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Electrodeposition of metal cations from the wet ionic liquid [EMIM][TFSI]

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Abstract

We investigated the deposition of silver, copper, and lead from the ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide [EMIM][TFSI] under potentiostatic conditions in the presence of water. This was part of a larger project involving the extraction of metal ions from mining waste into an ionic liquid, followed by electrodeposition so that the ionic liquid could be recycled. All three elements were deposited in metallic form by electrolysis in the ionic liquid, and the process was enhanced rather than hindered by the presence of water. The deposited metals did not adhere strongly to the cathode of the electrochemical cell, especially when Ebonex™ was used as the cathode. The deposition of silver showed little temperature dependence, and at temperatures close to ambient, the ionic liquid was not adversely affected. The deposits of copper and lead gradually re-dissolved after electrodeposition, suggesting that chemical re-oxidation of these metals by air is more facile in the ionic liquid than in water. Copper showed strong evidence of formation of a Cu^+ species upon reduction of Cu^{2+} (not seen in water); lead (Pb^{2+}) showed evidence of a time-dependent complexation with the anions of the ionic liquid.

Key words: electrodeposition; ionic liquids; possible application to mining wastes

1. Introduction

Ionic liquids (IL, salts with melting points $< \sim 100^\circ\text{C}$) typically have high chemical stability, negligible vapour pressure, and high ionic conductivity.¹ These properties are highly tunable by varying the structures of their constituent ions.² The literature on electrodeposition of metals from ionic liquids³ is mainly focused on obtaining novel forms of metal powders such as nano-particles,⁴ or on deposition of elements that cannot be reduced in water: semimetals such as germanium, and metals such as calcium and aluminum.⁵ These applications require scrupulously dry ionic liquids that have wide electrochemical windows.¹

World-wide demand for minerals produces large amounts of wastes.⁶ The present research considers the development of a possible technology for the remediation of toxic metals from aqueous mining wastes.^{7,8} This concept involves extraction of metal cations from the aqueous medium into an IL, using a supported liquid membrane. Subsequent electro-deposition of the elemental metals would regenerate clean IL for recycling back to the extraction step, with the metals recovered either as a saleable byproduct, or in the worst case in a form that could be readily land-filled. In contrast with the anhydrous conditions generally employed in previous studies, the IL would be wet. Hence, this exploratory study involves proof of concept for the electrodeposition of silver, lead and copper, from 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide [EMIM][TFSI] (**Figure 1**), with emphasis on whether the process is adversely affected by water.

2. Materials and Methods

1-Ethyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl) imide 99%, was purchased from Ionic Liquids Technologies, and stored by filling the bottle with argon after each use. Working solutions were prepared using silver (I) triflate (Sigma Aldrich $\geq 99\%$), lead (II) trifluoroacetate (Alfa Aesar, 98%) and copper (II) triflate (Alfa Aesar $\geq 99\%$).

Electrochemical studies: Cyclic voltammetry was conducted using DY2100 potentiostat software and a three-electrode cell comprised of a Pt working electrode (area 3.1 mm^2),

Pt foil counter electrode, and a Pt wire quasi-reference electrode, at a scan rate of 0.02 V s⁻¹. The working electrode was cleaned after each use with abrasive paper, and all electrodes were washed using ethanol, de-ionized water, and Milli-Q water, then oven dried; they were cooled for 5 min prior to voltammetric studies.

Electrolyses were conducted potentiostatically using a Princeton Applied Research Model 273A potentiostat/galvanostat (Gamble Technologies Limited, Mississauga, ON). Solutions were electrolyzed open to the air, except that argon was bubbled through those that had been previously dried in vacuum. Reactions were conducted using graphite or Ebonex® cathodes, Pt or Ti/IrO₂-Sb₂O₅ anodes, and Pt reference electrodes (~+0.7 V vs SHE), with gentle magnetic stirring.

Physical Studies: FTIR analyses were conducted on a solution of 50 mM (CF₃CO₂)₂Pb in [EMIM][TFSI] using Thermoelectron Nicolet 380 instrumentation with Ez-Omic software (Madison, WI). Sampling was obtained using attenuated total reflectance methods on a ZnSe crystal, with a resolution of 6 cm⁻¹, and 30 scans per acquisition.

²⁰⁷Pb NMR (Bruker Avance 300, Milton, ON) was conducted using 1.0 M Pb(NO₃)₂ in D₂O as a reference (δ = -2990 ppm), using 83.5 MHz instrumentation. IL solutions analyzed were 0.5M (CF₃CO₂)₂Pb in [EMIM][TFSI] with 10% v/v DMSO-d₆.

Quantitative water analyses were performed using a Metrohm 870 KF (Mississauga, ON) volumetric Karl Fischer titrator using the average of three injected samples of an approximate mass of 0.1 g.

Qualitative analysis: Silver was identified by dissolving the deposit in nitric acid and adding chloride to give a photosensitive precipitate. Copper was identified through its inability to dissolve in non-reducing acids (sulfuric acid, hydrochloric acid) and its solubility in nitric acid. Powder X-Ray diffraction using a 2-Theta goniometer configuration on an Agilent Technologies SuperNova X-ray diffractometer (Oxfordshire, UK) confirmed the identity of lead deposits.

Quantitative analysis: Silver remaining in solution was analyzed using a voltammetric calibration curve (see above). Copper analysis employed an Agilent 240 atomic

absorption spectrometer (Mississauga, ON) using a copper metal hollow cathode lamp and a calibration curve with copper (II) triflate. The samples run were prepared by taking 35 μL samples using a micropipette and dissolving them in water while stirring in a 5 mL volumetric flask. Lead was analyzed gravimetrically by washing the deposits with ethanol and water, followed by thorough drying. In later experiments, all metals were analyzed in triplicate using optical detection ICP, using a Varian Vista-MPX CCD Simultaneous ICP-OES with ICP Expert Software (Mulgrave Victoria, Australia). Wavelengths: silver, 328.068; copper, 327.395; lead, 220.353 nm; plasma gas flow, 15.0 L min^{-1} ; auxiliary gas flow, 1.50 L min^{-1} ; nebulizer gas flow, 0.70 L min^{-1} .

3. Results and Discussion

Dry [EMIM][TFSI] has an electrochemical window of 4.6 V (from -2.5 V to +2.1 V vs. Pt quasi reference electrode).⁹ The Digi-Ivy potentiostat used in this work had a range of only ± 2 V vs Pt (approximately -1.3 to +2.7 V vs. SHE), which was adequate for the present purposes. “Dry” IL was obtained by treating the solvent as supplied (950 ppm water by Karl-Fischer titration) in vacuum for 35 min. Upon adding water, the negligible voltammetric currents obtained with dry IL gave way to voltammograms showing the reduction and oxidation of water, and the electrochemical window shrank to ~ 2.3 V, as previously reported.¹⁰

The direct extraction of metal ions into ILs did not afford solutions of well-defined solute concentration. We therefore used metal triflates or trifluoroacetates to produce solutions with well-defined initial concentrations, rather than solutions produced by extraction from the aqueous phase. Reference silver solutions were prepared by dissolving Ag(I) triflate in [EMIM][TFSI] with gentle mixing. To prepare lead solutions, a weighed amount of lead (II) trifluoroacetate was vortexed with [EMIM][TFSI] in a volumetric flask for approximately 10-15 min; the flask was then warmed in a water bath while stirring the contents, and finally vortexed for 5 min. Copper (II) triflate, which is anhydrous, was negligibly soluble in dry [EMIM][TFSI], so the IL was saturated with water by forming an emulsion with water for 30 min before adding the copper salt, then vortexed for a few minutes to complete dissolution.

3.1 Silver

When silver was extracted into [EMIM][TFSI] from aqueous AgNO_3 , cyclic voltammetry at graphite showed a reversible reduction peak near -0.2 V vs. Pt (which has $E = +0.7$ vs SHE, and which was originally standardized vs SCE). The oxidation peak on the reverse scan was seen near +0.07 V (**Figure 2**) with a larger current with onset > 1 V due to oxidation of the water that was co-extracted into the IL (not shown). Cyclic voltammograms also showed a noticeable change between the first and subsequent cycles, possibly involving changes to the graphite surface during the oxidation step.¹¹ The peak current was proportional to $(\text{scan rate})^{1/2}$, showing that the reduction of Ag^+ was electrochemically reversible and took place under mass transport (**Supplementary Figure 1**).

Because [EMIM][TFSI] is more viscous than water, we anticipated faster mass transport and hence accelerated deposition in a warm solution. In practice, the peak current increased only two-fold between room temperature and 100°C (data not shown). The voltammetric current for the reduction of silver increased slightly with higher water content, showing that water in the IL would not inhibit electrodeposition. Previously, Basile et al. reported that increasing the water content from 60 ppm to 460 ppm lowered the peak current and shifted the potential for Ag^+ reduction to more negative values in the ionic liquid, $[\text{C}_4\text{mPyr}][\text{TFSI}]$ at a glassy carbon microelectrode.¹ They suggested that the cause was interaction of Ag^+ with the pyridinium nitrogen atom of $[\text{C}_4\text{mPyr}][\text{TFSI}]$, which is not present in [EMIM][TFSI].¹²

Planar graphite cathodes, formed by cutting 6 mm diameter graphite rods, were fitted into a 10 mL beaker that contained 5 mL of silver triflate in [EMIM][TFSI]. Initial electrolyses were carried out potentiostatically at -0.19 V vs Pt quasi reference electrode, and followed by cyclic voltammetry using a calibration curve prepared with standard solutions of silver triflate in [EMIM][TFSI] (**Supplementary Figure 2**). For this work the potentiostatic method was more convenient, and assured that first order kinetics would be followed. This avoided the issue of the competition between current controlled and mass transport controlled kinetics.

The reactions were run to ~50% conversion with water content up to near-saturation of ~10,000 ppm. The current density (reaction rate) increased significantly at higher water content; the current efficiency was essentially quantitative, independently of the water content (**Table 1**, entries 1, 3, and 4). The systematic trend of >100% CE in these experiments is almost certainly the result of experimental uncertainty, due to the experimental difficulty of calibrating the voltammetric method of quantitative analysis precisely. Later experiments were analyzed by ICP-OES, which gave more reproducible results.

The initial relationship between accumulated charge and time was relatively rapid, but then became linear (**Figure 3**). This was attributed to an initial deposition of silver onto graphite, with subsequent deposition onto a rough silver surface. The current density also increased at elevated temperature, as observed previously.¹³ At 78°C with IL as received (950 ppm water), the water content is recorded as “unknown” because the experiment was carried out in an open beaker, so water evaporated as the electrolysis progressed. Discolouration of the IL was observed above 78°C, suggesting decomposition. Although the cyclic voltammograms were run up to ~100°C, the electrodepositions were not run beyond 78°C once this discolouration was noticed. In addition, the inability to maintain a defined water concentration, because of evaporation at this elevated temperature, made the results ambiguous. However, the lack of a strong temperature effect was important for the proposed technology, because it rebutted any suggestion that the waste stream should be heated before electrolysis. Specific energies for silver deposition were approximately 3 kWh (kg Ag)⁻¹ in repeated experiments at ~10,000 ppm water, and double this at 78°C.

Later experiment employed EbonexTM cathodes (a conductive ceramic of approximate composition Ti₄O₇).^{14, 15} As at graphite, the silver deposit adhered poorly to the cathode and was easily removed. In experiments analyzed by ICP, silver was deposited from undried [EMIM][TFSI] with almost quantitative current efficiency at -0.27 V vs Pt. The rate increased when water was added to a total concentration of 10,000 ppm, with little reduction of the current efficiency (though the reaction was still considerably slower than in fully aqueous solution. At -0.40 V, the reaction was faster but somewhat less efficient, due to competing reduction of water (**Figure 4**).

3.2 Copper

Commonly available copper salts were insoluble in dry [EMIM][TFSI]. Saturation with water (~12,000 ppm) was necessary before adding copper triflate (a white powder). The resulting solution had the light blue colour characteristic of $\text{Cu}^{2+}(\text{aq})$.

Cyclic voltammetry of Cu(II) triflate in [EMIM][TFSI] at a Pt microcathode gave two reduction peaks experiments: one near -0.6 V and another near -0.3 V vs Pt quasi reference (**Figure 5**). These were assigned to the reduction of Cu(II) to Cu (I) and the subsequent reduction of Cu(I) to Cu(0),¹² based on the visual observation that no deposit was formed on the cathode upon electrolysis at -0.10 V even though current was flowing (showing that reduction was occurring), whereas rapid deposition of copper occurred upon electrolysis at ~ -0.60 V. A linear calibration curve for copper was obtained at the first reduction peak (**Supplementary Figure 3**) with $i(\text{peak}) \propto (\text{scan rate})^{1/2}$, indicating reduction under mass transport control (**Supplementary Figure 4**). At an Ebonex cathode, reduction peaks were observed with current maxima at -0.39 V and -1.02 V vs. Pt.

Graphite cathodes were not studied for the “bulk” deposition of copper, because the two reduction peaks were poorly separated, and so the appearance of the voltammograms changed with water content and temperature. Also, there was an initial confusion in identifying the electrolysis product at graphite – a black deposit (CuO) that dissolved easily in dilute mineral acids to give a faint blue aqueous solution of $\text{Cu}^{2+}(\text{aq})$. Murase et al. had identified a black deposit as Cu metal by XRD analysis, but from a different ionic liquid.¹⁶

In “bulk” (5 mL) solutions, the rate of loss of copper from the IL varied with the cathode (Pt < stainless steel < copper < graphite < Ebonex), giving a poorly adherent deposit, as with silver (**Supplementary Table 1**). Copper was distinguished from its oxides (CuO and Cu_2O) because the oxides were soluble in dilute mineral acids, whereas copper metal dissolved only in moderately concentrated nitric acid.

At Ebonex, copper deposition was observed visually upon electrolysis at -0.39 V, but was less efficient at -1.02 V due to preferential reduction of water to H_2 (supported by a large increase in current density when the solution was acidified). We cannot say

conclusively whether the deposition observed at -0.39 V was due to 2-electron reduction of Cu(II) to Cu metal, or to reduction of Cu(II) to Cu(I), followed by disproportionation in the somewhat aqueous medium. Evidence supporting the latter mechanism is that Cu(I) appears to be more stable in [EMIM][TFSI]. The oxidation of copper powder in contact with copper(II) triflate in [EMIM][TFSI] solution provided evidence for the reverse of disproportionation, literature precedent for which is the conversion of Cu(II) and copper metal to Cu(I) in [EMIM] [dicyanamide].¹² Additional evidence for accumulation of Cu(I) in solution during the electrolysis of copper triflate in [EMIM][TFSI], using an Ebonex cathode and Ti/IrO₂-Ta₂O₅ anode, was that there was initially no loss of copper from the solution, until 3 C of charge had passed (**Figure 6**). This suggests that any Cu metal that is deposited redissolves through the “reverse disproportionation” process – until the concentration of Cu(II) has become negligible. The deposition of copper was faster (and continuous from time zero) at more cathodic potentials, but the current efficiency was lower due to competing reduction of water.

When a solution of Cu(II) triflate was electrolyzed with sparging to remove water, copper was lost from solution with 80% apparent current efficiency. However, this was an artefact: the solution gradually became cloudy due to evaporation of water and precipitation of Cu(II) triflate, which redissolved when water was re-added.

Unexpectedly, the copper particles formed by electrolysis gradually dissolved when left in contact with the IL, with the smallest particles dissolving fastest. The oxidation of Cu metal by O₂ is thermodynamically favourable; it appears to be kinetically favourable in the ionic liquid, unlike in air or water, where it is so slow that copper is regarded as stable in these media. Besides molecular O₂ from the atmosphere, oxidizing species during the electrolysis include O₂ and hydroxyl radicals formed by the oxidation of water at the anode (balancing the reduction of Cu(II) at the cathode). Deposition of copper (or inhibition of redissolution) was mildly improved by excluding adventitious oxygen, by carrying out the electrolyses under a blanket of argon, and by using the dimensionally stable anode Ti/IrO₂-Ta₂O₅ to minimize the formation of hydroxyl radicals.¹⁷ The deposition of copper was very inefficient at elevated temperature, perhaps because of faster re-dissolution, unlike the deposition of silver, which was almost insensitive to temperature.

3.3 Lead

A solution of lead bis-trifluoroacetate in [EMIM][TFSI] (950 ppm water) showed a principal voltammetric reduction peak at ~ -1.3 V vs. Pt (more negative than that for silver or copper). However, the voltammograms changed in appearance with both water concentration (**Supplementary Figure 5**) and time (**Supplementary Figure 6**), showing that the interaction between Pb^{2+} and the IL is extremely complex. Hence the voltammograms represent contributions from both free and probably multiple forms of complexed lead cations. Most of the change occurred over ~ 2 h (the reduction peak near -1.3 V shifted to less negative potentials by about 0.1 V, while the broader peak near -0.6 V gained in intensity). Consequently, we could neither prepare calibration curves by voltammetry nor examine the effects of temperature and scan rate.

We suggest that aging caused a chemical change to the lead bis(trifluoroacetate) solution, perhaps due to complexation of Pb^{2+} with either the cation or more likely, the anion of the ionic liquid. We attempted to study this phenomenon by ^{207}Pb NMR (spin $\pm 1/2$, 22.6% natural abundance, receptivity $11.7\times$ that of ^{13}C), which has a particularly wide chemical shift range that is highly sensitive to both the number and type of atoms that is coordinated to the lead centre.¹⁸ Unfortunately, there is little information on the ^{207}Pb analysis of soluble Pb(II) compounds – most work on ^{207}Pb has involved soluble Pb(IV) and solid state Pb(II) systems.

We hoped to use NMR to follow chemical shift changes in fresh and aged solutions of lead bis(trifluoroacetate) in [EMIM][TFSI]. Reference spectra for $\text{Pb}(\text{NO}_3)_2$ in D_2O and $(\text{CF}_3\text{CO}_2)_2\text{Pb}$ were obtained in DMSO-d_6 using a deuterium lock to reference the signal due to ^{207}Pb , and hence avoid broadening the resonances due to small instrumental changes between pulses. Peak broadening, along with the relatively low concentration of Pb, obstructed our inability to observe ^{207}Pb NMR spectra in [EMIM][TFSI]. Hayamizu et al. have reported that the ^1H and ^{19}F NMR spectra of [EMIM][TFSI] show strong peak broadening,¹⁹ due to the T2 spin-spin relaxation time being much shorter than the T1 spin-lattice relaxation time.²⁰ We therefore hoped to observe “free” Pb^{2+} in a freshly prepared solution, followed by its “disappearance” due to peak broadening as it complexed to the IL. This was not feasible because the acquisition

of a ^{207}Pb NMR spectrum required > 2 h, by which time the presumed complexation had already occurred.

DFT calculations indicate that [TFSI] can act as a bidentate ligand, in which the oxygen atoms can coordinate a metal cation.²¹ FTIR spectrometry in the range 1100-1200 cm^{-1} gave tentative evidence for complexation of lead to the TFSI anion. The spectrum of the pure solvent agreed well with that reported.²² Subtraction of the spectrum of pure solvent from that of 50 mM lead bis(trifluoroacetate) in [EMIM][TFSI] showed changes in the S=O stretching frequencies near 1130 cm^{-1} . This is suggestive, but not diagnostic, of complexation between Pb^{2+} cations and TFSI anions (Supplementary Figure 7).

Electrolyses were carried out using graphite and Ebonex cathodes. At graphite, the grey deposit of lead from [EMIM][TFSI] was hard to distinguish from the colour of the cathode. With a Pt counter electrode, a dark, shiny red-yellow deposit of lead oxide, soluble in dilute mineral acid, appeared on the anode. This was not observed at Ti/IrO₂-Sb₂O₅. At Ebonex[®], the product comprised medium-to-small grey powder clusters, which were filtered, washed thoroughly, and dried before weighing. Possible errors include failure to capture the smallest particles, which would cause underestimation of the current efficiency, expressed as $(\text{mol Pb as weighed/mol e}^- \text{ from coulometry}) \times (2 \text{ mol e}^-/1 \text{ mol Pb})$. Powder x-ray diffraction confirmed that the particles were indeed lead, and not a lead oxide; the reference lead powder was obtained by electrochemical deposition of lead from lead nitrate solution (Supplementary Figure 8).

The current efficiency varied with both the water content and the aging of the solutions being electrolyzed (Supplementary Table 2). As with copper, the lead precipitate redissolved when left in contact with the IL after electrolysis, and solubilized completely within 24 h. Some of the smallest particles re-dissolved during the time that it took to filter the larger particles. There is literature precedent for oxidation and solubilization of metallic lead upon contact with oxygenated water through the historic use of lead pipes for drinking water, though this process is very slow.²⁰

Wet [EMIM][TFSI] gave faster electrodeposition but with a higher proportion of very small particles, whose redissolution may account in part for the lower current efficiency under these conditions (Figure 7). Aged solutions also had lower current

efficiency, consistent with complexation between Pb^{2+} and the IL. The specific energy consumption for deposition of lead from a 3 mM solution was slightly higher than from a fresh 20 mM solution, but with significantly lower current efficiency.

3.4 Metal mixtures

A single experiment with simultaneous deposition of silver, copper, and lead from [EMIM][TFSI] showed the expected preferential deposition $\text{Ag} > \text{Cu} > \text{Pb}$ at -1.2 V vs Pt, a potential that was sufficiently cathodic for all three metals to be deposited (**Figure 8**). No attempt was made in this work to achieve electroseparation.

4. Conclusions

In this study, silver, copper, and lead were electrodeposited from a representative IL, [EMIM][TFSI]. Current efficiencies approached 100% under potentiostatic conditions at which water reduction was minimized. Otherwise, the presence of water was not disadvantageous to the process. From the chemical perspective, the electrochemical behavior of silver was the most straight forward: copper showed evidence of the intermediate formation of a Cu(I) species in the IL, and lead showed evidence of complexation to the IL. The deposits of both copper and lead were found to redissolve in contact with the IL ($\text{Pb} > \text{Cu}$), suggesting that solvent [EMIM][TFSI] enhances the rate of the thermodynamically favourable oxidation process.

This work was carried out to offer proof of concept for electrodeposition from wet ionic liquids. Although not examined experimentally in this work, the literature on electrodeposition of metals from anhydrous ILs²³⁻²⁶ suggests that this should be a general phenomenon. More particularly, if this approach should be developed into a technology, we would use cation-selective ILs²⁷⁻³³ which would allow the recovery of specific contaminants from the waste stream. A further constraint is that the IL selected must have negligible solubility in water ([EMIM][TFSI] does not qualify). Otherwise the loss of IL to the aqueous phase during the extraction phase of the process (see Introduction) would make the technology completely uneconomic. No cost estimates for a technology have been made at this time, pending resolution of these critical issues, which must be explored in the next phase of the work.

A further consideration in the context of selective extraction into the IL is the need to discriminate against the uptake of Fe^{3+} , which has been shown by Hatfield et al.^{34,35} to interfere with the electrodeposition of copper (in that example) because of reoxidation of the deposited metal. In other words, Fe^{3+} ($E^\circ = +0.77$ V in aqueous solution) is easily able to oxidize both Cu and Pb metals.

To apply these results towards an eventual technology, we envisage a system in which the aqueous phase is in contact with a membrane-supported IL, with the metal cation(s) transported across the membrane from water into a separate compartment containing the IL. ILs are now available tailored for high affinity for specific metals, offering the option of selective extraction. Electrodeposition could then take place either in a separate chamber with a recycle loop, or even statically on the IL side of the supported membrane. With no requirement to keep the IL anhydrous, the electrodeposition unit could be open to the atmosphere, with facile periodic removal of the cathodes for metal recovery.

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Figure Captions

Figure 1. 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide [EMIM][TFSI].

Figure 2. Multiple cycles of voltammetry for the electrodeposition of Ag^0 at a graphite (pencil lead) microelectrode; continuous: first cycle; dashed: second and third cycle; dotted: ionic liquid alone.

Figure 3. Coulometry plot of the potentiostatic electrolysis of 22.11 mmol/L Ag^+ in [EMIM][TFSI] at -0.19 V vs. Pt reference electrode.

Figure 4. Depletion of silver in potentiostatic electrolysis of silver triflate in ionic liquid using Ebonex[®] cathode (-0.27 V vs. Pt wire reference electrode, diamonds, current efficiency 98% and at -0.40 V vs. Pt wire reference electrode, squares, current efficiency 79%) and in ionic liquid with added water (from 1000 to 10 000 ppm) using Ebonex[®] cathode (at -0.27 V vs. Pt wire reference electrode, triangles, current efficiency 91% at 75 min) compared with depletion of silver in potentiostatic electrolysis of silver nitrate in de-ionized water using Ebonex[®] cathode (at -0.27 V vs. Pt wire reference electrode, circles, current efficiency 85% at 40 min); anode: $\text{Ti}/\text{IrO}_2\text{-Sb}_2\text{O}_5$.

Figure 5. Overlay of the voltammograms of blank [EMIM][TFSI] and a solution of [EMIM][TFSI] containing 16.56 mmol/L of copper triflate using a platinum working electrode with a surface area of 0.0314 cm^2 .

Figure 6. Loss of total copper during potentiostatic electrolysis at high water and oxygen content (not dried and not sparged) at ambient temperature with quantification using FAAS.

Figure 7. Depletion of lead in potentiostatic electrolysis of lead (II) trifluoroacetate, in ionic liquid and 76 μL milliQ water using Ebonex[®] cathode (-1.204 V vs. Pt wire reference electrode) and $\text{Ti}/\text{IrO}_2\text{-Sb}_2\text{O}_5$ anode. Current efficiency: 111% (220 min).

Figure 8. Depletion of lead (diamonds), copper (squares) and silver (triangles) in potentiostatic electrolysis of a mixture of lead (II) trifluoroacetate, copper (II) triflate and silver (I) triflate using Ebonex[®] cathode (-1.204 V vs. Pt wire reference electrode) and Ti/IrO₂-Sb₂O₅ anode. Current efficiency: 26% for Ag (240 min), 29% for Cu (480 min) and 22% for Pb (480 min).

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Initial Ag ⁺ concentration (mM)	Temperature (°C)	Water content (ppm)	Current density (mA cm ⁻²)	Current efficiency (%)
16.03	20	1000	0.050	101
19.77	78	-unknown-	0.139	130
19.77	20	4500	0.120	109
19.77	20	9900	0.179	109

Table 1. Influence of temperature and water content in potentiostatic electrolysis of silver triflate in ionic liquid using graphite cathode (-0.19 V vs. Pt wire reference electrode).

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Figure 1. 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide [EMIM][TFSI]

Figure 2. Multiple cycles of voltammetry for the electrodeposition of Ag^0 at a graphite (pencil lead) microelectrode; continuous: first cycle; dashed: second and third cycle; dotted: ionic liquid alone.

Figure 3. Coulometry plot of the potentiostatic electrolysis of 22.11 mmol/L Ag^+ in [EMIM][TFSI] at -0.19 V vs. Pt reference electrode.

Figure 4. Depletion of silver in potentiostatic electrolysis of silver triflate in ionic liquid using Ebonex[®] cathode (-0.27 V vs. Pt wire reference electrode, diamonds, current efficiency 98% and at -0.40 V vs. Pt wire reference electrode, squares, current efficiency 79%) and in ionic liquid with added water (from 1000 to 10 000 ppm) using Ebonex[®] cathode (at -0.27 V vs. Pt wire reference electrode, triangles, current efficiency 91% at 75 min) compared with depletion of silver in potentiostatic electrolysis of silver nitrate in de-ionized water using Ebonex[®] cathode (at -0.27 V vs. Pt wire reference electrode, circles, current efficiency 85% at 40 min); anode: Ti/IrO₂-Sb₂O₅.

Figure 5. Overlay of the voltammograms of blank [EMIM][TFSI] and a solution of [EMIM][TFSI] containing 16.56 mmol/L of copper triflate using a platinum working electrode with a surface area of 0.0314 cm².

Figure 6. Loss of total copper during potentiostatic electrolysis at high water and oxygen content (not dried and not sparged) at ambient temperature with quantification using FAAS.

Figure 7. Depletion of lead in potentiostatic electrolysis of lead (II) trifluoroacetate, in ionic liquid and 76 μL milliQ water using Ebonex[®] cathode (-1.204 V vs. Pt wire reference electrode) and Ti/IrO₂-Sb₂O₅ anode. Current efficiency: 111% (220 min).

Figure 8. Depletion of lead (diamonds), copper (squares) and silver (triangles) in potentiostatic electrolysis of a mixture of lead (II) trifluoroacetate, copper (II) triflate and silver (I) triflate using Ebonex[®] cathode (-1.204 V vs. Pt wire reference electrode) and Ti/IrO₂-Sb₂O₅ anode. Current efficiency: 26% for Ag (240 min), 29% for Cu (480 min) and 22% for Pb (480 min).