

ELECTRODEPOSITION OF RARE EARTH METALS IN IONIC LIQUIDS

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Abstract

In this paper the available literature on the application of ionic liquids in rare earth metals electrodeposition, is briefly discussed and the main electrochemical properties of ionic liquids, in relation with such applications, are presented. In addition, the results of a preliminary investigation for the suitability of pyrrolidinium-based ionic liquids on the electrodeposition of lanthanum are presented.

Introduction

Production of rare earth metals and alloys are conventionally performed by high temperature molten salts electrolysis, which creates highly corrosive environment and demands high energy consumption. Recently, the use of organic solvents has been implemented for the electrodeposition of rare earths; however they were considered inadequate, due to their high volatility and their inflammability.

Ionic liquids gain increasing attention in the recent years, as electrolytes for the recovery of metals more electropositive than hydrogen. It concerns for salts that are generally liquid at ambient conditions, consisting of a bulky organic cation and a smaller organic or inorganic anion [1]. The variety, the combination, the position and the size of cations and anions adjust remarkable properties for ionic liquids, such as very low melting point, high chemical and thermal stability, negligible vapour pressure, ability to dissolve a wide range of organic and inorganic compounds, important ionic conductivity and broad electrochemical window [2]. These properties of ionic liquids, in combination with the non-flammability they present, render them advantageous for the electrodeposition of rare earth metals, in comparison with the organic solvents currently used [3-5].

Preliminary studies have proven that ILs are capable solvents and electrolytes of reactive metals, such as Li, Na, Al, Mg [6-8]. In this paper the applications of ionic liquids in the electrodeposition of rare earth metals are reviewed and preliminary results of the electrodeposition of lanthanum are presented.

Electrodeposition of rare earths in ionic liquids

The electrodeposition of rare earth elements from ionic liquids has been mainly investigated with four different families of ionic liquids based on their cation. It concerns for imidazolium, pyrrolidinium, ammonium and the phosphonium-based ionic liquids with a variety of anions.

Imidazolium-based ionic liquids

It is the most widely investigated family of ionic liquids for metals electrodeposition. Especially, the imidazolium chloroaluminate systems have been used successfully for the electrodeposition of Al and refractory metals such as Ta.

In the case of reduction of rare earth metals from imidazolium-based ionic liquids, Tsuda et al. [9-10] reported the co-deposition of La with Al from a LaCl_3 -saturated Emim- AlCl_3 system with excess of LiCl and SOCl_2 and not in pure Emim- AlCl_3 . The lanthanum content of the resulted Al-La alloy was 0.05% up to 0.50%, in terms of mass fraction. In addition, the co-deposition of La-Co alloys was studied in the ionic liquid Bmim- CF_3SO_3 using copper coils as cathodes [5]. Moreover, the co-deposition of Sm and Co in Bmim BF_4 was reported [5], through inductive effect and the content of Sm in the final alloy was estimated between 5% and 40%.

Lin [11] et al in 1993 approached the electrochemical behaviour of Ce(III)/Ce(IV) couple in the basic aluminium system ($\text{AlCl}_3 - \text{MeEtimCl}$) and via ultraviolet-visible spectroscopy it was stated that Ce(III) and Ce(IV) form complexes such as $[\text{CeCl}_6]^{x-}$, whereas $x=3$ and 2 respectively. Jagadeeswara et al. [12] researched the electrochemistry of the systems Ce(III), Sm(III) and Eu(III)/Eu(II) in BmimCl. The application of cyclic voltammetry and chronopotentiometry at platinum working electrode revealed the reduction of trivalent Ce and Sm ions to the divalent state at various temperatures and found them to be quasi-reversible reactions. In 2006, Yamagata et al. [13] studied the electrochemical behaviour of redox reactions Sm(III)/Sm(II), Eu(III)/Eu(II) and Yb(III)/Yb(II) in the ionic liquid Emim-TFSI through cyclic voltammetry and it was found to be quasi-reversible or irreversible.

Pyrrolidinium-based ionic liquids

Glukhov et al. [14] have stated the reduction of Y, Gd and Yb in the ionic liquid BMP- CF_3SO_3 on both, platinum and copper electrodes. On the voltammetric curves performed with the Pt electrodes in the systems Y and Gd with this IL, the observed cathodic peak with a maximum value of -2.6 V (rel. Ag/0.1 M Cl⁻) was attributed to the reduction of the trivalent cations to the metallic state. The electrodeposition of these metals was performed under potentiostatic or galvanostatic conditions and a tenuous black precipitate was formed on the electrode's surface. It was also shown that the reduction of Yb(III) to the metallic form occurs step by step via Yb(II) formation and the limiting stage of the cathodic process is the adsorption of the metal cation on the electrode. Legeai et al. [15] have shown that the reduction of La in OMP-TFSI is an irreversible reaction and that La electrodeposition in this ionic liquid under potentiostatic polarisation conditions -1.5 V (vs Ag/AgCl), for 120 min, at 298 K, resulted in the cathodic deposit of a thick La film of 350 nm.

In addition, Yamagata et al. [13] studied by cyclic voltammetry the redox reactions of the Sm(III)/Sm(II) couple in BMP-TFSI ionic liquid using a glassy carbon electrode and determined the redox reactions as quasi-reversible or irreversible. They also studied the electrochemistry of Yb(III) in BMP-TFSI by cyclic voltammetry and concluded to a cathodic and an anodic peak at around -0.95 V (vs Ag/Ag⁺), which considered attributable to the reduction of Yb(III) and the oxidation of Yb(II), respectively. The electrochemical behaviour of Eu(III) in BMP-TFSI was researched by Rao et al. [16] with glassy carbon and stainless steel electrodes, at various

temperatures. The cyclic voltammograms revealed a quasi-reversible behaviour of the redox couple Eu(III)/Eu(II) and an irreversible behaviour of the couple Eu(II)/Eu(0), which presented a cathodic peak attributed to the reduction of Eu(II) to the metallic state. In the same ionic liquid (BMP-TFSI) that contained also chloride anions, Hussey et al. [17] studied the electrochemical and spectroscopic behaviour of Nd(III) and Pr(III). According to their results, the electrolytic dissolution of both metals in this ionic liquid's system produces only the respective trivalent cations, which can be reduced to the Ln²⁺(II) state, but the resulting divalent species exhibit only transient stability, undergoing rapid disproportionation to Ln³⁺(III) and Ln⁰ states.

Ammonium based ionic liquids

Glukhov et al. [14] investigated the reduction of Y, Gd, Yb in the ionic liquid Bu₃MeN-CF₃SO₃ and concluded that the deposition of the above metals is only possible on a copper substrate and does not occur on a platinum one. Bhatt et al. [18] reported the reduction of selected lanthanide cations (La, Sm and Eu) to the zero-valent state in the ionic liquid Me₃NBu-TFSI. The lanthanide cations were introduced to the ionic liquid as the TFSI hydrate complexes. Cyclic voltammograms revealed a cathodic peak at -2.4 V vs Fc⁺/Fc for the lanthanum system attributed to the reduction to metallic state, whereas two peaks were observed for Sm- and Eu- systems, the less negative were associated with (III)/(II) reaction and the more negative with the reduction to the metallic state.

Phosphonium based ionic liquids

In 2008 Matsumiya et al. [19] studied the electrochemical behaviour of Sm(III) in the phosphonium based ionic liquids. The diffusion coefficients of Sm(III) were determined via cyclic voltammetry, chronoamperometry, chronopotentiometry and were estimated to be on the order of 10⁻⁸ cm²s⁻¹. It was stated that the trivalent samarium complexes in the phosphonium based ionic liquids were assumed to present higher ion mobility in respect to those in the ammonium ionic liquids, due to weaker interaction between the cation and the anion in phosphonium-based ILs. In addition, Kondo et al. [20] researched the suitability of P[₂₂₅]-TFSI for the electrodeposition of neodymium. The diffusion coefficient of Nd(III) was investigated by chronopotentiometry with cylindrically symmetrical diffusion and was estimated on the order of 10⁻¹¹ m²s⁻¹ at 100 °C. The cyclic voltammograms of Nd(III)/P[₂₂₅]-TFSI containing 0.5 mol dm⁻³ NdTFSI₃ presented an anodic and a cathodic peak currents that were attributed to the oxidation and the reduction of Nd(III), respectively. The reduction of Nd cation was observed at -2.5 V vs a platinum wire immersed in the solution used as a quasi-reference electrode, compensated for the Fc⁺/Fc redox couple. The electrodeposition of neodymium in the specific ionic liquid was performed by potentiostatic electrolysis at -3.1 V vs Fc⁺/Fc at 150 °C. A black electrodeposit was fine and formed uniformly neodymium particle and was observed by SEM and identified from the evaluation of EDX.

Moreover, the electrochemical behaviour and electrodeposition of dysprosium (Dy) in the phosphonium-based ionic liquid P[₂₂₅]-TFSI were investigated by Kurachi et al. [21]. The cyclic voltammetric measurements resulted in one step reduction of the trivalent dysprosium ion in phosphonium-based ionic liquid. On the other hand, no anodic peak ascribed to the oxidation of dysprosium metal was observed in this electroanalytical study. The diffusion

coefficient and the activation energy for diffusion of the trivalent Dy complex in this IL were also estimated, using semi-integral analysis. The diffusion coefficient of Dy(III) was calculated to be $2.0 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$ at 25 °C, closed to that of the trivalent lanthanoid ion such as Eu(III) and Sm(III) in phosphonium-based ionic liquids. In addition, the activation energy for diffusion was estimated to be 65 kJmol^{-1} (0.5 M) and 49 kJmol^{-1} (0.075 M).

Choline based ionic liquids

In 2012 Ishii et al. [22] investigated the physical and electrochemical properties of choline-based ionic liquids and their capacity to reduce iron and neodymium cations. The novel cationic blended ionic liquids which were constituted by the 2-hydroxyethyltrimethylammonium bis(trifluoromethylsulfonyl)imide Ch-TFSI and P_[225]-TFSI was applied for the electro-recovery of neodymium. In this study the starting materials were voice coil motors for hard disk drivers and the electrodeposits obtained were examined by SEM/EDX and XPS. According to the results of this study, iron group and rare earth metals can be recovered separately by electrodeposition in two stages.

Preliminary studies on lanthanum electro-recovery from pyrrolidinium-based ionic liquids.

Experimental work of the specific research focused on evaluating the use of pyrrolidinium-based ionic liquids for the electro-recovery of reactive metals, such as the Rare Earth Metals are. More precisely, the reduction of lanthanum in the ionic liquid N-butyl-N-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide (BMP-TFSI) was studied, at room temperature. BMP-TFSI was selected among the different pyrrolidinium-based ionic liquids, because it presents electrochemical stability under cathodic polarisation, satisfying ionic conductivity and it is an air and water stable electrolytic medium.

Materials and apparatus

The ionic liquid BMP-TFSI was supplied by Solvionic and Lanthanum nitrate hexahydrate was purchased by Alfa Aesar. The lanthanum nitrate salt was heated at 100 °C under vacuum for 72 h and was dissolved in pure acetone, where subsequently the proper amount of electrolyte was added to form a solution's concentration of the order of 0.06 M. The solution was placed at 60 °C under vacuum for approximately 2h to remove acetone and then at 100 °C under vacuum for 24 h to remove residual water.

Linear and cyclic voltammetry tests were performed in a three microelectrodes cell (PAR) connected to a VersaSTAT3 potentiostat (PAR); the obtained experimental data were analysed with the VersaStudio software (PAR). The working electrode was a platinum disk of $d = 1.98 \text{ mm}$, as a counter electrode a Pt wire immersed directly into the solution was used and finally, as a reference electrode the redox couple Ag/0,1 M AgNO₃ in acetonitrile was employed. The working electrode was polished with aluminum paste 1 μm on a velvet pad and electrochemically in 1 M sulfuric acid. Although BMP-TFSI exhibits hydrophobic characteristics and it is stable under normal atmospheric conditions, the cyclic voltammetry and chronoamperometry measurements were performed in a glove box, providing an inert atmosphere by purging nitrogen gas to minimise oxygen and moisture contamination. The morphology of electrodeposits was examined by Scanning Electron Microscope (JEOL6380LV), provided with Energy Dispersive Spectrometry.

Results

The electrochemical window was determined at room temperature by cyclic voltammetry and the cathodic limit of the electrolyte was determined at -3.5 V vs Ag/Ag⁺. Figure 1 shows the cyclic voltammogram recorded in the system BMP-TFSI/La. As it is obvious, a generation of an intense cathodic peak begins at -2.2 V vs Ag/Ag⁺, attributed to the reduction of trivalent lanthanum cation (La³⁺) to the metallic state. The absence of corresponding anodic peak on the reverse scan allows the assumption that lanthanum reduction is irreversible [15]. Moreover, the cathodic peak at -1 V is ascribed to the limited reduction of hydrogen cations, due to slight moisture [2] that inevitably was present and the narrow shoulder at -1,5 V is attributed to an adsorption La³⁺ reaction occurring on the electrode, prior to the reduction of lanthanum [14, 15].

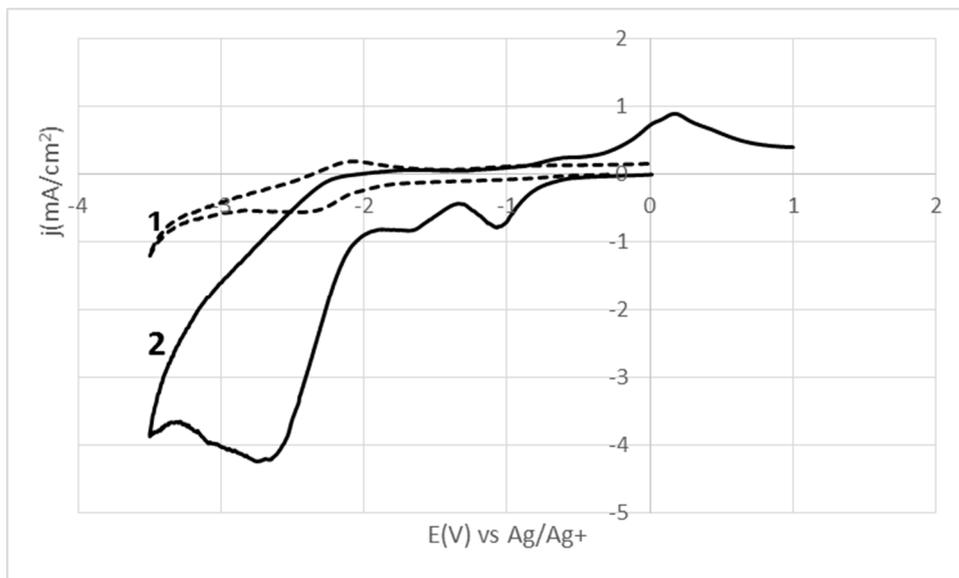


Figure 1: Cyclic voltammograms recorded with scan rate 20mV/s vs Ag/Ag⁺ on a Pt electrode at 25 °C: (1) BMP-TFSI and (2) for the solution of 0.06 M La(NO₃)₃ in BMP-TFSI.

Furthermore, the electrodeposition of lanthanum was realised on a copper substrate, under potentiostatic conditions for 5 h at -3.1 V (vs Ag/Ag⁺) at 25 °C. The electrodeposits were examined in SEM and EDS analysis (Figure 2) revealed the electrodeposition of lanthanum. The EDS analysis also revealed the existence of fluorine and sulfur that may occur, due to the TFSI anion adsorption on the electrode's surface that could explain the absence of anodic peak.

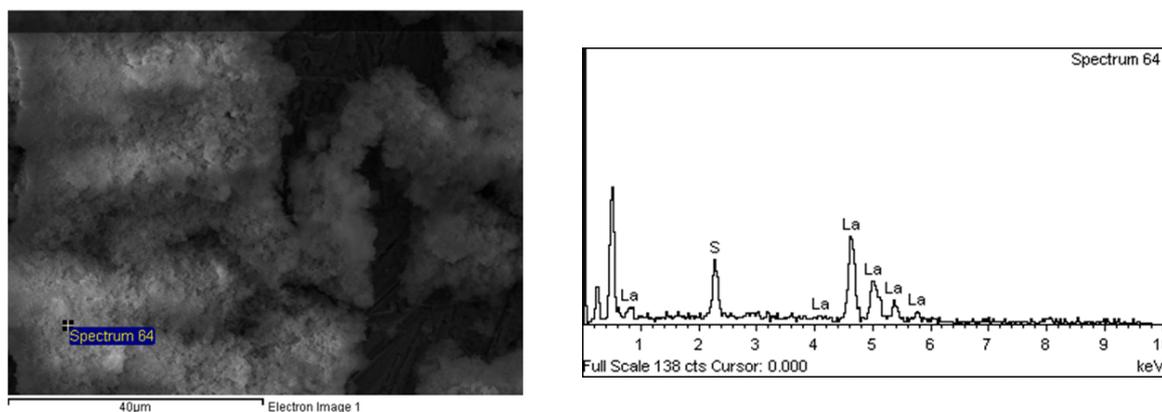


Figure 2: SEM image depicting the electrodeposits of lanthanum(left), EDS analysis of the electrodeposits(right)

Conclusions

Ionic liquids are promising electrolytes, suitable for the electrodeposition of rare earth metals. The research in this area has proven their ability to reduce and to permit the electrodeposition of drastic metals, without the drawbacks present in the currently used technology.

The preliminary electrochemical investigation of BMP-TFSI revealed its potential use for reduction of lanthanum and appears, due to its physicochemical properties, to be an appropriate medium for the electrodeposition of rare earth elements.

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