



Electrodeposition of transition metals from highly concentrated solutions of ionic liquids



Stefano Caporali^{a,c,*}, Patrick Marcantelli^a, Cinzia Chiappe^b, Christian Silvio Pomelli^b

^a Dipartimento di Chimica, Università di Firenze, via della Lastruccia 3-13, 50019 Sesto Fiorentino (FI), Italy

^b Dipartimento di Farmacia, Università di Pisa, Via Bonanno 33, 56126 Pisa, Italy

^c Consorzio INSTM, via Giusti 9, 50123 Firenze, Italy

ARTICLE INFO

Article history:

Received 24 July 2014

Accepted in revised form 14 January 2015

Available online 23 January 2015

Keywords:

Ionic liquids

Electrodeposition

Nucleation mechanism

SEM-EDX

Coatings

ABSTRACT

Five different ionic liquids (ILs), obtained by dissolving bistriflimide salts of Ag, Cu, Co, Ni and zinc in 1-butyl-3-methylimidazolium bistriflimide ([bmim][Tf₂N]) were synthesized and electrochemically characterized by means of cyclic voltammetry and chronoamperometry. Silver-bearing IL represents the simplest electrochemical system since silver is present as uncoordinated or weakly coordinated Ag⁺ ions. Homogeneous and crack-free silver coatings were potentiostatically obtained from this ionic liquid and the nucleation and growth mechanism were determined. In contrast, copper-cobalt- and zinc-bearing systems were highly moisture sensitive. The presence of large amounts of water changes the nature of the coordination species present in the solution, facilitating the electroreduction of the metal complexes. However, in hydrated solutions we observe simultaneous hydrogen evolution, which impairs the electrochemical investigation of the metal nucleation and growth mechanism. Nevertheless, metallic deposits were obtained and their morphologies investigated as a function of the deposition potential and water content. Conversely, within the investigated electrochemical window, the Ni-bearing IL does not form electroactive species.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Ionic liquids (ILs) are solvents constituted entirely by ions that have been demonstrated to be an interesting alternative to aqueous baths (for example, with respect to cyanide based baths) for metal electrodeposition [1,2] due to their intrinsic ionic conductivity, almost negligible vapor pressure, wide electrochemical window and low toxicity. Consequently, ionic liquids represent the ideal solvent for the electrodeposition of metals that cannot be deposited from aqueous solutions (e.g. Al, Mg, Nb, Ta, Ti and rare earths). Moreover, such solvents also offer several advantages for the electrodeposition of metals that are currently electrodeposited from aqueous solutions, e.g. Ag, Au, Cu Co, etc. ILs can be used with substrates composed of materials that are passivated in the presence of water; they allow the deposition of alloys with composition not achievable from aqueous media and nanostructured metallic deposits can be obtained more easily [3–10]. However, electrodeposition from ILs also has some limitations. The principal problem is that many metal salts are scarcely soluble in ILs. The low concentration of metal ions coupled with the relatively high

viscosity of the medium strongly limits the deposition rate achievable with these solvents that, in some cases, impairs their use for large scale applications. It has been recently observed that high concentrations of metal salts can be obtained by directly dissolving the metal salts in ILs having the same anion [11]. This approach allows the preparation of highly concentrated solutions of metal ions in ILs, from which, it is possible to electrodeposit metals at room temperature at a sufficiently high rate to make it a practically viable process.

In this communication we report an investigation of metal electrodeposition from five different highly concentrated ILs solutions obtained by dissolving metal bistriflimide salts in 1-butyl-3-methylimidazolium bistriflimide, [bmim][Tf₂N]. In some favourable cases the nucleation and growth mechanism have been also determined to gain insight into the morphology and structure of the deposits. Furthermore, in view of the clear potential for applications in the galvanic industry, the effects of current overpotentials as well as water uptake from the atmosphere have been evaluated and compared.

2. Experimental details

The ionic liquid mixtures were prepared by dissolving the required amount of metal Tf₂N salts in 1-butyl-3-methylimidazolium bistriflimide ([bmim][Tf₂N]) supplied by Solvionic and used as received. All the solutions were prepared maintaining constant the metal/ionic liquid molar

* Corresponding author at: Dipartimento di Chimica, Università di Firenze, via della Lastruccia 3-13, 50019 Sesto Fiorentino (FI), Italy. Tel.: +39 055 457 3119; fax: +39 055 457 3120.

E-mail address: stefano.caporali@unifi.it (S. Caporali).

ratio at 1:2. The electrochemical experiments were conducted using a PAR model 2273 potentiostat controlled by PowerSuite 2.58 software. A classical three-electrode setup was employed using a glassy carbon (GC) electrode (Metrohm mod 628, \varnothing 3 mm), a platinum grid (Goodfellow, 99.99, 0.25 mm mesh) and a gold wire (Goodfellow, 99.99, \varnothing 1 mm) as working, counter and quasi reference (QRE) electrodes, respectively. Before use, the metallic electrodes were cleaned by immersion in nitric acid 46%w for several hours, and then rinsed with distilled water and air-dried. The stability of QRE was checked with respect to the Ferrocene/Ferrocenium redox couple (5 mM solution) in aerated (“wet”) $\text{Ni}(\text{TF}_2\text{N})_2$: $[\text{bmim}][\text{TF}_2\text{N}]$ 1:2 molar by means of cyclic voltammetry (CV). The data displayed in Fig. 1 refer to the first, 50th and 100th consecutive cycles, and the 100th cycle of a second series recorded 12 h later (100th”). The voltammograms are characterized by an almost reversible one electron oxidation process and are comparable with the literature data for this redox couple [12,13]. The maximum anodic current (see inset Fig. 1) displays a slight shift as a function of time. Nevertheless, it was found to be stable enough (± 0.02 V) to allow the use of gold as quasi reference electrode (QRE). Even though slightly larger potential shifts cannot be excluded in the other ionic liquid systems a larger confidence value (± 0.05 V) is considered and all the potential values are referred to the Au. The GC electrode was polished with alumina (\varnothing 0.25 μm) and then rinsed several times with ethanol and distilled water. Pure (99.9%) silver wires (Goodfellow) were used as substrates for the morphological investigation of the deposits. In order to clean the silver surface before the electrodeposition, the wires were pickled in ammonia/ H_2O_2 for at least 5 min and then rinsed with distilled water and finally air-dried. All the electrochemical experiments were conducted in an in-house built small cell (0.5 ml volume) sealed for “dry” ILs and in an open vessel for “wet” ILs. Wet ILs were obtained by dissolving the metal salts (in some cases hydrated) in moisture saturated ILs, while the respective dry forms were obtained by drying overnight the mixture in a schlenk apparatus under vacuum. In order to avoid moisture uptake during the experiments, the small cell was kept under slight overpressure by a laminar nitrogen flush. Before and after the experiments the amount of water dissolved in the ILs was determined via Karl-Fisher titration (Hydranal, Sigma Aldrich) for both “dry” and “wet” system. The results of this analysis are summarized in Table 1.

Finally, the deposits obtained were rinsed with distilled water and acetone, and their morphology and chemical composition were investigated using a Hitachi 2300 SEM microscope coupled with an Energy Dispersive Microanalysis (EDX) system (NORAN NSS 300). The acceleration voltage used was 20 kV and the take off angle was 34.7° . Statistically representative quantitative analyses were achieved averaging the EDX results of four different spots, each of about 0.12 mm^2 , randomly

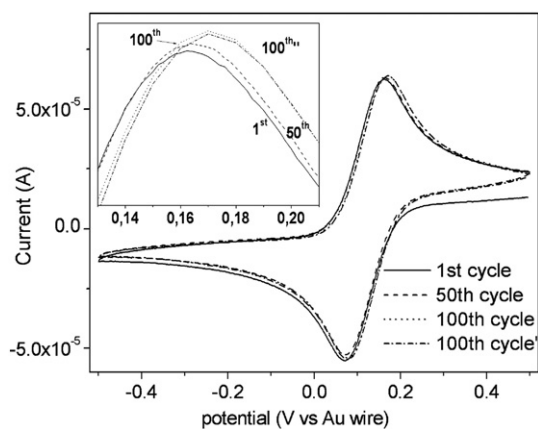


Fig. 1. The first, 50th and 100th cyclic voltammograms obtained on GC electrode in aerated $\text{Ni}(\text{TF}_2\text{N})_2$ $[\text{bmim}][\text{TF}_2\text{N}]$ 1:2 molar ratio containing 5 mM of ferrocene. Sweep rate 100 mV s^{-1} . The 100th cycle of a second series recorded 12 h later is also displayed.

Table 1

Moisture content as determined by Karl-Fisher titration in “dry” and “wet” ILs.

	“Dry” (ppm)	“Wet” (ppm)
$[\text{bmim}][\text{TF}_2\text{N}]$	300 ± 20	6000 ± 200
$[\text{bmim}][\text{TF}_2\text{N}] + \text{Ag}(\text{TF}_2\text{N})$	450 ± 20	9000 ± 300
$[\text{bmim}][\text{TF}_2\text{N}] + \text{Cu}(\text{TF}_2\text{N})_2$	$30,000 \pm 1000$	$50,000 \pm 5000$
$[\text{bmim}][\text{TF}_2\text{N}] + \text{Co}(\text{TF}_2\text{N})_2$	$14,000 \pm 500$	$80,000 \pm 5000$
$[\text{bmim}][\text{TF}_2\text{N}] + \text{Ni}(\text{TF}_2\text{N})_2$	$10,000 \pm 500$	$33,000 \pm 1000$
$[\text{bmim}][\text{TF}_2\text{N}] + \text{Zn}(\text{TF}_2\text{N})_2$	900 ± 100	$11,000 \pm 1000$

chosen on the surfaces of every sample. The peaks acquired were fitted by Gaussian curves applying the ZAF correction method.

3. Results and discussion

3.1. Silver

A typical cyclic voltammogram of AgTF_2N in $[\text{bmim}][\text{TF}_2\text{N}]$ for a 1:2 molar ratio solution recorded using a GC electrode is displayed in Fig. 2.

The voltammogram was obtained scanning the potential from +1.0 V to -1.5 V prior to switching the scan direction. The shape of the voltammogram is very similar to that obtained in diluted IL solutions [3,14–18] and is consistent with the silver deposition and stripping from an electrode surface. Significant differences were observed between the “dry” (H_2O 450 ± 20 ppm, see Table 1) and “wet” or “moisture saturated” (H_2O 9000 ± 300 ppm, see Table 1) systems. It is clearly evident that the electroreduction of Ag^+ is considerably favoured in the “wet” system, starting at about -0.30 V, whereas a much more negative value (-0.70 V) is required in the case of the “dry” system. In both cases the reverse sweep shows a current crossover and the reduction peak is dependent on the scan rate; increasing the scan rate, the peak value moves towards more negative values (Fig. 3).

Both of these observations are indicative that silver electroreduction follows a nucleation-growth mechanism [19–24]. As observed in other types of ionic liquids [24], in the wet system, the overpotential required to start the electroreduction is lower and the maximum current value is higher (see Fig. 3). This phenomenon can be partially attributed to the enhanced Ag^+ ion mobility due to the decreased viscosity of the electrochemical medium resulting from the presence of a larger amount of water. The plot of deposition currents as a function of the square root of the scan rate (see Fig. 3) displays linear trends compatible with a diffusion controlled process, for which the slope is proportional to the diffusion constant. It is clear as the electroactive species present in the “wet” system is more mobile than that in the “dry” one.

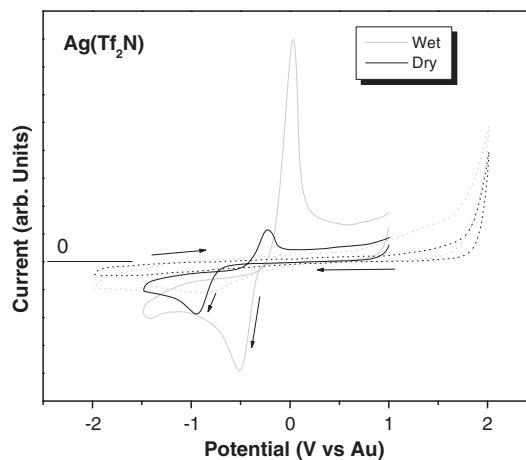


Fig. 2. Cyclic voltammograms of AgTF_2N on a GC electrode in “wet” and “dry” $[\text{bmim}][\text{TF}_2\text{N}]$ for a 1:2 molar ratio solution. Dotted lines represent the curve of “wet” and “dry” $[\text{bmim}][\text{TF}_2\text{N}]$ without silver. Sweep rate 100 mV s^{-1} .

Download English Version:

<https://daneshyari.com/en/article/1657253>

Download Persian Version:

<https://daneshyari.com/article/1657253>

[Daneshyari.com](https://daneshyari.com)