Contents lists available at ScienceDirect

## Electrochimica Acta



journal homepage: www.elsevier.com/locate/electacta

# Electrochemical deposition of silver from 1-ethyl-3-methylimidazolium trifluoromethanesulfonate

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#### ARTICLE INFO

Article history: Received 8 December 2010 Received in revised form 15 April 2011 Accepted 18 April 2011 Available online 23 April 2011

Keywords: Ag electrodeposition [EMIm][TfO] EQCM Physicochemical properties

#### ABSTRACT

Silver was successfully electrodeposited from the ionic liquid 1-ethyl-3-methylimidazolium trifluoromethanesulfonate ([EMIm][TfO]) containing silver ions in various concentrations. The electrochemical windows of the electrolytes were determined by cyclic voltammetry. Moreover, the conductivity and the viscosity–density product were studied with electrochemical impedance spectroscopy (EIS) and electrochemical quartz crystal microbalance (EQCM). Potentiodynamic and potentiostatic depositions were performed at different temperatures. The morphology of the deposited Ag layers depends on temperature and concentration. Thus, by choosing the right experimental conditions one can optimize the properties of the deposited layers. The thus obtained layers can be used in different surface finishing processes, such as in decorative plating, catalysis or for electrical contacts.

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#### 1. Introduction

Thin silver layers find various applications because of their special properties, such as good corrosion resistance, shiny surface (decorative purposes), antibacterial property and high electrical conductivity [1,2].

Silver electrodeposition from ionic liquids (ILs) presents an environmentally friendly alternative to the classical aqueous cyanide baths [1] or plating baths containing many organic and inorganic additives for suppressing the dendritic growth [3].

A recently published review [4] discusses some of the techniques and the ILs used so far for the electrodeposition of Ag from non-aqueous media. Further reports on Ag deposition from various ILs, with different Ag precursors as well as the deposit morphologies (nanowires, nanoparticles, thin layers) can be found in the literature [5–19].

In a previous study, Zein El Abedin and Endres studied the electrodeposition of thin Ag layers and Ag nanowires from a solution of AgTfO in [EMIm][TfO] onto Au, glassy carbon, and Au substrates evaporated on a polycarbonate membrane [6]. The deposits were prepared by cyclic voltammetry (CV) and chronoamperometric techniques, and they were characterized by SEM and XRD. The EQCM (electrochemical quartz crystal microbalance) technique was used by Serizawa et al. [13] and by Abbot et al. [16] when electrodepositing thin Ag layers on Au [13] or

Pt, Cu and Au substrates [16], in order to monitor *in situ* the electrodeposition process. The solutions used in these studies were silver bis(trifluoromethylsulfonyl)amide (AgTFSA) in 1-butyl-1methylpyrrolidinium bis(trifluoromethylsulfonyl)amide in [13] and AgNO<sub>3</sub>, AgCl, AgSO<sub>4</sub>, and Ag(CH<sub>3</sub>COO) in choline chloride based ILs (with ethylene glycol or with urea) in [16].

In the present study we investigated the electrodeposition of Ag from 1-ethyl-3-methylimidazolium trifluoromethanesulfonate ([EMIm][TfO]) with different concentrations of Ag(I) ions, using in situ microgravimetry (electrochemical quartz crystal microbalance, EQCM). Our study extends previous reports [6,13,16] that also applied the EQCM technique or that used [EMIm][TfO] containing AgTfO for Ag electrodeposition. In our case, all the measurements were performed in a controlled atmosphere (inside a glove box), while previously reported results were obtained in ambient atmosphere, under 50% humidity [6]. It is well known that even small traces of moisture and oxygen can have a strong influence of the electrochemical behaviour of an IL. We also investigated other combinations of IL and silver precursor by EQCM than in [13,16]. The comparison of the results obtained in this study with the previously published data should give a deeper understanding of the silver deposition process in ILs.

Although the electrodeposition of Ag from ILs has been reported before by other groups, very few attempts have been done in the literature to correlate the physicochemical properties of the plating solutions with the properties of the deposited layers. With this study we intended to fill this gap that exists in the literature: thus, we determined the electrical conductivity and the viscosity-density product of the electrolytes and we investigated



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<sup>0013-4686/\$ -</sup> see front matter © 2011 Elsevier Ltd. All rights reserved. doi:10.1016/j.electacta.2011.04.060



Fig. 1. Schematic representation of the set-up used for Ag dissolution.

the effects produced by the temperature and the concentration of Ag(I) on the physical properties of the electrolytes and on the electrodeposited layers. Moreover, using the EQCM technique, we studied *in situ* the electrodeposition process and we got information on the current efficiency and on the deposited masses, beside the viscosity–density product of the electrolytes.

#### 2. Experimental

#### 2.1. Preparation of AgTfO in [EMIm][TfO]

Several [EMIm][TfO] samples with different Ag(I) concentrations were prepared for the electrodeposition experiments. A stock solution was obtained by anodic dissolution of a Ag metal foil in the IL. This stock solution was then diluted to prepare the desired Ag(I) concentrations. [EMIm][TfO], purchased from Iolitec with a purity of 99 wt.%, a water content below 10 mg/kg, and an halide content below 100 mg/kg, was always handled under an argon atmosphere in a glove box. Two beakers connected via a U-shaped glass tube, which served as a salt bridge, were used to prepare the solutions (Fig. 1). One beaker contained the working electrode, which was an electrochemically activated Ag plate (99.995 wt.%, thickness 0.5 mm, approximate area of  $1 \text{ cm}^2$  per side), and the reference electrode (Ag wire, 99.995 wt.%, 0.25 mm diameter). The second beaker housed the counter electrode, which was again a silver plate similar to the working electrode. All Ag electrodes were electrochemically activated prior to the experiments by anodic dissolution (at 800 µA for ca. 10 min) to remove impurities from the surface. These solutions, in which the electrodes were dissolved anodically for cleaning, were disposed afterwards. Other cleaning procedures, such as polishing the electrodes with abrasive paper and a subsequent rinsing with doubly distilled water, ethanol, and acetone led to unsatisfactory results. Such pre-treatments introduced more impurities than they removed.

The setup for the dissolution experiment is presented in Fig. 1. On the left hand side the cation of the IL is reduced, forming radical intermediate products, which can react further to unknown coloured decomposition products. If these products would reach the beaker on the right side, the Ag(I)/[EMIm][TfO] solution would be contaminated. Hence, the reaction must be stopped before. The pure product IL solution and the contaminated IL have different shadings. The opening of the salt bridge, marked by an asterisk (\*), was connected to a syringe via a small flexible tube, with which a small vacuum slight underpressure was applied to fill the salt bridge with the IL. The dissolution of Ag was carried out galvanostatically. Therefore, the silver content in [EMIm][TfO] can be directly calculated using Faraday's law. Another method to assess the silver content was the determination of the mass loss of the silver electrode. In the following all the silver concentration will be given in terms of molality (mmol Ag(I) per kg IL). The stock solution was diluted to a concentration of 202.8 mmol/kg Ag(I). This solution was further diluted to 101.4 mmol/kg, 50.7 mmol/kg, and 25.3 mmol/kg. The underlying assumption in calculating the silver content was that no silver ions were lost due to cation migration towards the cathode. Since all diluted solutions were prepared from the same stock solution, the concentration ratios are correct even if the absolute concentration could be slightly different.

The water content of the ILs was determined by Karl Fisher titration, with a KF Coulometer from Metrohm, model 831. The accuracy of this device is  $\pm 5$  mg/kg.

#### 2.2. Conductivity of the electrolytes

An immersion conductivity cell from Metrohm (theoretical cell constant  $0.80 \, \text{cm}^{-1}$ ) was used to determine the conductivity of the ILs. The conductivity cell consisted of two Pt electrodes embedded in glass. The electrode fitted neatly into a temperature-controlled double jacket glass cell. The exact value of the cell constant was obtained from measurements at 25 °C in 0.1 M KCl Centripur electrolyte from Merck (specific conductivity, 12.8 mS/cm). These calibration measurements were the only ones performed outside the glove box.

The conductivity of the ILs was determined in the temperature range between 20 °C and 100 °C in the double jacket glass cell within an Ar filled glove box (MBraun, Germany). The temperature of the IL was measured with a thermocouple with an accuracy of  $\pm 0.1$  °C. The oxygen and moisture contents inside the glove box were always below 2.0 cm<sup>3</sup>/m<sup>3</sup>.

The impedance of the conductivity cell was determined with an IM6 device from Zahner Elektrik (Germany), in the frequency range from 10 kHz down to 1 Hz, at an amplitude of 50 mV.

#### 2.3. Electrodeposition of silver

The electrodeposition experiments were performed in a three electrode arrangement in a PTFE home-made electrochemical cell. The working electrode was an Au layer evaporated on a quartz crystal, the counter electrode was a Pt wire and the reference electrode was an Ag wire. The active area of the working electrode was ca.  $0.22 \text{ cm}^2$ . The quartz crystals with a resonance frequency of 10 MHz (AT cut) with Au electrodes on both sides were purchased from Vectron International, Germany. The counter and the reference electrodes were polished with abrasive paper, washed with doubly distilled water and dried under a N<sub>2</sub> flow. Afterwards, the counter electrode was heated in a butane flame to red glow.

A potentiostat from EG&G (Model 263) was used for electrochemical measurements. A network analyser (Agilent E5100) was used to monitor the shift of the resonance frequency and the dissipated energy of the quartz crystal. The latter was determined via the full width at half maximum of the resonance curve. From the shift of the resonance frequency one can calculate the deposited mass using the Sauerbrey equation [20].

The electrodeposition measurements were performed at different temperatures, from room temperature up to 100 °C. The temperature inside the electrochemical cell was controlled with an accuracy of 1 °C by a Wema temperature controller (Lüdenscheid, Germany). All electrochemical measurements were performed inside an Ar filled glove box.

The morphology of the deposited layers was studied by scanning electron microscopy (SEM model DSM 982 Gemini from Zeiss Oberkochen, Germany). Information on the composition of the Ag layers was obtained with an energy dispersive X-ray detector (EDX model Voyager III 3200 from SUS Pioneer), which was incorporated in the SEM device.

#### 3. Results and discussion

#### 3.1. Characterization of the pure ionic liquid

The ILs can contain traces of water that can strongly affect their physicochemical properties or their electrochemical window [21–24]. Usually, the conductivity of an IL increases and its viscosity decreases in the presence of water impurities [22,24], while the electrochemical window shrinks substantially [23,24]. The manifold effects of water on the conductivity and on the viscosity are often ignored. This is one of the reasons why data reported in the literature can differ significantly, especially when conductivities and viscosities of ILs are concerned [22 and references within].

Beside water impurities, further organic or inorganic impurities can be found in ILs, often remains from the synthesis [25]. Special attention was given so far to lithium impurities [25]. The group of Endres has impressively shown that with the *in situ*-STM one can detect the UPD of Li and that this can be mistaken for the deposition of another metal. Halide impurities (e.g., chloride) can generate unexpected side reactions at the counter electrode [25]. Moreover, it was shown that small amounts of chloride ions decrease the conductivity of the ILs [26].

In our case, two different production lots of [EMIm][TfO] were investigated (of 98 wt.% and 99 wt.% purity). The water content of the first lot was initially ca. 247 mg/kg, while the other lot contained initially just 2.1 mg/kg of water. Both types of ILs were dried prior to the experiments for 20 h under vacuum at 80 °C. The water content of the first lot decreased to 3 mg/kg after ca. 200 min and to 2.1 mg/kg after 20 h, while the water content of the second lot reached 1.7 mg/kg after 20 h of drying. Thus, with sufficient drying time one can reach practically the same water content in all lots, independent of their initial water content or of the presence of other impurities. The latter reveal themselves as a hue of the IL, ranging from light yellowish to dark brownish. It is difficult to identify the organic impurities, and this still remains an unresolved research issue. However, it seems that a minimum amount of water (ca. 2 mg/kg) has to be accepted with the drying procedure employed here. Furthermore, it is difficult to assess the influence of heating under vacuum on the organic impurities.

The electrochemical windows of the two dried ILs were approximately 5.4 V at 25 °C (Fig. 2, black line). The electrochemical window was determined by cyclic voltammetry at a scan rate of  $20 \text{ mV s}^{-1}$  with Pt plates and wires as working, counter and reference electrodes. The electrochemical window was considered to be the potential window defined by the two intersection points between the 'zero' line (which was defined by the potentials around the open circuit potential value) and the tangents to the reduction and respectively, to the oxidation potential limits, where the current increased strongly and continuously, indicating the decomposition of the ILs.

The presence of chloride impurities in the neat ILs can be crucial in our case (formation of AgCl). The precipitation of AgCl would lower the concentration of silver ions in our electrolytes. The EDX (energy dispersive X-ray) spectroscopic analysis of preceding experiments hinted that the precipitation of AgCl leads to an even larger loss of Ag(I) due to adsorption of Ag(I) at the surface of the AgCl precipitate, or to co-precipitation of Ag(I), or to inclusion of Ag(I) in the pores of the AgCl precipitate formed. Therefore, we checked for the presence of chloride in the neat ILs by cyclic voltammetry. Small amounts of NaCl were added to the neat ILs



**Fig. 2.** Cyclic voltammograms (20 mV s<sup>-1</sup>) of the neat IL [EMIm][Tf0] (black, continuous line) and of the IL spiked with a very small amount of NaCl (red, dashed line). Working, reference and counter electrodes were Pt plates and wires in these experiments. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)



**Fig. 3.** Specific electrical conductivity of IL containing different amounts of Ag(I) as a function of temperature. (-■-) neat [EMIm][TfO], (-•-) 202.8 mmol/kg Ag(I), (-▲-) 101.4 mmol/kg Ag(I), (-▼-) 50.7 mmol/kg Ag(I) (-◀-) 25.3 mmol/kg Ag(I). Inset in the figure shows the electrical conductivity of the neat [EMIm][TfO].

and the CVs of the spiked ILs were compared to those of the neat IL. We found new peaks in the spiked IL, which were attributed to the added NaCl (Fig. 2). As these peaks were absent in the neat IL we conclude that chlorine content of ILs is very low.

#### 3.2. Physicochemical properties of the IL based silver electrolytes

#### 3.2.1. Ionic conductivity

The ionic conductivity of the ILs was extracted from the impedance spectra (raw data not shown). The spectra were fitted with the commercial software package Origin. The equivalent circuit consisted of a series combination of a capacitance and a resistor. The capacitance reflects the double layers of the two Pt electrodes. The specific conductivity of the ILs can then be calculated from the fit value of the resistor, *R*, and the cell constant, *C*, according to Eq. (1) [26].

$$\sigma = \frac{1}{R}C\tag{1}$$

The conductivities of the pure IL (inset in Fig. 3) and the electrolytes containing various concentrations of Ag(I) (Fig. 3), were determined in the temperature range from  $10 \,^{\circ}$ C to  $100 \,^{\circ}$ C. The specific

conductivity increases more than 8 times at 100 °C compared to 10 °C (Fig. 3). Higher conductivities were found for the ILs containing Ag ions. The IL with 25.3 mmol/kg Ag(I) had the highest conductivity in the entire temperature range investigated here. Above this concentration of Ag the conductivity decreases with increasing Ag concentration (Fig. 3). The conductivity of the solution with 202.8 mmol/kg Ag(I) was just slightly higher than that of the pure IL.

The diameter of the silver ion ranges between 134 pm and 256 pm for coordination numbers between 2 and 8 [27]. This leads to ion volumes of  $1.26 \times 10^{-3}$  nm<sup>3</sup> and  $8.78 \times 10^{-3}$  nm<sup>3</sup>, respectively. The ion volume of the EMIm<sup>+</sup> ion is 0.156 nm<sup>3</sup> [28]. Due to its smaller size one would expect that the silver ion has a much higher mobility compared to the imidazolium cation, leading to an increased conductivity with increasing concentration. However, this is only the case for the sample with a concentration of 25.3 mmol/kg. If the concentration of Ag ions in the IL is higher than this value, it seems that the mobility of the ions is hindered. This fact can be due to an association of the ions [26].

#### 3.2.2. Viscosity-density product

Based on the Stokes–Einstein relation,  $D_i = RT/(6\pi\mu r_i)$  (*R* is the ideal gas constant, *T* the temperature,  $D_i$  the diffusion coefficient,  $\mu$  the dynamic viscosity,  $r_i$  the radius of the solvated ion) and the Nernst–Einstein relation,  $D_i = RT\lambda_i/(|z_i|F^2)$  ( $\lambda_i$  is the ionic equivalent conductance,  $z_i$  the number of proton charges carried by an ion, *F* the Faraday constant), one can obtain a relationship between the viscosity and conductivity. This approach works well for diluted aqueous solutions [29]. Generally, the conductivity is proportional to the diffusion coefficient and inversely proportional to the viscosity, which means that if the conductivity of the liquids increases with the temperature, their viscosity should decrease.

However, it seems that this approach cannot be applied to ILs [30]. Some researchers argue that the charge transport in ILs cannot be described properly by the Stokes–Einstein relationship [31]. Other groups showed that in some cases the Stokes–Einstein equation can be used for predicting the conductivity, or at least the order of magnitude of the conductivity, for room temperature ILs [32,33 and references within]. In molten salts (such as ILs) fluctuating empty spaces exist, due to thermal motions [32–34 and references within]. This model based on the conventional hole theory was applied to estimate the conductivities and viscosities of several ILs at ambient temperature [32,33].

Due to the lack of suitable theoretical models it is difficult to predict how the conductivity or the viscosity of ILs varies with the temperature [26]. Some authors use the Walden product, i.e., the product of the molar conductivity and the dynamic viscosity, to describe the properties of the ILs [26]. Other groups showed that the Walden product does not always describe properly the physicochemical properties of ILs [35]. Therefore, we decided to characterize separately the viscosity and conductivity of our ILs.

Conventional viscosimeters need a relatively large sample volume. We decided to determine the viscosity–density product of our ILs with the EQCM technique. In this case we can work with relatively small sample volumes (ca. 1 ml).

Kanazawa and Gordon [36] showed that the shift of the resonance frequency of a quartz crystal is proportional to the square root of the viscosity-density product of the adjacent liquid layer, Eq. (2).

$$\Delta f = -f_0^{3/2} \sqrt{\frac{n\rho\eta}{\pi\rho_q\mu_q}} \tag{2}$$

In Eq. (2) *n* is the overtone number (*n*=1,3,5,...),  $\rho$  and  $\eta$  are the density and the viscosity of the liquid, and  $\rho_q$  and  $\mu_q$  are the density and shear modulus of the quartz crystal. It has been shown that Eq.

**Fig. 4.** Viscosity-density product of the IL as a function of temperature.  $(-\blacksquare-)$  202.8 mmol/kg,  $(-\bullet-)$  101.4 mmol/kg,  $(-\bullet-)$  50.7 mmol/kg Ag(1),  $(-\bullet-)$  25.3 mmol/kg Ag(1),  $(-\bullet-)$  25.3 mmol/kg Ag(1),  $(-\bullet-)$  neat [EMIm][TfO].

(2) can be successfully applied to determine the viscosity of a series of ILs [37–39].

The product  $\rho \cdot \eta$  of our electrolytes decreased with increasing temperature (Fig. 4). At a given temperature, the product  $\rho \cdot \eta$ increases with increasing concentration of Ag ions in the ILs in the range from 50.7 mmol/kg to 202.8 mmol/kg. The product  $\rho \eta$  was lowest at a relatively low concentration of Ag(I) (25.3 mmol/kg), at room temperature, and it was the highest for the most concentrated solution (202.8 mmol/kg) in the whole temperature range investigated here. The values for the product  $\rho \cdot \eta$  obtained at the lowest concentration of Ag(I) (25.3 mmol/kg) at temperatures higher than 20 °C were practically the same as those obtained for the solution containing 50.7 mmol/kg Ag(I). For the neat [EMIm][TfO] IL, the product  $\rho \cdot \eta$  was almost similar to that obtained in a 101.4 mmol/kg Ag(I) for the temperature range from 20 °C to 100 °C. Thus, adding small amounts of Ag(I) to the IL induced a decrease of the product  $\rho \cdot \eta$  for these solutions when compared to the neat IL, while further increase of the Ag(I) concentration will induce higher  $\rho \cdot \eta$  values. These results show a nice correlation between the conductivities and the  $\rho \cdot \eta$  results of the ILs used, within the temperature range from 20 °C to 100 °C. Thus, for the solution that presented a lower conductivity (e.g., 202.8 mmol/kg Ag(I)) we obtained the highest  $\rho \cdot \eta$  values, while for a solution that presented a high conductivity (e.g., 25.3 mmol/kg Ag(I)), we obtained low  $\rho \cdot \eta$  values.

#### 3.3. Electrochemical characterization

#### 3.3.1. Cyclic voltammetry

Cyclic voltammograms started at the open circuit potential (OCP) towards the cathodic regime at a scan rate of  $20 \text{ mV s}^{-1}$ , and were recorded in a temperature range from  $20 \degree$ C to  $100 \degree$ C. Simultaneously to the CVs experiments, the EQCM data were acquired. Thus, we could follow *in situ* the deposition and the dissolution process in the four Ag containing ILs.

A typical CV is shown in Fig. 5. The cathodic wave can be associated with the deposition of Ag, while the anodic peak is due to Ag dissolution. No crossover between the cathodic and anodic branches was found. In other literature reports for other ILs systems at temperature below 200 °C a crossover between the cathodic and anodic branches was observed [10,17,18]. The peaks are relatively broad in the ILs with higher Ag(I) concentrations (202.8 mmol/kg, Fig. 5A). Sharp peaks were obtained usually in the anodic potential regime in the ILs having lower Ag concentrations (25.3 mmol/kg), while the cathodic peaks were typically broader (Fig. 5B).





**Fig. 5.** Cyclic voltammograms  $(20 \text{ mV s}^{-1})$  at different temperatures in a 202.8 mmol/kg Ag(1) in [EMIm][TfO] (A) and in 25.3 mmol/kg Ag(1) in [EMIm][TfO] (B). Black, continuous line shows the measurements at 20 °C, red dashed line is for 50 °C, green dotted line is for 80 °C and blue dashed-dot is for 100 °C. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)

For a given scan rate, the cathodic peak shifted towards more anodic potential values, while the anodic peak shifted towards more cathodic potential values with increasing temperature. The spacing between the anodic and cathodic peak increases with increasing scan rate. This indicates that the electrode reaction follows quasireversible kinetics. The shift of the peak potential results from the limiting charge transfer rate, which occurs together with the mass transport of the electroactive species. The latter is favoured by the decrease of the viscosity and the increase of the conductivity of the electrolytes with increasing temperature. As expected, higher currents were usually obtained at higher temperatures.

One can determine the current efficiency from the EQCM data. By multiplying the slope of a mass vs. charge plot with the Faraday constant, one can obtain the apparent molar mass of the reacting species. In our case (Ag deposition), this apparent molar mass should be 107.9 g/mol. The ratio between the apparent molar mass calculated from the EQCM data and the theoretical molar mass of Ag will give the current efficiency of the deposition process.

The apparent molar mass calculated from the EQCM data was often lower than the theoretical value. Thus, the current efficiencies of the Ag(I) electroreduction process varied generally between 80 and 100% in the potential ranges and at temperatures

Table 1	1
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Correlation between the current efficiencies calculated from the EQCM data and the potential applied in the potentiodynamic experiments at  $20 \, mV \, s^{-1}$  in Ag(1)/[EMIm][TfO] solutions.

Ag concentration (mmol/kg)	<i>T</i> (K)	Potential range (V)	Current efficiency (%)
202.8	203 15	0.18 to 0.26	51
202.0	233.13	-0.18  to  -0.20	96
202.8	373 15	-0.57 to -0.55	82
202.0	525.15	-0.1  to  -0.15	100
202.8	353 15	-0.2 to -0.0	100
202.0	555.15	-0.05 to -0.15	00
202.8	373 15	-0.2 to -0.0	100
202.0	575.15	-0.07 to -0.1	03
101 /	203 15	-0.38  to  -0.0	63
101.4	293.15	-0.08 to -0.13	100
101 /	373 15	-0.2  to  -0.0	70
101.4	525.15	-0.1  to  -0.15	90
101 4	252 15	-0.2 10 - 0.0	90
101.4	555.15	-0.0910 - 0.10	92
101 4	272 15	-0.4 10 - 0.0	05
101.4	575.15	-0.08 to -0.1	9J 74
50.7	203 15	-0.3 to -0.0	74
50.7	233.13	-0.00 to -0.13	100
50.7	373 15	-0.2 to -0.0	82
50.7	525.15	-0.04 to -0.00	03
50.7	353 15	-0.01  to  -0.06	78
50.7	555.15	-0.04 to -0.00	01
50.7	272 15	-0.17  to  -0.06	20
30.7	575.15	-0.02  to  -0.00	02
25.3	203 15	-0.25 to $-0.0$	52 77
23,3	233.13	-0.01 to -0.05	08
25.3	323 15	-0.2 to $-0.3$	76
23,3	525.15	$-0.00\ to -0.5$	84
25.3	353 15	-0.5  to  -0.01	80
23,3	555,15	-0.45 to $-0.6$	88
25.3	373 15	-0.06 to $-0.09$	82
23,3	575,15	-0.00 to -0.09	93
		-0.1010-0.20	55

investigated here (Table 1). This indicates that other processes occur in parallel to the Ag deposition. These processes could be a partial decomposition of the cation of the IL (which could be electrochemically induced), or/and the generation of another species that can be adsorbed and desorbed very easily from the working electrode surface, or/and the formation of a soluble species (see also the EDX results, in Section 3.4).

A shoulder appears in the cathodic scan of the cyclic voltammograms at ca. -0.3 V in the ILs containing a low amount of Ag(I) (Fig. 5B). This shoulder is more clearly visible when the reduction of Ag(I) in [EMIm][TfO] was carried out at  $100 \,^\circ$ C (Fig. 5B). The apparent molar masses associated with that second cathodic wave were higher than those corresponding to the first peak. A possible explanation is that two silver species are present in the electrolytes, which are reduced at different potentials. However, the exact mechanism of the reduction of these Ag species is not clear yet. The EQCM data indicates however that the reduction of the silver species that occurs at more anodic potential is a process with a lower current efficiency than the reduction of the silver species that occurs more cathodically.

A typical mass vs. charge diagram is shown in Fig. 6. With increasing temperature, more Ag was deposited due to the decrease of the viscosity and the increased mass transport. During the anodic sweep the deposited Ag is not dissolved completely. Such behaviour is often observed in ILs [40].

# 3.3.2. Potentiostatic deposition of Ag layers from IL based electrolytes

Potentiostatic depositions were carried out at -0.1 V, -0.2 V and -0.3 V in all four electrolytes and in the temperature range from 20 °C to 100 °C. The current efficiencies obtained at a deposition potential of -0.1 V are summarized in Table 2. The current



**Fig. 6.** Mass-charge balance during potentiodynamic experiments performed at 20 mV s<sup>-1</sup> and at different temperatures for 202.8 mmol/kg Ag(1) in [EMIm][TfO]. Black, continuous line shows the measurements at 20 °C, red dashed line is for 50 °C, green dotted line is for 80 °C and blue dashed-dot is for 100 °C. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)

efficiencies have been calculated as already mentioned above from the ratio between the apparent molar mass obtained from the EQCM data (obtained at its turn from the linear portions of the mass vs. charge diagrams) and the theoretical molar mass of Ag.

#### Table 2

Current efficiencies (in %) obtained during the potentiostatic experiments at -0.1 V for 1800 s as a function of temperature.

Ag(I) concentra- tion/(mmol/kg)	20°C	50°C	80°C	100°C
202.8	79	95	89	92
101.4	96	100	97	86
50.7	98	99	96	90
25.3	100	98	79	98

High current efficiencies, with values between 80% and 100%, were obtained in all the electrolytes used (Table 2) and for all three deposition potentials used (-0.1 V, -0.2 V and -0.3 V) (not shown). No significant trends of the current efficiency with the temperature or with the deposition potential were observed.

#### 3.4. SEM characterization

Uniform layers with a shiny metallic visual appearance were obtained by potentiostatic deposition. The morphology of some Ag layers is shown in Fig. 7. The morphology of the layers deposited at -0.1 V were very similar to those obtained at -0.2 V, for identical temperatures and Ag(I) concentrations (not shown). When the deposition was carried out at 20 °C, the layer contained mainly fine grains. Larger grains were obtained at 100 °C. This is probably due to the improved mass transport. Ordered grains, that resembled a hexagonal structure, were observed in the deposits prepared at 100 °C in the most concentrated solution (202.8 mmol/kg)



**Fig. 7.** Scanning electron micrographs of Ag layers obtained by potentiostatic deposition (E = -0.2 V) at a deposition time of 1800 s. (A) T = 20 °C, 25.3 mmol/kg Ag(I); (B) T = 100 °C, 25.3 mmol/kg Ag(I); (C) T = 20 °C, 50.7 mmol/kg Ag(I); (D) T = 100 °C, 50.7 mmol/kg Ag(I); (E) T = 20 °C, 101.4 mmol/kg Ag(I); (F) T = 100 °C, 101.4 mmol/kg Ag(I); (G) T = 20 °C, 202.8 mmol/kg Ag(I); (H) T = 100 °C, 202.8 mmol/kg Ag(I).



Fig. 7. (Continued)

(Fig. 7H). Moreover, the grains of the deposits formed at  $100 \,^{\circ}$ C in 202.8 mmol/kg were smaller than those obtained at  $100 \,^{\circ}$ C in less concentrated solutions. The reason why the intermediate concentrations exhibit the extreme deposition morphologies could be attributed to the interference of several competing influence factors. The intermediate concentrations exhibit high conductivities and low viscosity–density products; this could be one significant factor. One big unknown is the nuclei formation process. Are more nuclei formed at low temperature as at higher temperature? Or do the nuclei coalesce better at higher temperature, when more ions reach the electrode due to better migration? Moreover, maybe the nuclei themselves are more mobile at higher temperatures.

EDX analysis proved that the deposits consist of Ag (ca. 93-96 wt.%) and C (ca. 4-7 wt.%). The carbon signal is probably due to rests of IL trapped between the grains.

The granular morphology of our Ag layers is similar to that reported by other groups onto Au substrates, in the other ILs [13,15,16], or in [EMIm][TfO] with 50% humidity [6], but completely different from the dendritic or filiform morphology that one can obtain from aqueous electrolytes [3].

#### 4. Conclusions

This paper is dedicated to studying the electrodeposition of Ag from [EMIm][TfO] and to correlate the physical properties of the solution used with the properties of the deposited layers as a function of temperature and the concentration of Ag(I).

Silver electrodeposition was successfully carried out in the IL [EMIm][TfO]. The EQCM technique was used to monitor the viscosity–density product of the electrolytes and to obtain *in situ* information on the electrodeposited mass.

Different concentrations of Ag(I) were established via electrochemical dissolution of Ag and subsequent dilution. The electrical conductivity of the electrolytes was determined by EIS measurements. The conductivity increased with increasing temperature, while the viscosity-density product decreased. The solution containing 25.3 mmol/kg Ag(I) had the highest conductivity at a fixed temperature in comparison to the solutions containing more Ag ions or to the neat IL. Simultaneously, the viscosity-density product of the solutions containing 25.3 mmol/kg and 50.7 mmol/kg Ag(I) was the smallest from all the solutions investigated here. This behaviour could be attributed to the specific interaction of Ag ions with the ions of the IL. The cyclic voltammetry coupled with the EQCM allowed us to identify the potential regions where elemental Ag is obtained and the potential regions where Ag dissolves. The current efficiency was calculated in different potentiostatic and potentiodynamic experiments, and at different temperatures. The deposition conditions influenced the morphology of the layers. The smallest grain sizes were obtained for the layers electrodeposited from the 50.7 mmol/kg Ag(I) solutions at 20 °C and the biggest grain sizes for the layers obtained from 101.4 mmol/kg Ag(I)solutions at 100 °C. The higher the temperature is, the bigger the particles grow. This is most likely due to a facilitated mass transport towards the electrode at higher temperatures.

#### References

- [1] A.J. Bard (Ed.), Encyclopedia of Electrochemistry of the Elements, vol. VIII, Dekker, NY, USA, 1978.
- [2] Electroless and electrodeposition of silver, in: M. Schlesinger, M. Paunovic (Eds.), Modern Electroplating, fourth ed., John Wiley & Sons Inc., New York, 2000 (Chapter 5).
- [3] G. Papanastasiou, D. Jannakoudakis, J. Amblard, M. Froment, J. Appl. Electrochem. 15 (1985) 71.
- W. Simka, D. Puszczyk, G. Nawrat, Electrochim. Acta 54 (2009) 5307. [5]
- I. Kazeminezhad, A.C. Barnes, J.D. Holbrey, K.R. Seddon, W. Schwarzacher, Appl. Phys. A 86 (2007) 373.
- S. Zein El Abedin, F. Endres, Electrochim. Acta 54 (2009) 5673.
- [7] K. Peppler, M. Pölleth, S. Meiss, M. Rohnke, J. Janek, Z. Phys. Chem. 220 (2006) 1507
- [8] W. Dobbs, J.-M. Suisse, L. Douce, R. Welter, Angew. Chem. 118 (2006) 4285.
- [9] S.A. Meiss, M. Rohnke, L. Kienle, S.Z. El Abedin, F. Endres, J. Janek, ChemPhysChem 8 (2007) 50.
- [10] A. Safavi, N. Maleki, E. Farjamia, Electroanalysis 21 (2009) 1533.
- [11] T. Murakami, Y. Kogo, K. Waku, H. Hayashi, A. Kishimoto, Electrochemistry 77 (2009) 645
- S. Arimoto, H. Kageyama, T. Torimoto, S. Kuwabata, Electrochem. Commun. 10 (2008) 1901.
- [13] N. Serizawa, Y. Katayama, T. Miura, J. Electrochem. Soc. 156 (2009) D503.
- A.I. Bhatt, A.M. Bond, J. Electroanal. Chem. 619-620 (2008) 1.
- [15] D. Borissov, C.L. Aravinda, W. Freyland, J. Phys. Chem. B 109 (2005) 11606. [16] A.P. Abbott, S. Nandhra, S. Postlethwaite, E.L. Smith, K.S. Ryder, Phys. Chem.
- Chem. Phys. 9 (2007) 3735. R. Bomparola, S. Caporali, A. Lavacchi, U. Bardi, Surf. Coat. Technol. 201 (2007)
- 9485 [18] P. He, H. Liu, Z. Li, Y. Liu, X. Xu, J. Li, Langmuir 20 (2004) 10260.

- [19] N. Serizawa, Y. Katayama, T. Miura, Electrochim. Acta 56 (1) (2010) 346.
- [20] G. Sauerbrey, Z. Phys. 155 (1959) 206.
- L. Aldous, D.S. Silvester, C. Villagrán, W.R. Pitner, R.G. Compton, M.C. Lagunas, C. Hardacre, New J. Chem. 30 (2006) 1576.
- [22] J.A. Widegren, E.M. Saurer, K.N. Marsh, J.W. Magee, J. Chem. Thermodyn. 37 (2005) 569.
- [23] A.M. O'Mahony, D.S. Silvester, L. Aldous, C. Hardacre, R.G. Compton, J. Chem. Eng. Data 53 (2008) 2884.
- B.D. Fitchett, T.N. Knepp, J.C. Conboy, J. Electrochem. Soc. 151 (7) (2004) E219. F. Endres, A.P. Abbott, D.R. MacFarlane (Eds.), Electrodeposition from Ionic Liq-[25]
- uids, Wiley-VCH, Weinheim, Germany, 2008, p. 369. [26] Peter Wassescheid, Tom Welton (Eds.), Ionic liquids in Synthesis, second ed.,
- Wiley-VCH, Weinheim, Germany, 2008, p. 141. [27]
- R.D. Shannon, Acta Crystallogr. A32 (1976) 751.
- [28] I. Krossing, J.M. Slattery, C. Daguenet, P.J. Dyson, A. Oleinikova, H. Weingärtner, J. Am. Chem. Soc. 128 (2006) 13427. [29] John Newman, K.E. Thomas-Alyea, Electrochemical Systems, third ed., Wiley-
- Interscience, NJ, USA, 2004, p. 283.
- [30] A. Jarosik, S.R. Krajewski, A. Lewandowski, P. Radzimski, J. Mol. Liq. 123 (2006) 43
- [31] M.A. Vorotyntsev, V.A. Zinovyeva, M. Picquet, Electrochim. Acta 55 (2010) 5063.
- [32] H. Zhao, Z.-C. Liang, F. Li, J. Mol. Liq. 149 (2009) 55. [33] A.P. Abbott, ChemPhysChem 6 (2005) 2502.
- [34] A. Doi, J. Non-Cryst. Solids 311 (2002) 207.
- [35] M. Nakahara, K. Ibuki, J. Phys. Chem. 90 (1986) 3026. [36] K.K. Kanazawa, J.G. Gordon, Anal. Chem. 57 (1985) 1770.
- G. McHale, C. Hardacre, R. Ge, N. Doy, R.W.K. Allen, J.M. MacInnes, M.R. Brown, [37] M.I. Newton, Anal. Chem. 80 (2008) 5806.
- [38] A. Bund, E. Zschippang, ECS Trans. 3 (2007) 253.
- [39] A. Ispas, A. Bund, F. Endres, ECS Trans. 16 (49) (2009) 411.
- [40] A. Ispas, B. Adolphi, A. Bund, F. Endres, Phys. Chem. Chem. Phys. 12 (2010) 1793.