STUDIA UNIVERSITATIS BABEŞ-BOLYAI, CHEMIA, LIII, 1, 2008

In memoriam prof. dr. Liviu Oniciu

ELECTROCHEMICAL INVESTIGATION OF SILVER / SILVER ION COUPLE REVERSIBILITY IN CHOLINE CHLORIDE - UREA BASED IONIC LIQUID

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ABSTRACT. Cyclic voltammetry and electrochemical impedance spectroscopy were used for studying both cathodic and anodic processes on Pt electrode in an ionic liquid as electrolyte support at 70^0C temperature. Air and water stable solutions containing Ag^+ ion (0.14M, 0.282M and 0.565M $AgNO_3$) are based on choline chloride (ChCl) and urea (1: 2) mixtures. Voltammograms were recorded using scan rates in 10-200 mV/s range. It is shown that the Ag^+/Ag couple on Pt electrode exhibits almost reversible behavior in ChCl-urea electrolyte support at 70^0C, with diffusion control of cathodic process and a stripping anodic process. The diffusion coefficient of Ag^+ ion was estimated. Impedance of Pt electrode has been measured as a function of frequency for different overpotential values in the region of beginning and current peak Ag deposition. The non-uniformity of Ag deposited surface is one of the main factors determining the depressed shape of the impedance semicircle in Nyquist spectra. The values of fitting parameters for impedance data were calculated and the simulated curves have agreed with the experimental ones. Considerations regarding the use of Ag/Ag^+ ion couple as reference electrode in electrochemical experiments with ChCl based ionic liquids are made.

INTRODUCTION

Room temperature (or ambient temperature) ionic liquids based on choline chloride (ChCl) are of interest for last years. The preparation and applications of this new class of ionic liquids containing a quaternary ammonium salt (ChCl chemical compound is 2 hydroxy-ethyl-trimethyl-ammonium) mixed with hydrogen bond donor species, as amides, carboxylic acids, ethylene glycol etc., were described first by Abbott *et al*. [1-3]. Among the electrochemical applications, these ionic liquids can be used for the deposition of a range of metal coatings [4-6] including Zn, Cr, Sn, Cu, Ag at high current efficiency; also, they are well suited for metal electropolishing [7].

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Recently, we reported some data [8] about cyclic voltammetry experiments and demonstrated that the Ni electrodeposition process in ChCl - urea and ChCl - malonic acid systems as ionic liquids represents an environmentally friendly alternative for the classic electrodeposition techniques in aqueous solutions which are used in present at industrial scale. The new proposed technique is an ecological procedure because the ionic liquid is air and moisture stable and its components are both common chemical compounds: chloride choline, which is used for chicken feed as vitamin B4 and urea, which is a common fertilizer.

The electrodeposition of silver as pure metal or its alloys is a technological process involved in a variety of finishing processes, an example being in electronics for the manufacture of printed circuit boards. Also, the electrodeposition and electrodissolution of silver in aqueous solutions were extensively studied in the past years in relation to silver recovery from photographic wastes. Silver deposits can be obtained from aqueous solutions in various conditions regarding composition, structure, aesthetic aspect, thickness and deposition rate. Obviously, a better approach of the silver electrodeposition kinetics was achieved by determining the diffusion and kinetic parameters and also establishing the mechanism of electrode process. The study of the mechanism of cathodic process of silver ion in thiosulphate aqueous solution performed by Gonnissen *et al.* [9] is an example. However, regarding the electrochemistry of silver in ionic liquids we found out that it is a lack of information about the electrode process kinetics and diffusion.

The present paper aimed to illustrate the electrochemical reversibility of Ag/Ag^+ ion couple in choline chloride - urea mixture as ionic liquid by showing the similar electrochemical behavior as in aqueous solutions or molten salts. To the authors knowledge, cyclic voltammetry and electrochemical impedance spectroscopy for Ag deposition and dissolution on Pt inert electrode in such ionic liquids have not been applied, yet. The obtained value of diffusion coefficient of Ag^+ ion may also be compared with other similar values in different electrolytes. Moreover, since we have used a quasi-reference electrode consisting in a silver wire immersed in the investigated ionic liquid, the results may allow us to make some considerations regarding the use of Ag / Ag^+ ion couple as reference electrode in ionic liquids.

RESULTS AND DISCUSSION

The electrochemical experiments were carried out firstly in supporting electrolyte consisting in choline chloride - urea mixtures (1: 2, in moles) as binary ionic liquids, in order to know the potential window and potentially electrochemical reactions occurring on Pt electrode. Also, in our preliminary determinations with gradually additions of $AgNO_3$ in the above ionic liquid we found out a decrease in the specific electrical conductivity at a constant temperature for concentrated solutions, whereas the increase of temperature leads in all systems to an important increase in conductivity.

Cyclic voltammetry measurements

Cyclic voltammetry curves were recorded for studying both cathodic and anodic processes on Pt electrode in pure ionic liquid as electrolyte support at 70^{0}C constant temperature using scan rates in 10-200mV/s range.

An example of typical cyclic voltammogram recorded in choline chloride – urea mixture (1: 2, in moles) at 70^{0}C is shown in Fig. 1, indicating a potential window on Pt electrode from about +1.4 V to –1.2 V (electrode potentials *vs.* Ag quasi reference). During the cathodic scan the current density was lower than 0.5 mAcm^{-2}. It is worth to mention that on the cathodic branch of voltammograms two consecutive reduction waves appear at potentials around –0.35 V and –0.8 V, respectively, with a current amplitude that increases at faster scan rates.

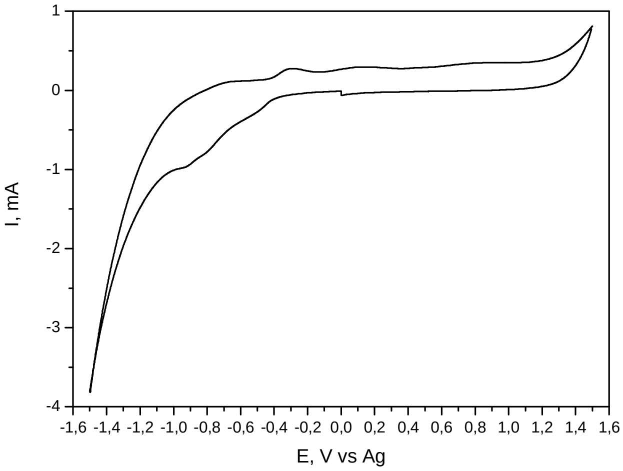


Figure 1. Cyclic voltammogram for Pt electrode (0.5 cm^2) in choline chloride - urea mixture (1: 2, in moles) at 70^{0}C; 10 mV/s scan rate.

It was considered that the existence of such waves with limiting currents less than 1 mAcm^{-2} is due to the presence of small amounts of H$^+$ ion in binary ionic liquid, resulted by dissociation of water molecules that surely are present in our experiments. In anodic direction, the current is almost zero in -0.9 ÷ +1.2 V potential range, with a continuous increasing at more positive values.

We performed voltammetric measurements in air and water stable solutions containing concentrations of Ag^+ ion of 0.14M, 0.282M, 0.565M $AgNO_3$, respectively, and choline chloride (ChCl) with urea (1: 2) mixture as electrolyte. Figures 2-4 show cyclic voltammograms recorded with various scan rates at 70^0C constant temperature, in the same potential range. Starting from the stationary potential (0V *vs.* Ag quasi reference electrode), all figures show clearly the beginning of cathodic deposition process with a current peak located at electrode potentials in the range -0.1 ÷ -0.3V, followed by a quite large potential region of limiting currents.

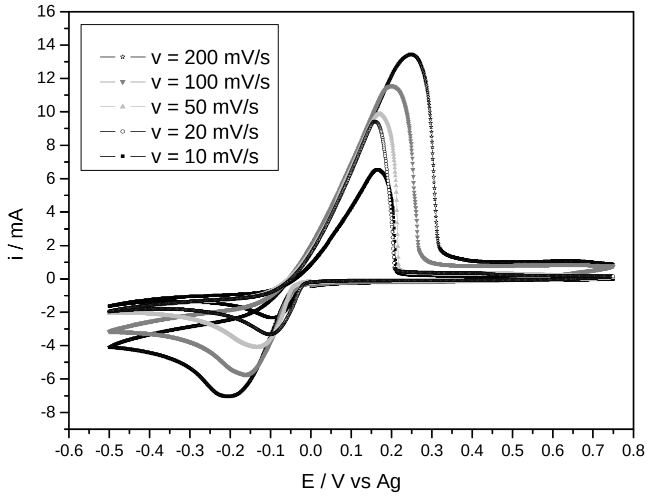


Figure 2. Cyclic voltammogram for 0.14M $AgNO_3$ in ChCl+urea (1:2) with Pt electrode (0.5 cm^2) at various scan rates, 70^0C.

In experiments with a further polarizing the Pt electrode (not shown), a continuous increasing of cathodic current at more negative potentials, generally more negative than -1.2V, was recorded, proving a supplementary process of ionic liquid solvent together with the massive deposition of Ag on working electrode. In all voltammograms, by returning the electrode potential in the anodic direction, a single well pronounced peak was obtained, with a peak potential situated at +0.2 ÷ +0.4V. This clearly seen anodic peak having the increasing amplitude for higher concentrations and scan rates is surely due to the silver stripping process onto the platinum electrode. Next increasing of current at potentials more positively than +1.2V (not shown, too) was attributed to the anodic process of supporting electrolyte, being probably the chlorine evolution.

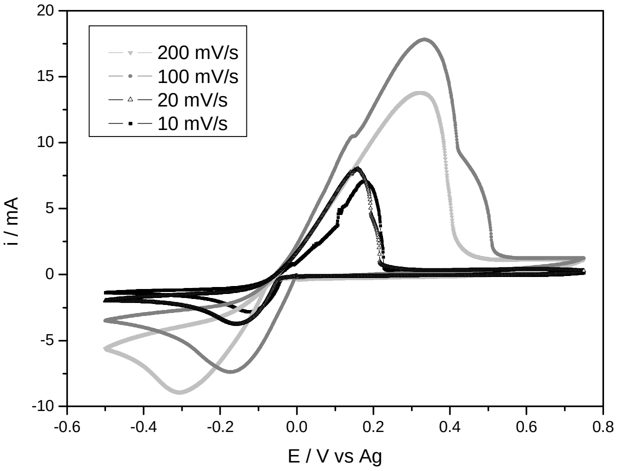


Figure 3. Cyclic voltammogram for 0.282M $AgNO_3$ in ChCl+urea (1:2) with Pt electrode (0.5 cm^2) at various scan rates, 70^0C.

Referring to the silver electrodeposition and electrodissolution, it is worth to note that for each silver ion concentration, the increase of scan rate entails the increase of both cathodic and anodic peak currents. However, it was remarked the gradual shift of peak potentials in cathodic and anodic direction, respectively (*ie* an increase of ΔE_p difference by increasing scan rate). An explanation would be the IR ohmic drop owing to the gradually diminishing of electrical conductivity of ionic media by adding $AgNO_3$ amounts in ChCl+urea ionic liquid.

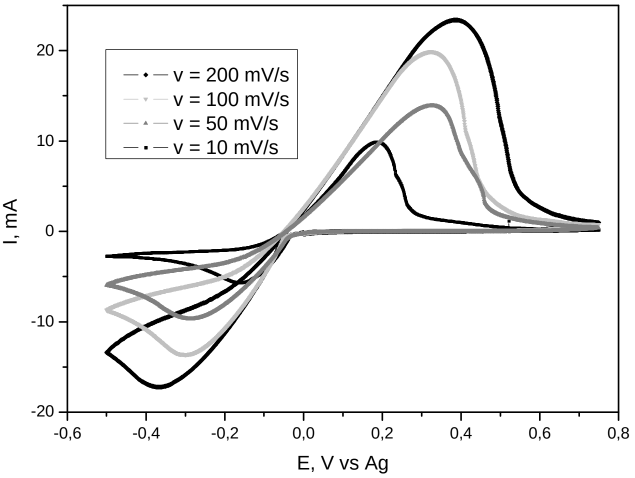


Figure 4. Cyclic voltammogram for 0.565M $AgNO_3$ in ChCl+urea (1:2) with Pt electrode (0.5 cm^2) at various scan rates, 70^0C.

This phenomenon, already noticed in our conductivity measurements, is related to the existence of ionic complexes (in form of chloride complex ions) between choline chloride and urea as components of ionic electrolyte. We consider new bonds formation with introduced silver ions, which become chloride ionic complexes. According to the mechanism suggested by Gonnissen [9], the silver deposition involves these complexated silver ions, with the following scheme:

$$\mathrm{AgL_n} \Leftrightarrow \mathrm{AgL} + (n\text{-}1)\,\mathrm{L} \qquad (1)$$

$$\mathrm{AgL} + e^{-} \Leftrightarrow \mathrm{Ag} + \mathrm{L} \qquad (2)$$

The symbol L means the ligand present in the electrolyte, *ie* choline chloride as component in our system.

Thus, the reaction follows a chemical-electrochemical (CE) mechanism. The first chemical reaction is a rapid process, so that it does not affect the overall reaction rate. It involves the partial decomplexation of AgL_n species in the bulk of solution, considered as an equilibrium reaction, this being too fast to be detected. Then, AgL intermediate species are reduced at the electrode in the electrochemical step with a reversible single electron transfer. The results of our investigations suggest for the cathodic process to be diffusion controlled, especially for more diluted ionic liquids and for small scan rates, where the IR ohmic contribution in ΔE_p separation may be not important.

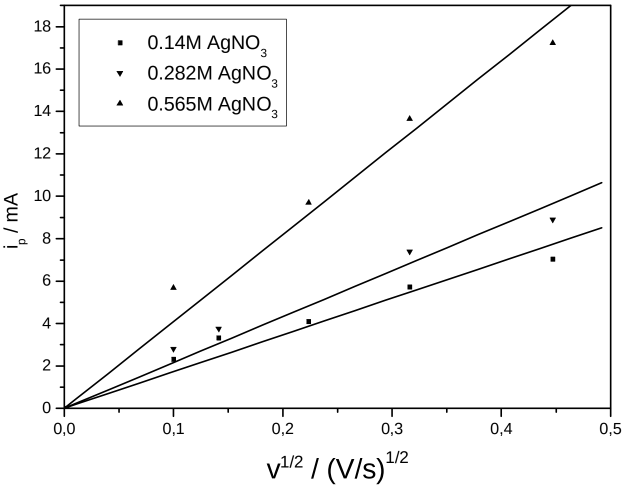


Figure 5. Cathodic peak current (i_p) *vs.* square root of the scan rate ($v^{1/2}$) for the three Ag^+ concentrations in ChCl+urea (1:2); Pt electrode ($0.5 cm^2$), 70^0C.

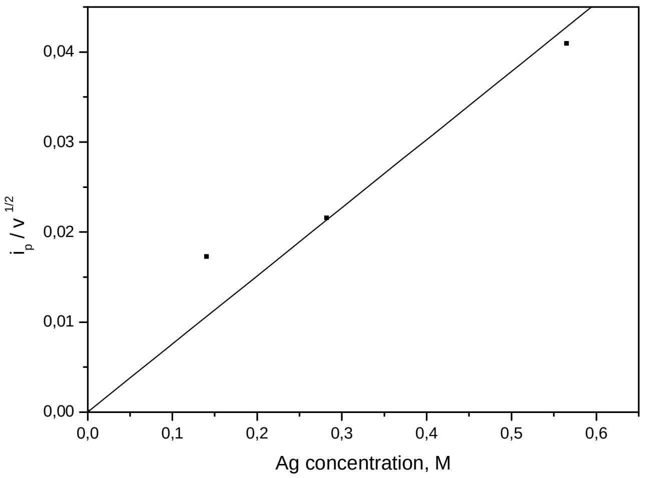


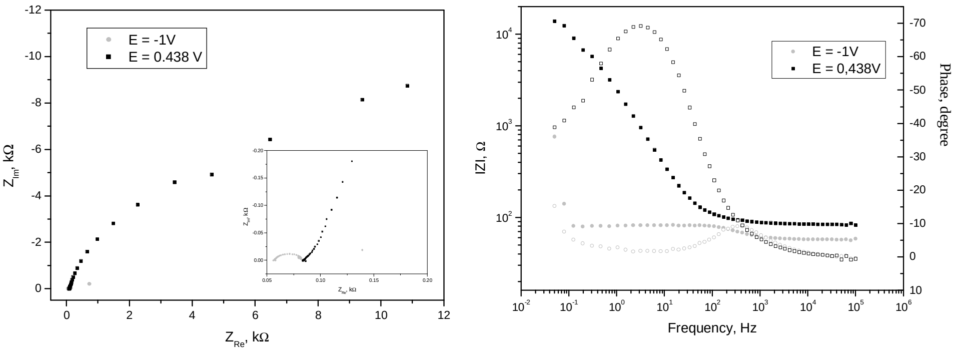
Figure 6. The $i_p / v^{1/2}$-c dependence for cathodic silver deposition in ChCl+urea ionic liquid; Pt electrode (0.5cm^2), 70^{0}C.

A quantitative analysis of the CVs varying both scan rate (v) and Ag$^+$ concentration (c) is presented in Figs 5 and 6. These figures show that the cathodic peak current (i_p) is almost linearly proportional to square root of the scan rate ($v^{1/2}$); this invariance of current function $i_p/v^{1/2}$ with scan rate accompanied by a linear $i_p / v^{1/2}$ - c dependence allowed us to calculate the diffusion coefficient using the well-known Randles-Sevcik equation for reversible processes. A value of diffusion coefficient for complexed silver ion of 0.36 $\times10^{-6}$ cm^2/s was estimated from Fig. 6, whereas a higher value, of 0.92 $\times10^{-6}$ cm^2/s, was computed considering the data of diluted solution (0.14M), only (Fig. 5). Taking into account the lack of information about the diffusion data in ionic liquid media, we have compared the diffusion coefficient obtained in diluted solution with similar measurements in aqueous solutions and found out them being quite close to the previous data reported for silver ion in thiosulphate solutions from photographic wastes (D=0.5 $\times10^{-5}$ cm^2/s at room temperature [10,11]).

It also resulted that the Ag$^+$/Ag couple on Pt exhibits almost reversible behavior in ChCl-urea electrolyte support at 70^{0}C, with diffusion control of cathodic process and a rapid charge transfer.

The a.c. impedance measurements

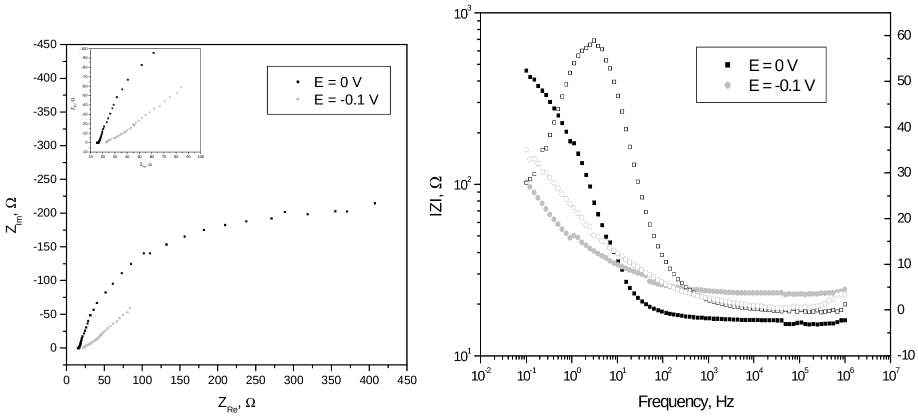
The *a.c.* frequency response of the supporting electrolyte system (pure ChCl+urea ionic liquid) was investigated at different electrode potentials, where some increases of current were observed. Figure 7 presents the Nyquist and Bode spectra, illustrating the absence of any cathodic process in the region of less negative potentials. Here, the *a.c.* frequency response is almost totally capacitive (for instance, the phase angle of 70^0 is closed to theoretical value, 90^0). However, due to water impurities, probably, the cathodic process has modified drastically the a.c. response at –1V potential, where the phase angle is around 10^0 and the charge transfer resistance (diameter of semicircle) decreases with three orders of magnitude.



a) b)

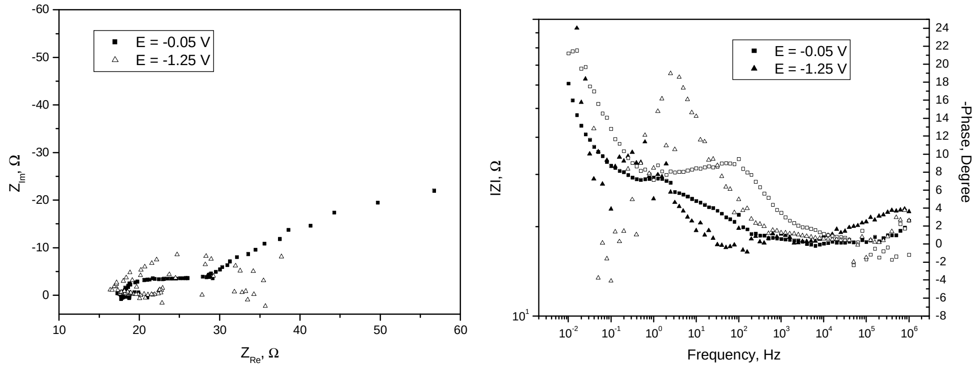
Figure 7. Nyquist (a) and Bode (b) diagrams of ChCl+urea (1:2) with Pt electrode (0.5 cm^2) at two potentials: 0.438V and –1V.

Impedance investigations in solutions containing choline chloride (ChCl) with urea (1: 2) mixture as electrolyte and 0.14M, 0.282M, 0.565M $AgNO_3$, respectively, are also performed at different electrode potentials, *ie* at the beginning of silver deposition and within the potential region of peak current or limiting current. As in CV experiments, a quite different behavior of the a.c. impedance was noticed in the region near equilibrium potentials (E=0 V *vs*. Ag pseudo-reference electrode), compared to the region of a massive Ag deposition. The impedance spectra as Nyquist diagrams (Figs. 8a-10a) show clearly at less cathodic polarization the capacitive semi-circles in the region of high frequences, followed by a linear dependence of imaginary part of impedance against the real part. The values of charge transfer resistance (the diameters) drastically decreased with 2-3 orders of magnitude in the potential region of continuous deposition. The shape of depressed semi-circles may be attributed to the non-uniformity of silver deposit onto platinum surface, especially after the first nuclei of electrocrystallised silver occur forming a monolayer. Thus, during *a.c.* measurements at higher negative overpotentials a roughness of cathode surface has continuously increased. Generally, the value of the real part of impedance determined by extrapolation of capacitive arc to zero frequency decreases with an increase of cathodic overpotential (indicating a diminution of the charge transfer resistance), and increases with a decrease of Ag^+ ion concentration.



a) b)

Figure 8. Nyquist (a) and Bode (b) diagrams of silver electrodeposition from 0.14M $AgNO_3$ in ChCl+urea (1:2) with Pt electrode (0.5 cm^2) at two potentials: 0V and -0.1V

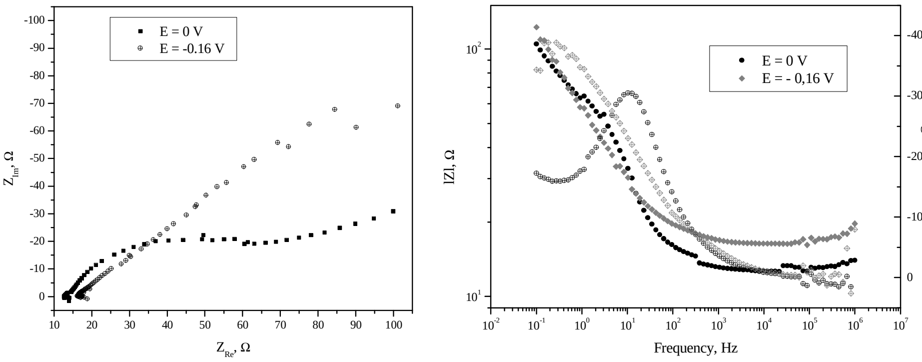


a) b)

Figure 9. Nyquist (a) and Bode (b) diagrams of silver electrodeposition from 0.282M $AgNO_3$ in ChCl+urea (1:2) with Pt electrode (0.5 cm^2) at two potentials: -0.05V and -1.25V

The same behavior is evidenced in all Bode diagrams (Figs. 8b-10b). The capacitive response at potentials near 0V is illustrated by a phase angle of about 60^0 and large values of impedance. In the potential region of continuous silver deposition, the phase angle decreases at values around

20^0 and less. Moreover, the large linear portions of impedance variation with frequency for more negatively polarised samples are correlated with the thickening of silver film onto platinum electrode. Corespondingly, at lower frequencies a Warburg impedance appears.



a) b)

Figure 10. Nyquist (a) and Bode (b) diagrams of silver electrodeposition from 0.565M $AgNO_3$ in ChCl+urea (1:2) with Pt electrode (0.5 cm^2) at two potentials: 0V and -0.16V

We consider that the above interpretation of impedance of Pt electrode in Ag^+ ion containing electrolyte measured at different overpotentials and for different silver concentrations was consistent to the above described reaction mechanism.

Impedance data were simulated by proposing an equivalent electric circuit (Fig. 11). This model of interface is composed of the electrolyte resistance, R_S, connected with a constant phase element, CPE (which is a non-ideal capacitor), in parallel with the charge transfer resistance, R_{ct}, which describes the electrochemical reaction under activation control; finally, a Warburg element (W) which represents a diffusion controlling step was added in series with the charge transfer resistance.

The constant phase element CPE replaces the capacity of the electric double layer for a better fitting; it takes into account the deviation from pure capacitive behavior, having the impedance given by the expression:

$$\mathrm{CPE} = \frac{1}{\mathrm{T}}\left(\frac{1}{\mathrm{j}\omega}\right)^{\mathrm{p}} \tag{3}$$

where for the exponent value p=1, CPE reduces to a ideal capacitor with a capacitance T and, for p=0 value, to a simple resistor. In the above expression the other significations are: ω – the angular frequency of *ac* voltage and j – the imaginary vector unit ($j=\sqrt{-1}$).

The Warburg impedance has a resistive part (W-R) and a capacitive part (W-CPE), for this last component (capacitive part) considering an expression similar with eq. (3). However, since W represents the diffusive component of equivalent circuit the exponent p was considered around a constant value, p=0.5. The values of circuit parameters resulted from fitting procedure are given in Table I. An example of both experimental and fitted data is represented in Figure 12.

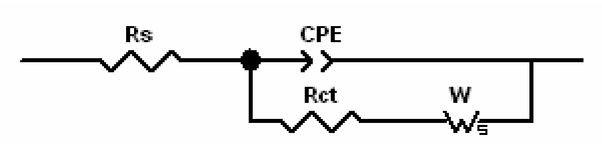
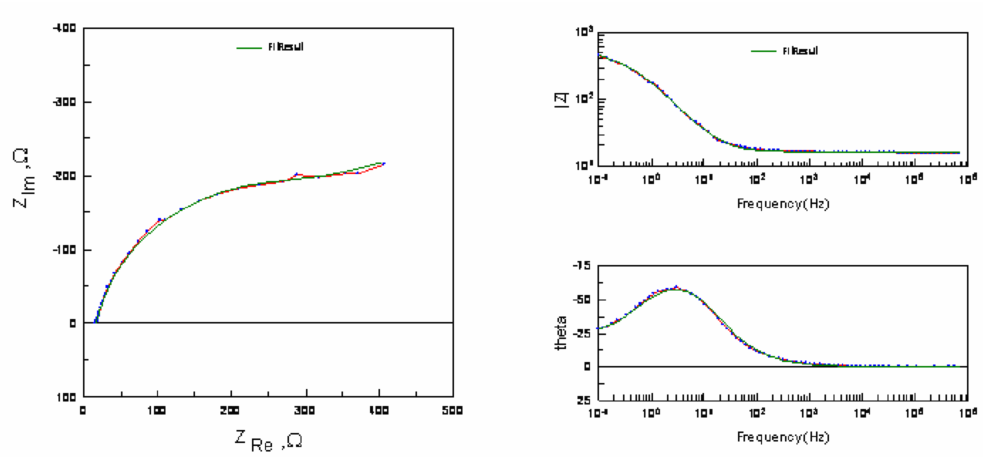


Figure 11. The proposed equivalent electrical circuit used for fitting impedance data. The significances of circuit parameters are given in text.



a) b)

Figure 12. Nyquist and Bode diagrams of silver electrodeposition from 0.14M $AgNO_3$ in ChCl+urea (1:2) with Pt electrode (0.5 cm^2) at 0V electrode potential. Dotted lines represent the experimental data; the continuous lines show the fitted points using the model circuit from Figure 11.

As can be seen from Table I, the ohmic resistance of electrolyte has almost a constant value, of around $10\Omega cm^2$. We have noticed that for relatively diluted solutions the charge transfer resistance, R_{ct}, decreases with shift of the electrode potential towards negative direction. This behavior corresponds to a more intensive rate of charge transfer after the first silver layer was deposited on Pt, leading to the increasing the exchange currents.

Table 1 shows that at near equilibrium potentials (zero values of E), with increasing silver concentration in binary ionic liquid there is also a continuous decreasing in diffusion resistance (W-R). On contrary, in the region of intense silver deposition (-0.1V to -0.2V) W-R has a slightly increase. This constitutes an evidence for a diffusion control of cathodic process. As a consequence, we confirm the chemical step (1) as a rapid one, the diffusion of complexated Ag ion to the electrode surface being the rate-determining step. Taking into account an approximately constant value of CPE-p exponent (p is mostly in the 0.6-0.86 range) we can compare the values of CPE-T at each potential; the increasing of double layer capacitance with cathodic overpotential would be explained by an increasing in the surface area of electrode, which is due to the further silver deposition on the electrode.

Table 1.

Fitted parameters for silver electrodeposition on Pt electrode (0.5cm^2) in ChCl+urea (1: 2) ionic liquid at 70^{0}C

Circuit parameter	0.14M $AgNO_3$		0.282M $AgNO_3$			0.565M $AgNO_3$	
Potential	0V	-0.1V	-0.05V	-0.12V	-1.25V	0V	-0.16V
R_s, Ω	16.12	23.05	17.94	11.17	19.19	12.96	16.55
CPE-T, μF	1019	4009	2827	498	1563	1834	5931
CPE-P	0.86	0.60	0.70	0.81	1.24	0.73	0.57
R_{ct}, Ω	409.4	20.0	9.4	5.0	8.0	49.9	148.2
W-R, Ω	280.4	411.7	45.8	589.8	5.8	21.0	626.9
W-T, μF	5340	21290	37330	45400	480	500	6140
W-P	0.55	0.54	0.53	0.5	0.74	0.001	0.84

About the using of Ag/Ag+ ion couple as the reference electrode in ionic liquid media

In our experiments we have arbitrarily chosen a quasi-reference electrode consisting in a silver wire immersed in the ionic liquid containing Ag^+ ion (ChCl + urea + $AgNO_3$ (or AgCl)). This convenience of use has led to the frequent employment. It has advantage of achieving quickly its equilibrium potential and reproducibility and of maintaining its potential well with time, making it particularly well suited to act as a comparison. The results about reversible behavior of silver/silver ion couple may lead to some interpretations regarding the use of this couple as reference electrode in ChCl based ionic liquids.

It is well known that a reference electrode ideally provides a fixed reference potential against which the potential of the working electrode is measured. Conventionally, its Galvani electric potential is set equal to zero. One of the most common used reference electrodes in electrochemical studies undertaken in aqueous media is the silver/silver chloride (Ag/AgCl) electrode with NaCl or KCl aqueous solutions in concentration ranging from 1M to saturation. Sometimes, this electrode is also used in experiments in non-aqueous media being easier to construct and with potentials established rapidly and reproducibly.

However, the electrode potential difference between two electrodes immersed in electrolytes in contact with each other involves supplementary potentials, apart from ohmic potential drop term (IR). Thus, a salt bridge may give rise to a liquid junction potential which may alter the imposed potential of working electrode from potentiostat. For good results, the liquid junction potentials at the reference electrode/salt bridge and salt bridge/working solution interfaces must have similar magnitudes but opposite polarities and will, therefore, cancel each other. The complexity of problem is related to knowledge of the free energies of solvation for charged (cation) or neutral particles transferred between the aqueous and organic solvent; for minimizing errors these transfer free energies should be the same from solvent to solvent. It follows that in electrochemical measurements using non-aqueous solutions an electrochemical series can be established for each solvent [12]. The problem is how the potentials of such a series would compare with the corresponding potentials in water.

In conditions where AgCl is soluble in a non-aqueous solvent, the working electrode potential is measured against Ag/non-aqueous solution containing Ag^+ ion (commonly as $AgNO_3$) reference couple. For example, we have used a nonaqueous Ag/Ag^+ system (10^{-2}M $AgNO_3$ + 0.1M tetra-n-butylammonium perchlorate, CH_3CN) as reference electrode in acetonitrile [13]. In cyclic voltammetry experiments carried out in molten nitrates (300-600^{0}C), we also employed a silver wire immersed in a melt containing $AgNO_3$ with a concentration about 10^{-2}M in the studied molten nitrate electrolyte [14,15].

Working in medium and high temperature molten halides or carbonates, within 450-1000^{0}C range, the choosing of an appropriate reference electrode is much more difficult. Using LiCl-KCl melts, the reference electrode was a Ag wire immersed in silver ion containing melt (1M AgCl in LiCl-KCl eutectic) placed in a separated compartment [16]. Usually, especially at high temperatures, a metal electrode (Pt, Al, W, Ni etc.) simply immersed in the melt is frequently used as quasi-reference electrode in molten electrolytes where no established reference electrode couple exists [17].

The use of such quasi-reference electrodes for experiments in ionic liquids was reported by many authors. For example, Bakkar and Neubert [18] employed a Pt wire directly placed in the electrochemical cell during corrosion studies carried out in ChCl binary mixtures (with urea, ethylene glycol, glycerol, malonic acid). A silver wire as quasi-reference electrode was used recently by Abbott *et al.* during studies of either stainless steel electropolishing [7] or deposition of metals and alloys [19-21] in deep eutectic solvents based on choline chloride. We consider that employing a Ag wire immersed in an ionic liquid with a certain content in chloride ions such as ChCl ionic complex species, a half-cell reaction of AgCl film formation occurs:

$$Ag(solid) + Cl^-(ionic\ liquid) \Leftrightarrow AgCl(solid) + e^- \qquad (4)$$

This process of film formation on Ag quasi-reference electrode has advantages of achieving the equilibrium potential in short time, reproducibility and maintaining electrode potential with time, making it particularly well suited to act as a comparison.

CONCLUSIONS

Both voltammetric and electrochemical impedance measurements showed a quite reversible and diffusion controlled process of silver deposition in choline chloride + urea mixture at 70^0C, where one electron transfer process is preceded by a chemical step of delivering of electroactive species. Thus, the diffusion of complexated silver ion with choline chloride was considered as rate-determining step.

Additionally, the EIS data exhibit a non-uniformity of electrodeposited silver layer onto platinum substrate as well as change in behavior of cathodic process at more negative potentials. The experimental impedance data were fitted using a single electric circuit as model, with the values of circuit parameters in good agreement with the experimental data. The use of Ag/Ag^+ reference electrodes for experiments in ionic liquids was finally discussed.

EXPERIMENTAL SECTION

Cyclic voltammetry and electrochemical impedance spectroscopy investigations were conducted in ChCl-urea-$AgNO_3$ ionic liquid media. The binary ChCl-urea system as supporting electrolyte was separately prepared with analytical grade choline chloride (Merck) and urea (Fluka) in the corresponding amounts for 1: 2 (in moles) mixtures. $AgNO_3$ was dissolved as precursor of Ag^+ ion in concentrations in the range of 0.14 - 0.565 M, the molarity values being calculated using own experimental data of ionic liquid density (work in progress). The electrochemical cell (50 cm^3) contained a Pt foil (0.5 cm^2) as working electrode, a large platinum plate (4 cm^2) as auxiliary electrode, and a Ag wire placed in the same electrolyte (a quasi reference electrode). In the experiments a computer driven Autolab PGSTAT 302 potentiostat was used. Voltammograms were recorded using scan rates in 10 -200mV/s range. The impedance was measured in the potentiostatic conditions with a sinusoidal potential perturbation of the peak to peak amplitude equal to 10 mV at frequency sweep from 1 MHz to 0.01 Hz at different electrode potentials. Zview 2.80 software (Scribner Assoc. Inc.) was used for fitting impedance data. All electrochemical tests were carried out in a quiescent aerated ionic liquid at 70^0C.

ACKNOWLEDGEMENT

The financial support within the PNCDI-2, Parteneriate Romanian Programme - project nr.31066/2007 is gratefully acknowledged.

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