

# Cathodic Deposition of Pb from Ionic Liquids Based on Choline Chloride

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**Abstract:** This paper reports the electrodeposition of Pb films on Pt using ionic liquids based on choline chloride: ethylene glycol eutectic mixture (ChCl-EG, 1:2 moles) in the 45-65 °C temperature range. Lead ion (as PbCl<sub>2</sub>) was dissolved in ChCl:EG ionic liquid at concentrations in the range of 1-5 mM. The mechanism of Pb electrodeposition was investigated by cyclic voltammetry and electrochemical impedance spectroscopy. Cyclic voltammograms show a single cathodic peak of Pb deposition, with an amplitude increased with Pb<sup>2+</sup> concentration, scan rate or temperature. Nyquist and Bode impedance spectra show differences in Pt behavior due to its polarization at various cathodic potentials.

**Keywords:** lead, choline chloride : ethylene glycol eutectic, ionic liquid, electrodeposition

## 1. Introduction

Besides the common use in lead - acid batteries and in plating of electronic components, metallic lead is an attractive element, due to its superconductivity in some conditions [1]. Electrodeposition from aqueous solution is a current technique for obtaining lead films with appropriate properties. Dubois *et al.* [2] reported that lead nanowires grown *via* electrodeposition in the nanopores of track-etched polymer membranes possess the characteristics of superconductivity. Using such procedure, Pb nanowires were prepared by pulse electrodeposition [3]. Lead is also involved in PbTe and PbSe electrodeposition using aqueous media, both semiconductors being useful in thermoelectronic, optoelectronic, spintronic devices and photovoltaic converters [4].

However, lead is one of the most toxic elements which have strong negative effect on plants as well as on human and animal health. Although the hazards posed by lead are recognized for decades, only in recent years the legislation stimulates the restriction of its use. In the European Community there is a clear tendency to phase out the use of dangerous lead technologies. Therefore, there is the need to develop alternative electrolytes which can be used in place of lead containing aqueous electrolytes. The proposed solutions should be ionic liquids.

Ionic liquids are electrolytes forming liquids that consist only in cations and anions. They have received great interest recently because of their unusual properties: are miscible with certain organic solvents and/or water, good solubility of inorganic and organic materials, non-flammable and thermally stable. Room-temperature ionic liquids are the promising electrolytes for the electrodeposition of various metals, alloys or semiconductor compounds [5,6]. The advantages of these novel baths include: electroplating of very electronegative metals, *e.g.* Mg, Al, Ta, Nb, Mo, W; significantly reduced hydrogen evolution as compared with the acidic aqueous baths; lower electrical energy consumption comparing with

processes in aqueous solutions. Ionic liquids show reasonable ionic conductivity (similar to most non-aqueous electrolytes), have a large potential window and extremely low vapor pressure.

Reports of the electrodeposition of lead from ionic liquid media are relatively fewer, in spite of its many advantages, including cost-effectiveness, large-scale production and precise control of composition and thickness of materials [7]. In recent years an important progress has been obtained on the extraction and separation of nonferrous metal in ionic liquids by metal oxide processing. Thus, the protonated betaine bis (trifluoromethyl sulfonyl)imide ([Hbet][Tf<sub>2</sub>N]) was used as ionic liquid for solubilization of lead oxide (PbO) [8,9].

It has also recently been shown that a new ionic liquid can be formed as eutectic mixture of choline chloride (2 hydroxy-ethyl-trimethyl-ammonium, **ChCl**) with a hydrogen bond donor species such as a glycol, amide or carboxylic acid [10]. In this deep eutectic solvent the solubility of metal salts or oxides is increased, a fact that has importance in the recovery of corresponding metals [11]. For instance, using such ionic liquids containing ChCl, Abbott *et al.* [12] have succeeded to recover metallic lead together with other non-ferrous metal (zinc, cadmium etc.) by processing of electric arc furnace dust.

In the present work the electrodeposition of Pb films using the eutectic of choline chloride and ethylene glycol (1:2 moles) as supporting electrolyte is reported. The procedure of electrodeposition applied is an environmentally friendly method compared with the conventional methods of electrodeposition using aqueous baths, because of replacement of many hazardous and toxic materials currently used in galvanic industry.

In spite of the lack of data of solubility of lead salts, it is expected for Pb precursor (PbCl<sub>2</sub>) to dissolve in a large amount in ChCl based ionic liquids. Cyclic voltammetry and electrochemical impedance spectroscopy (EIS) were chosen as electrochemical techniques in order to evidence electrochemical couples of deposition/ dissolution of Pb.

## 2. Experimental

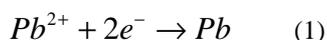
The supporting electrolyte was prepared by mixing choline chloride (ChCl, Aldrich 99%, used as purchased, without recrystallization or drying) with ethylene glycol (EG, Aldrich 99%). By gently heating the two components in a 1:2 mole ratio (at 80°C), a homogeneous colorless ionic liquid is formed. PbCl<sub>2</sub> (Merck) reagent as precursor of Pb<sup>2+</sup> ions was also used as received, being dissolved in the prepared supporting electrolyte ChCl-EG. In order to calculate the solution molarities we used a density value for ChCl-EG of 1.09 gcm<sup>-3</sup>, determined in our laboratory in the temperature range of 45-65°C.

An AUTOLAB PGSTAT 12 Ecochemie potentiostat provided with a frequency response analyzer was used for cyclic voltammetry and impedance spectroscopy measurements. A platinum sheet (0.5 cm<sup>2</sup>) was used as working electrode, whereas the auxiliary electrode was a platinum mesh. A silver wire immersed in the working electrolyte (constituted from ionic liquid containing lead ions) was used as a quasireference electrode. The Pt working electrode was polished with alumina paste, rinsed, and dried before every measurement. Cyclic voltammograms were recorded at scan rates from 5 mVs<sup>-1</sup> to 100 mVs<sup>-1</sup>. EIS characterization was carried out in 100 kHz ≥ f ≥ 0.1 Hz frequency range with an *ac* voltage amplitude of ±10 mV; the impedances of the Pt cathode polarized gradually in the range of 0.2 V to -0.7 V (versus Ag quasireference electrode), were represented as Nyquist and Bode spectra.

## 3. Results and Discussion

Previously, a typical cyclic voltammograms of ChCl-ethylene glycol (1:2 moles) ionic liquid supporting electrolyte recorded on Pt electrode for a large range of potentials was reported [13]. It was noticed the large domain of potentials (from -0.9 V to +1.25 V) representing the potential window for selected ionic liquid, which is about two times wider in comparison with similar parameter of aqueous solutions (1.23V).

Cyclic voltammetry measurements were carried out, within 45 - 65°C temperature range, in order to investigate the electrochemical reversibility of electrode process and the appropriate potential range for electrodeposition / dissolution of single metal films. Typical cyclic voltammograms recorded on Pt electrode in ChCl-ethylene glycol eutectic in the absence of solution stirring are presented in Figs. 1-3. As Fig. 1 illustrates, for 10mM Pb<sup>2+</sup> concentration the metallic Pb started to deposit at -0.37 V, and displayed an increasing current during the negative going scan, with a cathodic peak within -0.42 ÷ -0.45 V potential range followed by a limiting current up to -0.75 V. The electrode process may be described by the simple reduction of lead ions:



Both peak current and limiting current increase with scan rate, suggesting the diffusion control of this quite

reversible process. A new increase of current at more negative potentials than -0.8 V was attributed to the cathodic process of ionic liquid (of choline cation).

In the corresponding positive going scan, two or three anodic peaks were successively noticed and their behavior is more complex. Thus, in Fig. 1 the first oxidation peak (at -0.22 V for slowest scan rate) is followed by a second anodic peak of smaller amplitude (at -0.1 V for 10 mVs<sup>-1</sup>) and a third broader peak (rather a plateau) at positive potentials. Increasing the scan rate, the currents increased but the second peak becomes a shoulder. This behavior was similar for all faster scans.

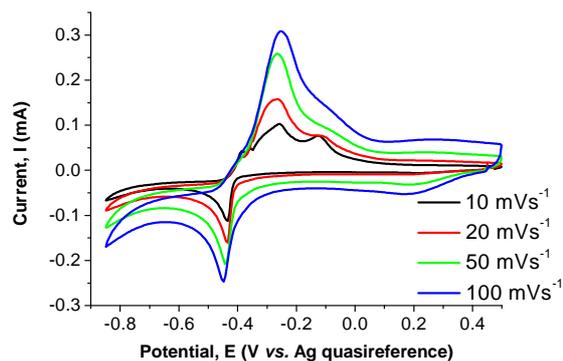


Figure 1. Cyclic voltammograms for 10 mM PbCl<sub>2</sub> dissolved in ChCl-EG (1:2 moles) eutectic at different scan rates; temperature 45°C

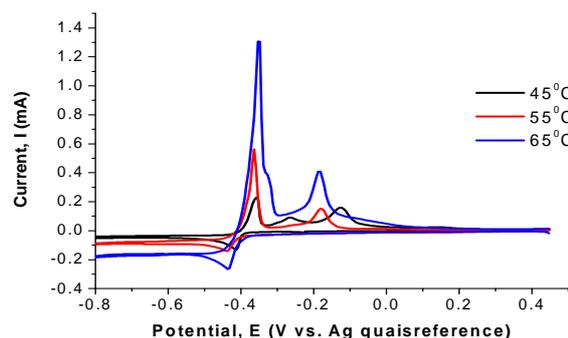


Figure 2. Cyclic voltammograms showing the influence of temperature for 10 mM PbCl<sub>2</sub> dissolved in ChCl-EG (1:2 moles) ionic liquid at constant scan rate of 5mVs<sup>-1</sup>

Fig. 2 presents comparatively the voltammograms at constant scan rate of 5 mVs<sup>-1</sup> for the same Pb<sup>2+</sup> ion concentration and three temperatures. The shapes of cathodic branches are very similar, with increase of peak currents with temperature. In the anodic scan, there are more clear potential differences between first peak and third peak during oxidation sequence. Decreasing the Pb<sup>2+</sup> concentration in the electrolyte led to a more pronounced cathodic plateau instead of a peak, with significant decrease of currents. For instance, working at 2.5 mM Pb<sup>2+</sup> concentration, Fig. 3 shows a dependence on scan rate of cathodic limiting currents together with two evidenced anodic peaks.

The interpretation of the anodic branch of voltammograms is difficult. According to the order of occurrence during the potential scan towards positive

potentials, we may assign the first anodic peak to the oxidation of deposited lead, to  $\text{Pb}^{2+}$  ions; this is not a reversible process, its peak potential being shifted towards positive with scan rate. The third anodic peak should correspond to the subsequent oxidation of  $\text{Pb}^{2+}$  to  $\text{Pb}^{4+}$  onto Pt surface and this process diminishes for faster scan rates. The shoulder (or peak) appeared between these processes may be due to an oxidation (also at  $\text{Pb}^{2+}$ ) of metallic Pb first deposited cathodically as monolayer by so called UPD (underpotential deposition), a phenomenon which is expected during formation of Pb nuclei onto Pt surface.

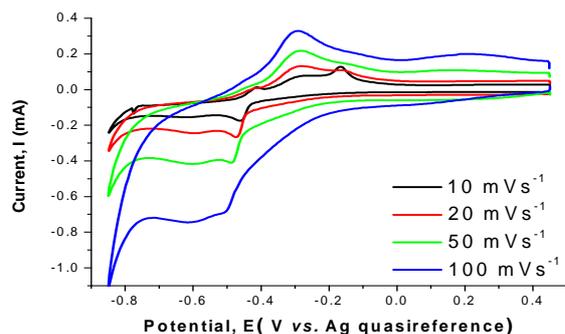


Figure 3. Cyclic voltammograms for 2.5 mM  $\text{PbCl}_2$  dissolved in ChCl-EG (1:2 moles) eutectic at different scan rates; temperature 80°C

In a quantitative analysis of cyclic voltammograms, it has been seen that both cathodic and anodic peak currents increase with scan rate and temperature. As Fig. 4 shows, linear dependences of cathodic current with square root of scan rate are obtained for three  $\text{Pb}^{2+}$  concentrations at 65°C constant temperature; also, the slopes of the straight lines obtained in all three cases increase with  $\text{Pb}^{2+}$  concentration, proving a diffusion-controlled deposition process of lead. This fact should allow us to calculate the diffusion coefficients of  $\text{Pb}^{2+}$  ionic species using the well-known Randles-Sevcik equation for a metal deposition (a process where the thermodynamic activity of solid deposit may be considered unity) [14]:

$$I_{pc} = 0.6401 n F A c \sqrt{\frac{n F}{RT}} v D \quad (2)$$

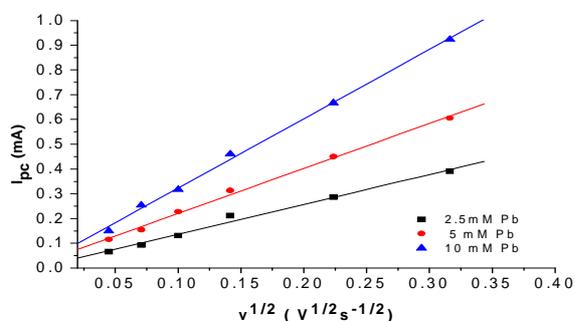


Figure 4.  $I_p - v^{1/2}$  linear plots for cathodic deposition of Pb films on Pt ( $0.5 \text{ cm}^2$ ) using ChCl-EG (1:2 moles) eutectic; temperature 65°C

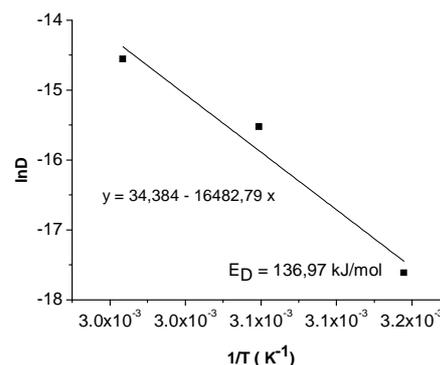


Figure 5. The semilogarithmic Arrhenius plot of  $\ln D$  vs.  $1/T$  for cathodic deposition of Pb films on Pt ( $0.5 \text{ cm}^2$ ) using ChCl-EG (1:2 moles) eutectic as electrolyte; 10 mM  $\text{Pb}^{2+}$  ion concentration

In Eq. (2),  $n$  is the number of electrons changed in electrode process ( $n=2$ );  $F$ ,  $R$  and  $T$  are the Faraday number, ideal gas constant and absolute temperature, respectively;  $A$  – the surface area of electrode ( $A=0.5 \text{ cm}^2$ );  $v$  – the scan rate;  $D$  – the diffusion coefficient of ionic species.

Using the above equation and the slopes of  $I_{pc} - v^{1/2}$  linear dependences, the obtained  $D$  values for  $\text{Pb}^{2+}$  ion were of the order of  $10^{-7}$ - $10^{-6} \text{ cm}^2 \text{ s}^{-1}$  in the temperature domain of 45-65°C. It is to mention that the order of magnitude for diffusion coefficient of  $\text{Pb}^{2+}$  ion in ionic liquids is generally lower than in aqueous solutions (where  $D$  is about  $10^{-5} \text{ cm}^2 \text{ s}^{-1}$  for  $\text{Pb}^{2+}$  ion); this is expected for diffusion of  $\text{Pb}^{2+}$  ion in our ChCl-ethylene glycol ionic liquid that has higher values of viscosity and density as aqueous media.

In Fig. 5 the Arrhenius semi-logarithmic plot is presented. From the slope of this linear dependence a value of  $137 \text{ kJmol}^{-1}$  of the activation energy of diffusion of  $\text{Pb}^{2+}$  ion in the selected ionic liquid was estimated.

More information about the cathodic process is obtained by applying the electrochemical impedance spectroscopy technique for  $\text{Pb}^{2+}$  / ChCl-EG ionic liquid system.

In the followings we present both Nyquist and Bode diagrams obtained experimentally by shifting gradually the electrode potential toward more negative values. To choose the potential range we have used the cyclic voltammograms. Figure 6 shows clearly that the polarization from -0.2V to -0.4V results in decreasing of diameters of capacitive semicircles up to  $440 \Omega \text{ cm}^2$ , suggesting an increased rate of deposition of metallic Pb. Correspondingly, the maximum of Bode angle decreases from  $-72^\circ$  to  $-58^\circ$ , a value rather attributed to a diffusion-controlled deposition process. By continuing the polarization at more negative potentials the increase of semicircle diameter demonstrates that the cathodic peak potential (around -0.4 V) was exceeded, proving the diminution of faradaic process in more negative potential range.

In a separate series of experiments we performed electrolysis at 65°C by keeping the electrode potential at constant value of -0.4 V (vs. Ag quasireference) and

recording Nyquist and Bode diagrams after different time intervals. The obtained results for 10 mM  $\text{Pb}^{2+}$  concentration are presented in Fig. 7. As the inset in Fig. 7-a shows the smallest semicircle diameter was obtained at the initial time and in this case the corresponding capacitive loop is followed by a straight line with an approximately  $45^\circ$  slope. This is typically for a film deposition process with a diffusion-control due to the mass transport of ionic species reacting to cathode.

The following impedance records show only Nyquist semicircles, which is characteristic for a charge-transfer control.

Electrolyses at prolonged time led to gradually increased diameters of semicircles proving a decrease of charge transfer rate during thickening of metallic deposit. Correspondingly, Bode diagrams presented a gradual increase of impedance modulus together with an increase from  $-30^\circ$  (the most conductive film, thin Pb film) to  $-65^\circ$  (pseudo-capacitive, the thickest Pb film) of maximum phase angle.

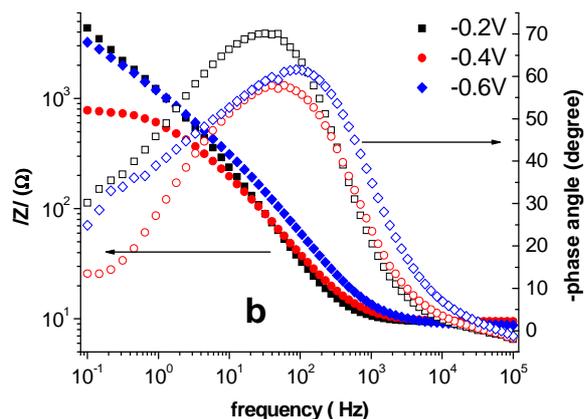
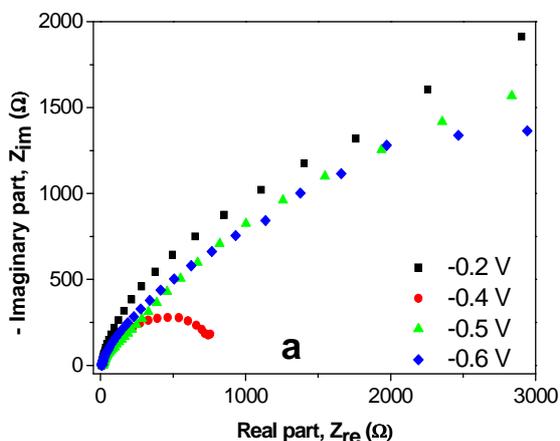


Figure 6. Nyquist (a) and Bode (b) diagrams recorded at different polarizations of the Pt electrode ( $0.5 \text{ cm}^2$ ) in  $\text{ChCl-EG}$  (1:2 moles) eutectic containing  $2.5 \text{ mM PbCl}_2$ ; temperature  $65^\circ\text{C}$ .

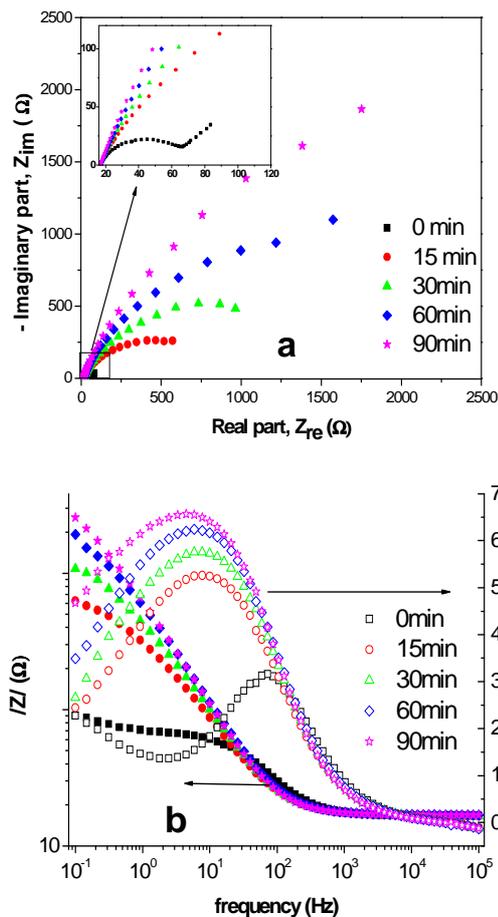


Figure 7. Nyquist (a) and Bode (b) diagrams recorded at  $-0.4 \text{ V}$  constant polarization of the Pt electrode ( $0.5 \text{ cm}^2$ ) in  $\text{ChCl-EG}$  (1:2 moles) eutectic containing  $10 \text{ mM PbCl}_2$ ; temperature  $65^\circ\text{C}$ ; electrolysis times up to 90 min. **Inset**: high frequency data on an enlarged scale.

## 4. Conclusions

Cyclic voltammetry and electrochemical impedance spectroscopy were successfully used for investigation of lead deposition from a room temperature ionic liquid (choline chloride: ethylene glycol eutectic). Both techniques gave information about the electrode potentials of deposition and dissolution of Pb, as well as about the mechanism of electroreduction and electrooxidation.

The novelty of this work consists in using the choline chloride : ethylene glycol (1:2 moles) eutectic as supporting electrolyte instead of an aqueous solution.

By working in the  $45\text{--}65^\circ\text{C}$  temperature range we demonstrated that electrodeposition of Pb is a cathodic process controlled by diffusion, a fact that allowed to estimate the diffusion coefficients of  $\text{Pb}^{2+}$  ion in the choline chloride : ethylene glycol (1:2 moles) ionic liquid, as well as the activation energy of diffusion.

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