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New insight into indium electrochemistry in a Tf_2N-based room-temperature ionic liquid

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ABSTRACT

The electrodeposition of indium is reported in a new weakly hygroscopic piperidinium-based ionic liquid (1-butyl-1-ethyl-piperidinium bis(trifluoromethylsulfonyl)imide) that allows electrodeposition to be performed without a glove box. The electrochemistry of indium is thoroughly investigated and the drawbacks of using metal chloride precursors in Tf_2N-based electrolytes are highlighted using cyclic voltammetry and stripping experiments. Voltammograms revealed complex electrochemical behaviour and several cathodic and anodic signals that could be attributed to the formation of indium chloro complexes during the scan, due to changes in the concentration ratio $[Cl^-]/[In(III)]$ of interfacial species during the In(III) reduction reaction. A procedure for the electrodeposition of indium avoiding the use of the indium chloride precursor is then proposed. It offers an improved morphology of the electrodeposit and an increase in faradic yield from 33% to 85% compared to chloride-containing RTILs.

1. Introduction

Electrochemical deposition (ECD) of indium is of great interest for the production of thin-film semiconducting compounds such as InSb, InAs and $Cu(In,Ga)(S,Se)_2$, widely used in electronic and opto-electronic devices (e.g. detectors, lasers, photovoltaic devices and light-emitting diodes). ECD using indium-containing compounds in aqueous media has been extensively described in the literature [1,2]. It has been emphasised that deposition efficiency is limited by H^+ reduction.

Low melting-point ionic liquids or room-temperature ionic liquids (RTILs) are a new class of non-aqueous solvents considered as promising electrolytes for ECD of high quality thin films, since hydrogen is not evolved in these media [3–9]. They are liquid at or below room temperature and they display, in particular, high ionic conductivities and wide electrochemical windows [10]. Two main families of RTILs are commonly used for ECD purposes: halide-based compounds, also called first-generation RTILs, and second-generation "air- and water-stable" RTILs. Numerous examples of the use of first-generation RTILs for the ECD of single metals and alloys have been reported [11]. However, these chloroaluminate RTILs, combining aluminum chloride and dialkylimidazolium or dialkylpyridinium chloride, are highly hygroscopic and so have to be protected from moisture by working in a glove box. The use of RTILs has greatly increased since Riechel and Wilkes reported the first second-generation, air- and moisture-stable RTILs with either tetrafluoroborate or hexafluorophosphate as anions [12]. More recently, RTILs containing anions such as tri-fluoromethanesulfonate, bis(trifluoromethanesulfonyl)imide or tris(trifluoromethanesulfonyl)methide were synthesised and attracted attention because of their low viscosity, low hygroscopy and low reactivity towards moisture [13]. However, currently developed and commercialised electrolytes still have to be used in a dry atmosphere for ECD applications and so cannot be considered as viable electrolytes by the electroplating industry.

In addition, contrary to common belief, second generation RTILs are not "supersolvents" in which all kinds of materials can be easily dissolved. Due to the poor solvating power of

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these RTILs, composed of weakly coordinating anions, and to their moderate polarity, the solubility of inorganic ionic compounds in second-generation RTILs is actually very low unless chloride salts are used. However, the introduction of chloride ions in electroplating baths leads to undesirable chlorine gas evolution at the anode during ECD, makes the RTIL more hygroscopic and leads in some cases to complex electrochemical behaviour.

ECD of indium has recently been studied in an air- and moisture-stable RTIL, using a chloride salt as the indium cation source [14]. In these conditions, the In(III)/In(0) electrochemical system is far from simple, involving several reduction steps that are difficult to explain and require complex optimisation of ECD experimental parameters for high quality film synthesis. Also, in this earlier work, experiments were carried out in highly restrictive conditions, i.e. in a glove box with water and oxygen concentration levels below 1 ppm. This was because the electrolytic solutions used, consisting of a 1-butyl-1-methyl-pyrrolidinium bis(trifluoromethylsulfonyl)imide ($BMPTf_2N$) RTIL containing $InCl_3$ as the metal precursor, was too hygroscopic to perform the ECD experiments in ambient atmosphere.

In this paper, we report the electrodeposition of indium in a home-made weakly hygroscopic piperidinium ionic liquid (1-butyl-1-ethyl-piperidinium bis(trifluoromethylsulfonyl)imide: $BEPipTf_2N$) that allows electrodeposition to be performed without the need of a glove box. The synthesis and some physical and chemical properties of several piperidinium-based RTILs are first related. We then present a detailed study of the electrochemical behaviour of $InCl_3$ in the $BEPipTf_2N$ RTIL. The strong influence of chloride ions on the In(III)/In(0) electrochemical system and electrodeposition faradic yield is highlighted. We finally propose a procedure for the electrodeposition of indium in a chloride-free electrolyte to avoid the drawbacks of using a chloride-based precursor metal in a Tf_2N-based RTIL.

2. Experimental

Ionic liquids were prepared according to the published procedure of Triolo et al. [15], modified. Briefly, the nitrogen-based heterocycle yielded the corresponding ammonium salt by reaction with alkyl bromide. Bromide anion was then replaced by bis(trifluoromethylsulfonyl)imide (Tf_2N^-) by vigorous stirring of the alkylammonium bromide with an aqueous solution of lithium bis(trifluoromethylsulfonyl)imide ($LiTf_2N$, Solvionic, 99+%). After metathesis was complete the ionic liquid was extracted with dichloromethane (Sigma–Aldrich, >99.5%) and dried under reduced pressure for 3 h. Synthesised ionic liquids were characterised by nuclear magnetic resonance (NMR) analysis (Bruker Spectrospin DRX 300 MHz Ultrashield).

The density, viscosity and conductivity of RTILs were determined as a function of water content determined by Karl Fischer coulometric titration (Metrohm 831KF coulometer) using Hydranal 34843 Coulomat AG-H (Fluka) as titrant.

The density measurements were performed with a DSA 5000 thermo-regulated digital densimeter (Anton Paar). The apparatus measures densities using an oscillating U-tube with an accuracy of $0.00001\ g/cm^3$ and temperature controlled to within 0.001 °C.

All measurements were conducted at $20.005 \pm 0.004\ ^\circ C$. The density was calculated from the quotient of the period of oscillations of the U-tube and the reference oscillator: density = $K_A \times Q^2 \times f_1 - K_B + f_2$, where K_A and K_B are constants specific to the apparatus, Q is the quotient of the period of oscillation of the U-tube divided by the period of oscillation of the reference oscillator and f_1 and f_2 are correction terms for temperature, viscosity and non-linearity.

All rheological measurements were performed using an AMVn automated microviscosimeter (Anton Paar). The apparatus measures viscosities in a 0.3–2500 mPa s range using the rolling ball/falling ball principle, which consists in measuring ball rolling time in a diagonally mounted glass capillary filled with the sample. Ball rolling time was measured with an accuracy of 0.002 s at a temperature controlled to within 0.001 °C.

All measurements were made at 20.00 °C with a 70° inclination angle of the capillary, and the dynamic viscosity η was calculated using the formula $\eta = K_1 \times (\rho_K - \rho_P) \times t_1$, where K_1 is the calibration constant of the measuring system, ρ_K is the ball density, ρ_P is the density of the measured sample and t_1 is the ball rolling time.

Conductivities of RTILs were measured using a Tacussel Electronique CDRV62 conductimeter/resistivitimeter with a platinum 2-electrode cell (Materials Mates). The cell was calibrated with 5×10^{-3} to 3.3×10^{-2} KCl solutions, and the data were recorded at a frequency of 62 Hz.

The solubility of water in the RTILs was determined by Karl Fischer coulometric titration after RTIL contact with distilled water. The water content of water-saturated RTILs in equilibrium with water was measured by mixing water and each RTIL for 24 h. The two-phase system was then centrifuged and the RTIL water content was measured.

Electrochemical experiments were carried out using a PGP201 potentiostat (Radiometer Copenhagen) and a Tacussel Electronique potentiostat (101T and PJT24-1). Before electrochemical experiments the electrolytic solution was de-aerated and dried down to a water content below 50 ppm by dry argon bubbling. In(III) solutions were prepared either by dissolution of $InCl_3 \cdot 4H_2O$ (Sigma–Aldrich, 97%) or by electrochemical potentiostatic dissolution of a soluble indium anode (Alfa Aesar, 99.99%) in the selected ionic liquid at ambient temperature. It appeared that $InCl_3 \cdot 4H_2O$ salt was readily soluble in the ionic liquid and concentration values up to 0.25 M were easily achieved. All experiments were performed at 60 °C to lower RTIL viscosity and increase mass transport. Electroanalytical studies were carried out using a conventional three-electrode electrochemical cell, with a platinum disk ($19.6\ mm^2$) as working electrode, glassy carbon as counter electrode and an AgCl-covered Ag wire (Alfa Aesar 99.999%) as pseudo-reference electrode. This latter was separated from the bulk solution by a salt bridge, containing only the RTIL electrolyte, in order to avoid the variations of its potential as a function of Cl^- concentration in the bulk. This pseudo-reference electrode was prepared by chemical oxidation of an Ag wire in a $FeCl_3$ aqueous solution, and carefully dried before use. Square platinum plates (Goodfellow, Lille, France, 99.99%, area $25.0\ mm^2$) were used as substrates for the electrodeposition of indium. Electrodeposition was achieved by controlled potential electrolysis in steadily stirred $BEPipTf_2N$ containing In(III). Before the electrochemical experiments were carried out, the working electrode was polished with SiC abrasive papers and 1 μm diamond paste, and then soaked in deionised water and acetone. After electrodeposition, the indium-coated square platinum plate electrodes were immediately transferred from the electrodepositing baths into acetone to remove residual RTIL.

The surface morphology and grain size of the deposits were determined using a scanning electron microscope (FEG-SEM) (Philips XL30), equipped with an energy dispersive spectrometry (EDS) detector. Structural characterisations were conducted by X-ray diffraction (XRD) using a Bruker diffractometer (D8 Advance, Cu $K\alpha_1$ radiation).

ECD faradic yields were determined by atomic absorption spectrometry (Varian AA240FS) after chemical dissolution of the deposits in 3 M HNO_3.