different potentials, and (b) comparison of the theoretical non-dimensional plots for instantaneous (continuous line, NI-3D<sub>diff</sub>) and progressive (dashed line, NP-3D<sub>diff</sub>) nucleation controlled by diffusion of three-dimensional centers obtained from reference 27, with experimental data obtained from Figure 6a.

respective curves that were adjusted to a NI-3D<sub>diff</sub> model coupled with a bi-dimensional instantaneous process (NI-2D). This bi-dimensional process can be considered the product of an electrochemical reaction when the electrodic substrate is covered with a ZnO layer. This result implies that at long time, only a second process is coupled to those nucleuses that are formed in the active sites on the substrate. Previous studies<sup>19</sup> confirm that the ZnO nanowire electrodeposition from a ZnCl<sub>2</sub>/DMSO solution form highly oriented structures, being coherent with an instantaneous nucleation and growth mechanism.

#### ZnCl<sub>2</sub> + LiCl media

The chronoamperometric curves are affected by the presence of LiCl in the electrolytic solution because (as

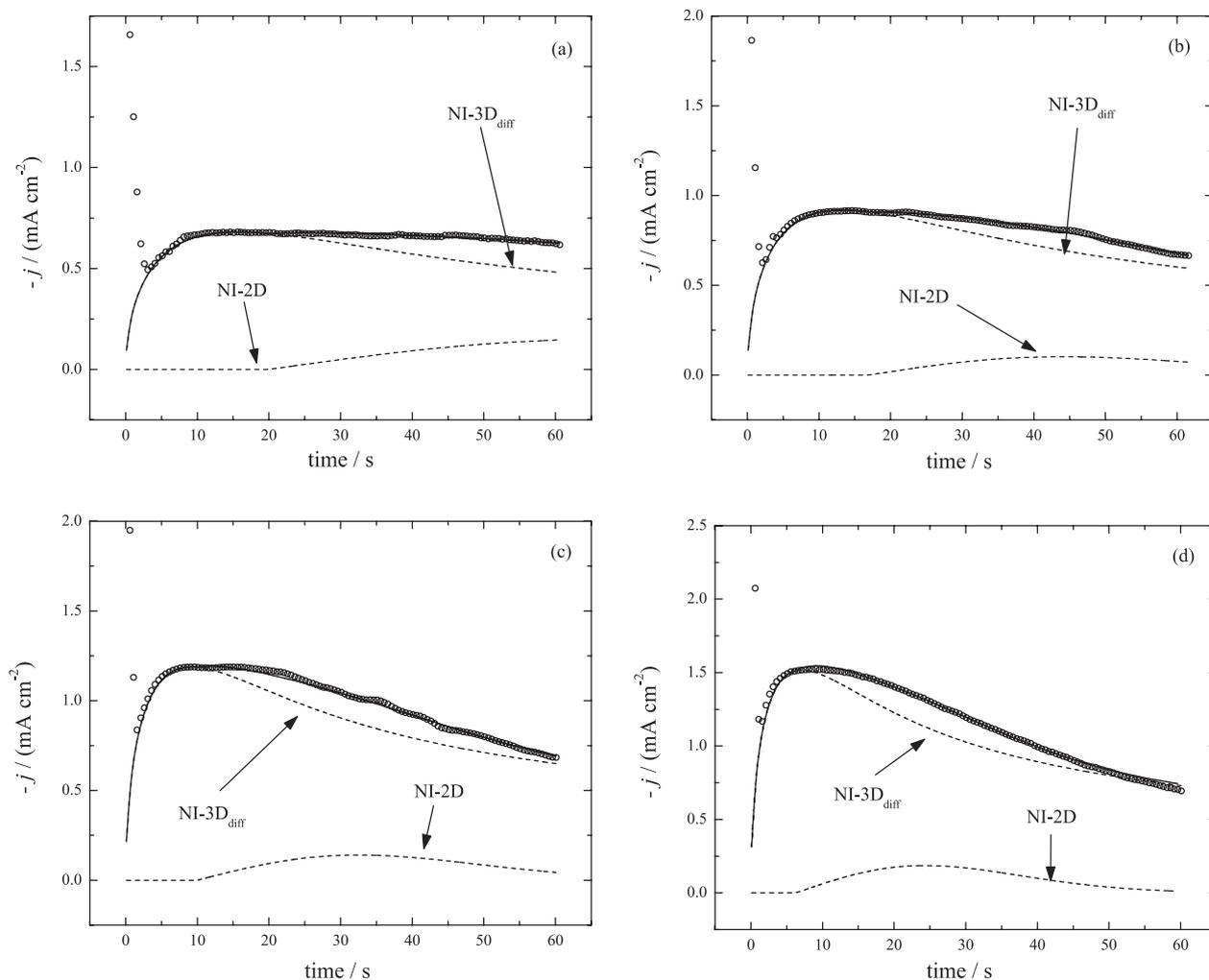
discussed before) Cl<sup>-</sup> ions reduce the available free Zn(II) concentration. Furthermore, as a consequence of the low effective free Zn(II) concentration in the interface, at high chloride concentration (*i.e.*, [LiCl] =  $0.1 \text{ mol L}^{-1}$ ), ZnO is not formed on the gold surface (the curves are not dependent on the applied potential). However, when the LiCl concentration is  $\leq 0.075 \text{ mol L}^{-1}$ , a clear dependence of the curves with the applied potential is observed, confirming the ZnO formation on the electrode surface. Figure 8 shows the chronoamperometric curves obtained from a  $0.05 \text{ mol L}^{-1} \text{ ZnCl}_2 + 0.075 \text{ mol L}^{-1} \text{ LiCl}$  solution in DMSO that is saturated with molecular oxygen at  $85^\circ \text{C}$  at different potentials.

Due to the employment of a non-dimensional analysis to differentiate between instantaneous and progressive three-dimensional nucleation processes, these curves cannot be adjusted with this procedure. In these cases, at short times, the deconvolution analysis (Figure 9) shows that they can be adjusted employing an instantaneous bi-dimensional nucleation (NI-2D) instead of a three-dimensional nucleation process. At longer times, the curves are adjusted with a progressive three-dimensional nucleation that is controlled by diffusion (NP-3D<sub>diff</sub>).

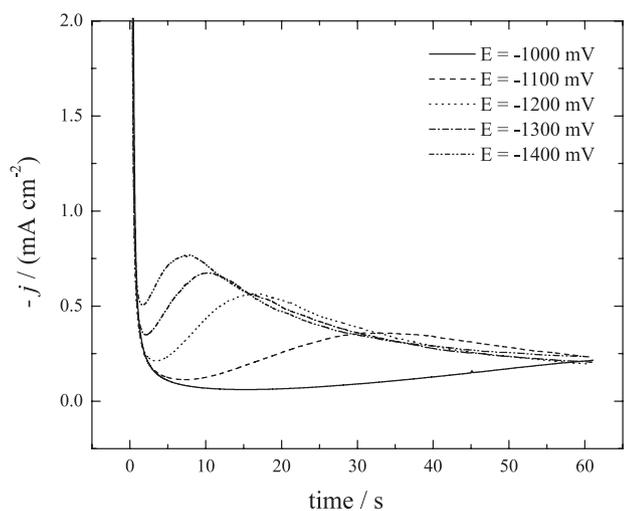
These results show that the presence of a chloride excess in solution is decisive in the nucleation and growth process of the ZnO from DMSO solutions. When the films are obtained from a ZnCl<sub>2</sub> solution without additional chloride in solution, the nucleation and growth follow an instantaneous mechanism. On the other hand, when the films are obtained from a ZnCl<sub>2</sub> + LiCl solution, the mechanism changes to a progressive nucleation and growth.

This change can be due to an adsorption process between chloride ions and the electrode surface. This effect has been previously observed with different anions<sup>15</sup> and specifically with chloride<sup>17</sup> during the ZnO electrodeposition on conducting glass substrate in aqueous media. Thus, in absence of chloride excess ([LiCl] = 0), the surface is free of any adsorbed species (*i.e.*, chloride ions) because they are forming complex with Zn(II) in solution. In these conditions, the electrodeposition will take place only on the active sites of the surface, being in accord with an instantaneous nucleation. Figure 10 represents a scheme of these processes.

The film growth will be on these nucleus forming highly oriented films. However, when an excess of chloride ions is present in solution, an adsorptive process can occur between these ions and the gold surface. Thus, the active sites of the electrode surface will be blocked and the nucleation will follow a progressive mechanism. The observed bi-dimensional process in all the curves (Figure 9) can be



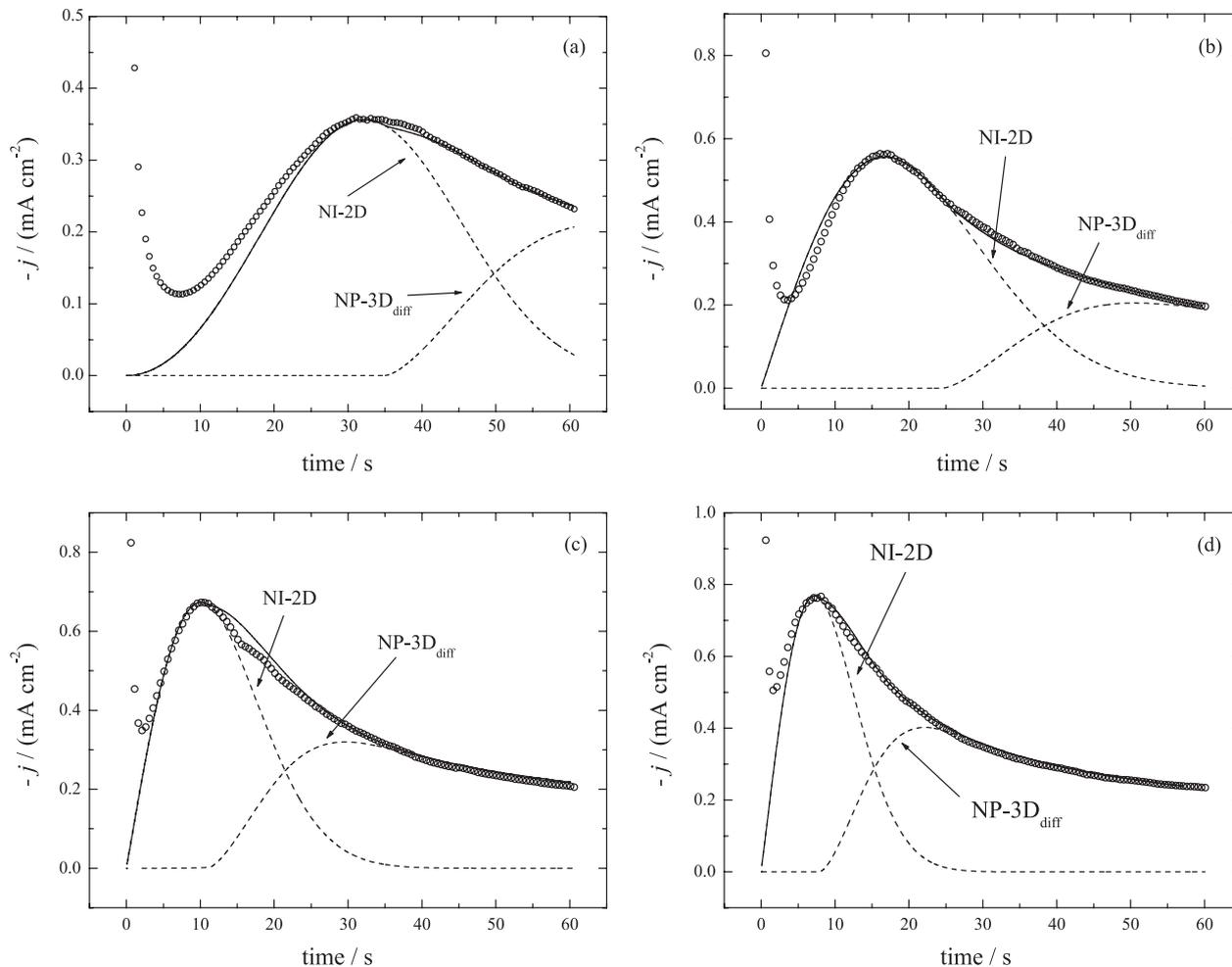
**Figure 7.** Deconvolution analysis of the chronoamperometric curves obtained at different potential from a  $0.05 \text{ mol L}^{-1} \text{ ZnCl}_2$  solution in DMSO at  $85^\circ \text{C}$  saturated with molecular oxygen at different potentials (open circles): (a)  $E = -1000 \text{ mV}$ , (b)  $E = -1100 \text{ mV}$ , (c)  $E = -1200 \text{ mV}$  and (d)  $E = -1300 \text{ mV}$ . In all the cases, the curves were adjusted with an instantaneous three-dimensional nucleation controlled by diffusion (NI-3D<sub>diff</sub>), together with an instantaneous bi-dimensional nucleation (NI-2D) (dotted lines). The continuous line represents the contribution of NI-3D<sub>diff</sub> + NI-2D.



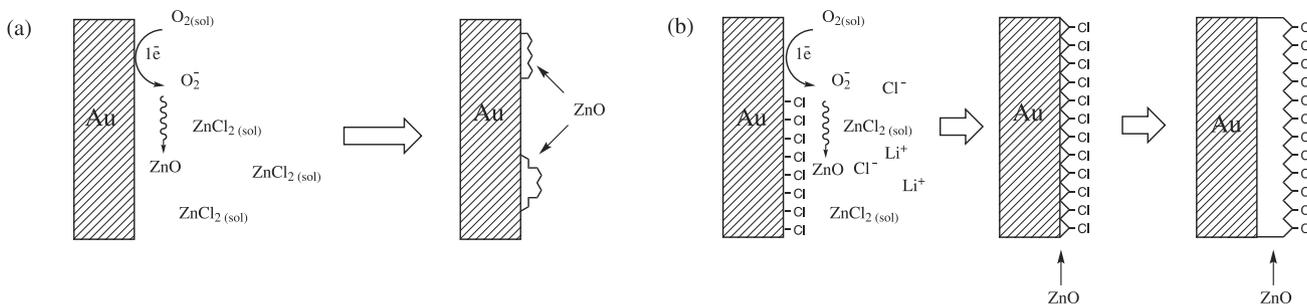
**Figure 8.** Chronoamperometric curves for the ZnO electrodeposition on a gold electrode from a  $0.05 \text{ mol L}^{-1} \text{ ZnCl}_2 + 0.075 \text{ LiCl}$  solution in DMSO at  $85^\circ \text{C}$  saturated with molecular oxygen at different potentials.

associated with the formation of a thin layer of ZnO on the gold electrode. The three-dimensional process is product of the ZnO electrodeposition on the ZnO that was previously formed with a layer of adsorbed chloride.<sup>17</sup> The latter is a progressive process that is controlled by diffusion. If the film is formed through a progressive mechanism, the crystals will be small and randomly oriented, forming highly polycrystalline films.

These results agree with those obtained during the ZnO nanowire electrodeposition from DMSO solution employing an alumina membrane as template.<sup>19</sup> Highly oriented nanowires are obtained from a  $\text{ZnCl}_2$  solution, being coherent with an instantaneous nucleation and growth mechanism. Polycrystalline nanowires are obtained when an excess of chloride is present in solution, confirming that their growth through a progressive mechanism.



**Figure 9.** Deconvolution analysis of the chronoamperometric curves obtained at different potential from a  $0.05 \text{ mol L}^{-1} \text{ ZnCl}_2 + \text{LiCl}$   $0.075 \text{ mol L}^{-1}$  solution in DMSO at  $85^\circ \text{C}$  saturated with molecular oxygen at different potentials (open circles); (a)  $E = -1100 \text{ mV}$ , b)  $E = -1200 \text{ mV}$ , c)  $E = -1300 \text{ mV}$  and (d)  $E = -1400 \text{ mV}$ . In all the cases, the curves were adjusted with a progressive bi-dimensional nucleation (NI-2D), following with a progressive nucleation controlled by diffusion (NP-3D<sub>diff</sub>). The continuous line represents the sum of NP-3D<sub>diff</sub> + NI-2D.



**Figure 10.** Scheme of electrodeposition of ZnO from DMSO solution employing molecular oxygen as oxygen precursor from different electrolyte composition: (a)  $\text{ZnCl}_2$  solution, following an instantaneous growth, and (b)  $\text{ZnCl}_2 + \text{LiCl}$  solution, following a progressive growth.

## Conclusions

Differences between the voltammetric responses were found between  $\text{Zn}(\text{ClO}_4)_2$  and  $\text{ZnCl}_2$  in DMSO solution at a gold electrode (in absence and presence of molecular oxygen) which were explained in terms of the type of coordination between Zn(II) and chloride ions and how it is

affected by the presence of perchlorate ions. It is proposed that the latter ones favor a change of coordination from a stable octahedral to a less stable tetrahedral complex in the electrolytic solution.

When chronoamperometric measurements were carried out in  $\text{Zn}(\text{ClO}_4)_2$  media, it was not possible to analyze the nucleation and growth mechanism because

the rds is not an electrochemical step. In  $\text{ZnCl}_2$  and  $\text{ZnCl}_2 + \text{LiCl}$ , the rds is associated to the electrochemical reduction of molecular oxygen, allowing in both cases the analysis of nucleation and growth mechanism. The chronoamperometric curves from  $\text{ZnCl}_2$  solution were adjusted with an instantaneous three-dimensional nucleation that is controlled by diffusion and coupled with an instantaneous bi-dimensional nucleation. The curves from  $\text{ZnCl}_2 + \text{LiCl}$  solution were adjusted to a progressive bi-dimensional nucleation mechanism, followed by a diffusion that is controlled progressive nucleation mechanism. These results agree with previous results that were obtained during the electrodeposition of ZnO nanowires on alumina membranes from different DMSO solutions. In agreement with a progressive nucleation and growth mechanism, ZnO nanowires were polycrystalline when obtained from  $\text{ZnCl}_2 + \text{LiCl}$  solutions. When they were obtained from  $\text{ZnCl}_2$  solution, a preferential crystallographic orientation was obtained, being consistent with an instantaneous nucleation and growth mechanism.

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