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DIFFUSION-CONTROLLED REDUCTION OF Sb^{3+} AND Cu^{2+} TO METALS FROM IONIC LIQUIDS CONTAINING CHOLINE CHLORIDE

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Sb^{3+}/Sb and Cu^{2+}/Cu couples were studied at 60°C in ionic liquids containing choline chloride (ChCl) using cyclic voltammetry. ChCl-oxalic acid binary mixture was used as electrolyte and Pt and glassy carbon were the working electrodes. $SbCl_3$ and $CuCl_2$ as precursors were introduced into the ChCl-oxalic acid ionic liquid as solvent. Families of cyclic voltammograms were recorded for ionic concentrations of 5-16 mM Sb^{3+} and 8-20 mM Cu^{2+}. The peak current – square root of scan rate plots are straight lines passing through origin, thus demonstrating the diffusion control of cathodic processes. The diffusion coefficients of Sb^{3+} and Cu^{2+} ionic species were found to vary with the chemical nature of working electrode and of investigated electrolytes, partly reflecting the difference between complex species which may be present in ionic liquid.

Keywords: antimony(III) ion, copper(II) ion, ionic liquids, diffusion coefficient, cyclic voltammetry

1. Introduction

Antimony is considered a semi-metal with gap energy of 0.18 eV (at 4.2 K) between the conduction and valence bands, so it has an unusual transport for both electrical charge carriers - electrons and holes. It is a component of many alloys and semiconductor compounds, such as SbTe, SbSe, InSb or $InAs_{1-x}Sb_x$.

Copper as pure metal and alloys is a well-known electrical conductor and has many industrial and decorative applications, being also regarded as precursor for the production of semiconductor compounds. The electrodeposited copper is widely used in the corrosion and wear-resistant coating industry.

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It has been found in experiments with traditional ionic liquids that, by dissolving either CuCl or $CuCl_2$ in the solvent, the reduction of Cu^{2+} to metallic Cu occur in two steps: in the first step Cu^+ is formed, in the second step the metal is deposited. This means that a disproportionation (comproportionation) reaction takes place and, whatever cupreous or cupric salt is dissolved, the electrolyte contains both copper mono- or copper divalent ions.

In the field of metal electrodeposition, ionic liquids (liquids at temperatures below 100°C) offer a number of advantages against aqueous electrolytes or organic media, such as lower vapor pressure, larger electrochemical window, or not generating additional risks of environmental pollution. From literature we noticed that experiments with electrodeposition of antimony and copper as pure metals using ionic liquid media are relatively fewer reported. Historically, most of such electrochemical studies employed molten chloroaluminates, imidazolium or pyrollidinium salts as electrolytes. Antimony deposits with good adhesion on the substrate were obtained by electrolysis of traditional ionic liquids at room temperature [1-7]. Studies of Cu electrodeposition from traditional ionic liquids were also reported by many authors [8-18].

An alternative for traditional ionic liquids are deep eutectic solvents based on choline chloride (or other choline salts or hydroxide). These media that are considered a new class of ionic liquids, have a lot of advantages since they are easier to be prepared, stable to air and humidity, less toxic, readily biodegradable and cheaper. In general, there are composed by binary mixtures of choline chloride (*2-hydroxy-ethyl-trimethyl ammonium chloride*, **ChCl**) with compounds that play role of hydrogen bond donors (amides, alcohols, carboxylic acids) [19,20]. These ionic liquids are expected to be ideal electrolytes for electrodeposition of coatings. A potential advantage refers to obtain crystalline deposits through direct electrodeposition without subsequent annealing. ChCl-based ionic liquids have been used in our previous works [21-25] for electrodeposition of Sb metal or Sb-based semiconductors. Also, the results obtained by other authors [26-36] indicated that the electrodeposition of Cu may be also more facile in such media, making these ionic liquids an interesting alternative for large-scale production in industrial applications. In general, for both antimony and copper electrodepositions the potentiostatic plating was carried out within the mass transfer controlled region of potential, where is the fastest possible rate, necessary for industrial processes.

Cyclic voltammetry (CV) technique was used extensively for electrochemical studies of diffusion-controlled processes, since it provides valuable information about the deposition domain of potentials, useful for obtaining coatings with the best quality characteristics. Also, the diffusion coefficients of ions may be calculated from CV results. In this regard, we mention that Schiffrin [37, 38] presented the application of cyclic voltammetry to insoluble product deposition and established a different form of Randles-Sevcik equation (peak current vs. square root scan rate dependence), taking into account the variable thermodynamic activity of deposited metal species.

With this in view, this paper presents some experimental results dealing with voltammetric investigation at $60^{o}C$ of Sb and Cu electrodeposition /dissolution in ChCl-oxalic acid (OxAc) ionic liquid. From our best knowledge the ChCl-OxAc ionic liquid was not used for systematic research of cathodic processes of Sb^{3+} and Cu^{2+} ions. We also aim to calculate the diffusion coefficients of Sb^{3+} and Cu^{2+} in ChCl-OxAc ionic liquid.

2. Experimental

We prepared in the first step the binary mixtures of choline chloride (99%, Aldrich) with oxalic acid dihydrate (Aldrich) in the 1:1 mole ratio. The reagents were used as received. The mixture was heated to $90^{0}C$ to form a homogeneous and colorless liquid. $SbCl_3$ (Alfa Aesar) and $CuCl_2\cdot 2H_2O$ (Aldrich) were used as precursors for ionic species of Sb^{3+} and Cu^{2+}, respectively, and were used as received. The ionic concentrations were 5-16 mM Sb^{3+} and 8-20 mM Cu^{2+}, calculated from densities of ionic liquids measured in our laboratory.

Cyclic voltammograms were recorded at different scanning rates (3-200 mV/s) by employing either Biologic - SP 150 or Zahner elektrik IM 6e potentiostats. The temperature was maintained constant at $60^{o}C$.

The electrochemical cell contained a Pt plate ($0.5\ cm^2$) or vitreous carbon disc ($0.07\ cm^2$) as working electrode, a larger Pt plate as auxiliary electrode, and a Ag wire immersed in the ionic liquid as quasi-reference electrode. The working electrode was mechanically polished with up to 2000 grit sandpaper, cleaned successively with HNO_3 solution, washed with running water and distilled water and then dried before each measurement.

3. Results and discussions

3.1. Electrode processes of Sb^{3+} in ChCl-OxAc ionic liquid

Figs. 1-3 show comparative families of cyclic voltammograms (CVs) recorded on Pt in ChCl-OxAc ionic liquid with 5, 8 and 10 mM $SbCl_3$ dissolved. The voltammograms indicate that the electrodeposition and stripping dissolution of antimony metal occur at peak potentials within -0.15V ÷ - 0.25 V cathodic range and 0 V ÷ 0.08 V anodic range. Generally there are no “nucleation loops" for cathodic processes at the selected potential limit were the scans were reversed, that is typical for electrodeposition processes which do not require nucleation overpotential. The final increase of cathodic current at the most negative potential is attributed to the reduction of cholinium cation (from the ionic liquid solvent) and the final increase of anodic current is attributed to the oxidation of Cl^- ions existing also in solvent. Beside the Sb^3/Sb couple, voltammograms in Figs. 2 and 3 show clearly a second redox couple, namely Sb^{5+}/Sb^{3+} couple, located at 0.8 V more positive potential. The responses of both couples, expressed as current densities, are increased with Sb^{3+}concentration. Also, they are increased with scan rate, and the peak potentials move towards negative or positive direction thus increasing ΔE_p. However, the large ΔEp difference between the anodic and cathodic peaks corresponding to Sb^{3+}/Sb couple is comparable to the ΔEp values reported by other authors [5].

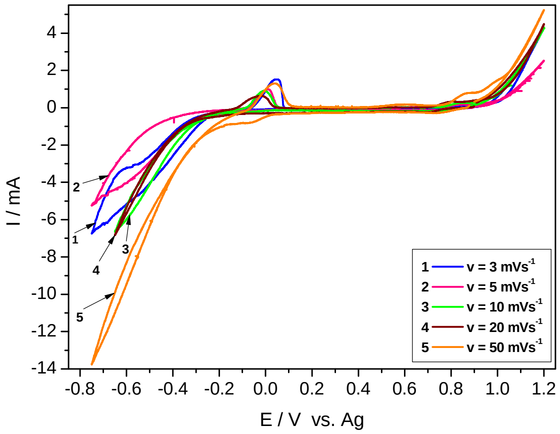

Fig. 1. CV curves on Pt electrode, 60^0C, from ChCl-OxAc + 5 mM $SbCl_3$ ionic liquid

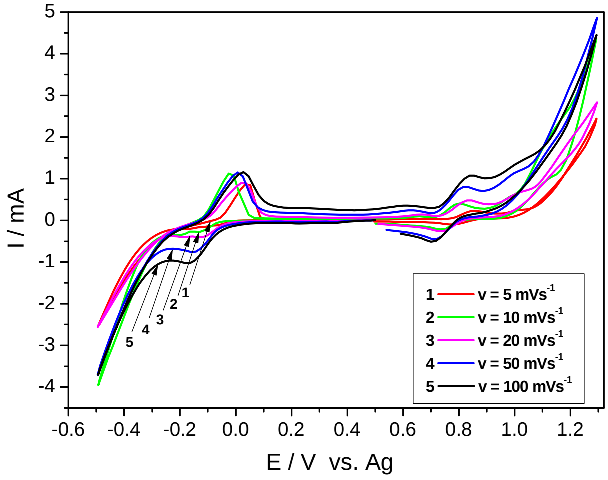

Fig. 2. CV curves on Pt electrode, 60^0C, from ChCl-OxAc + 8 mM $SbCl_3$ ionic liquid

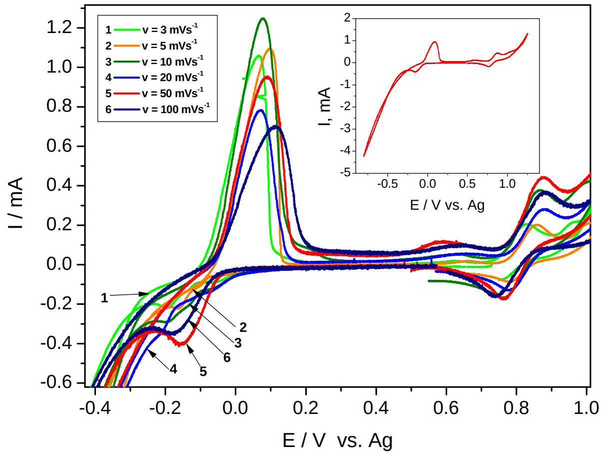

Fig. 3. CV curves on Pt electrode, 60^0C, from ChCl-OxAc + 10 mM $SbCl_3$ ionic liquid. Insert: CV curve for entire potential domain, 50 mV/s scan rate

The voltammograms recorded on glassy carbon electrode (GC) are shown in Figs. 4 and 5; we selected only cathodic/anodic peaks for deposition/stripping dissolution of antimony metal. In general, the shape of CV curves recorded using GC electrode is similar with those using Pt electrode, having the same order of magnitude of current densities, but with more pronounced shifts of peak potentials when scan rate was increased.

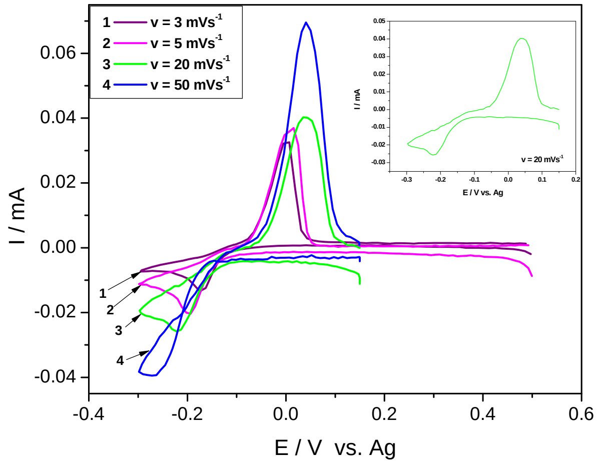

Fig. 4. CV curves on GC electrode, 60^0C, from ChCl-OxAc + 8 mM $SbCl_3$ ionic liquid. Insert: separate CV curve for 20 mV/s scan rate

We can consider that on both Pt and GC electrodes the reduction of Sb^{3+} is a quasi-reversible process with three electron-transfer, and the cathodic shift of the reduction peak can be due partially to a high uncompensated ohmic drop which is usually in ionic liquid media. This process of Sb^{3+} reduction is not a totally irreversible process because the reverse reaction of the electrode process (stripping of antimony layers from Pt or GC surface) occurs.

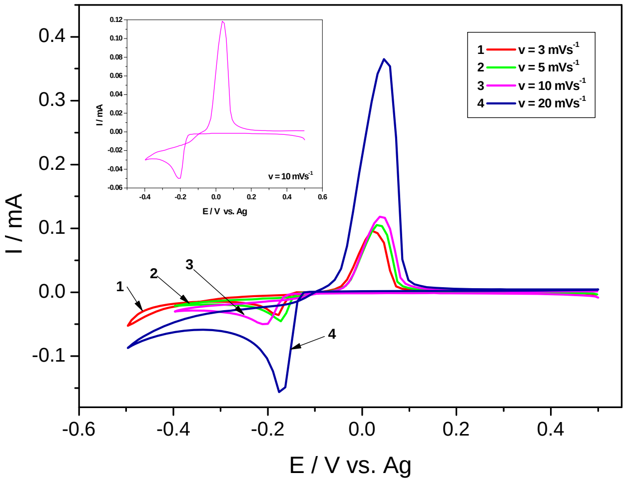

Fig. 5. CV curves on GC electrode, 60^0C, from ChCl-OxAc + 16 mM $SbCl_3$ ionic liquid.
Insert: separate CV curve for 10 mV/s scan rate

In order to demonstrate the mass-transport control (diffusion control) of cathodic process, we represented the plots of cathodic peak current (I_p) *versus* the square root of scan rate ($v^{1/2}$). Some examples of the resulted straight lines are shown in Fig. 6 for Pt electrode.

For determining the diffusion coefficient (D) of Sb^{3+} we used the equation deduced by Schiffrin [37,38]:

$$I_p = 0.62nF\left(\frac{nF}{RT}\right)^{1/2} C \cdot D^{1/2} \cdot A \cdot v^{1/2} \tag{1}$$

where n - number of electrons transferred; F – Faraday constant; A - surface area of working electrode; C – $SbCl_3$ molar concentration, R and T having their usual meanings. Using the slopes of I_{pc} *vs.* $v^{1/2}$ dependences, the averaged values of diffusion coefficients of 2.32 x10^{-7} cm^2/s for Pt electrode and 0.92x10^{-7} cm^2/s for GC electrode were obtained taking n=3, R=8.314 J mol^{-1} K^{-1}, T=333.15 K. Table 1 and Table 2 list the obtained data at different Sb^{3+} concentrations for Pt and GC electrodes, respectively.

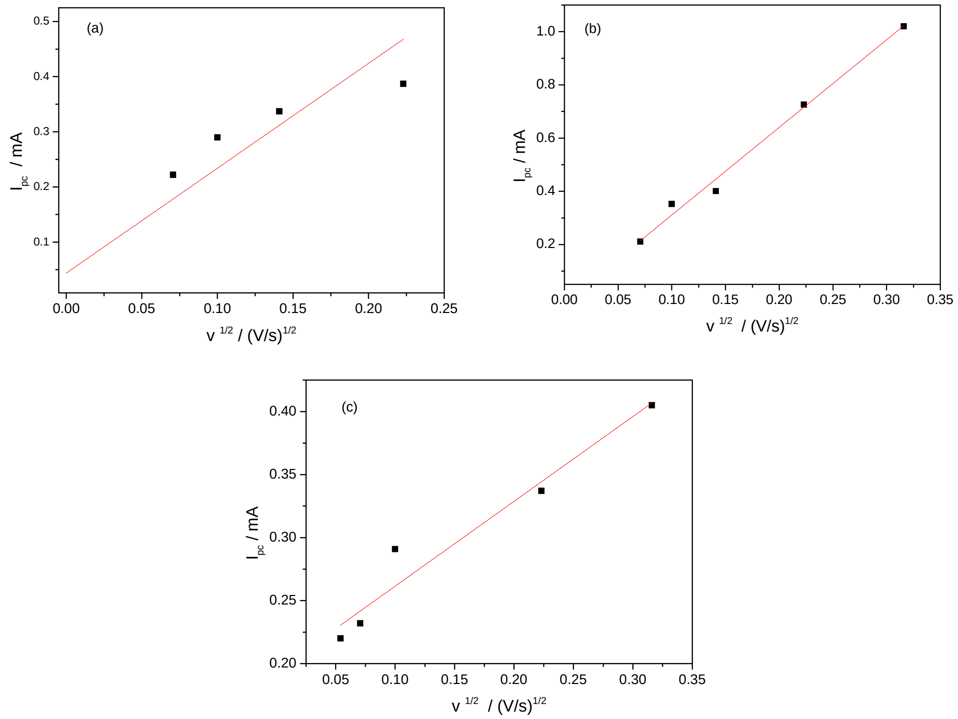

Fig. 6. I_{pc} *vs.* $v^{1/2}$ plots on Pt electrode from ChCl-OxAc electrolytes containing various Sb^{3+} concentrations: a - 5 mM $SbCl_3$; b - 8 mM $SbCl_3$; c - 10 mM $SbCl_3$

Table 1

Diffusion coefficients of Sb^{3+} ion at 60°C, calculated for different systems ChCl + OxAc + x mM $SbCl_3$ using Pt as working electrode

x mM $SbCl_3$	$D \times 10^7$ (cm^2/s)
5	4.15
8	1.88
10	0.94

Table 2

Diffusion coefficients of Sb^{3+} ion at 60°C, calculated for different systems ChCl + OxAc + x mM $SbCl_3$ using glassy carbon (GC) as working electrode

x mM $SbCl_3$	$D \times 10^7$ (cm^2/s)
8	0.46
10	1.37

One should take into account that even though the $D_{Sb^{3+}}$ values obtained in this work varied with increasing antimony ion concentration and nature of electrode, however they are in relatively good agreement with the $D_{Sb^{3+}}$ value (1.19×10^{-6} cm^2/s at 60°C) in ChCl-urea liquid ionic reported by Mares et al. [25].

The differences may be due to different nature electrode, glassy carbon having an inert surface. Another reason may be a variation in concentration of antimony ions present in the electrolyte. It is well-known that $SbCl_4^-$ complex species occurs in all choline chloride based ionic liquids due to existence of a high concentration of Cl^- anions. A decrease in $SbCl_4^-$ concentration may be possible when a high amount of $SbCl_3$ is dissolved, with a corresponding increase of concentration for the Sb^{3+} free ions. Thus the gradual decrease of $D_{Sb^{3+}}$ with Sb^{3+} concentration can be explained (see Table 1). Values for $D_{Sb^{3+}}$ in the case of GC electrode are both obtained in high concentration domain, so the difference may be consider irrelevant.

3.2. Electrode processes of Cu^{2+} ions in ChCl-OxAc ionic liquid

Figs. 7 and 8 show comparatively cyclic voltammograms recorded on Pt in ChCl-OxAc + $CuCl_2$ electrolytes at two Cu^{2+} concentrations and various scan rates. Also, our results are in very good agreement with other published works [26-36] because two reduction peaks and two oxidation peaks can be observed in all cases. However, in our experimental conditions, with $CuCl_2$ as solute, we consider that the peaks, or limiting currents (the case of diluted electrolyte, Fig. 7), recorded within -0.25V ÷ -0.40 V potential range may be attributed to Cu^{2+}/Cu process, with direct deposition of Cu metal. Peak currents or limiting currents increase with scan rate and Cu^{2+} concentration. The anodic stripping peaks at potentials about -0.25 V occur on the oxidation branch of CVs and correspond to Cu^+ ions formation by metal dissolution. The second anodic peaks, located at about 0.6 V, are attributed to Cu^+/Cu^{2+} oxidation; they are followed (after returning of the scan in negative direction) by a Cu^{2+}/Cu^+ reverse process at about 0.45 V (located, therefore, at more positive potential than copper deposition).

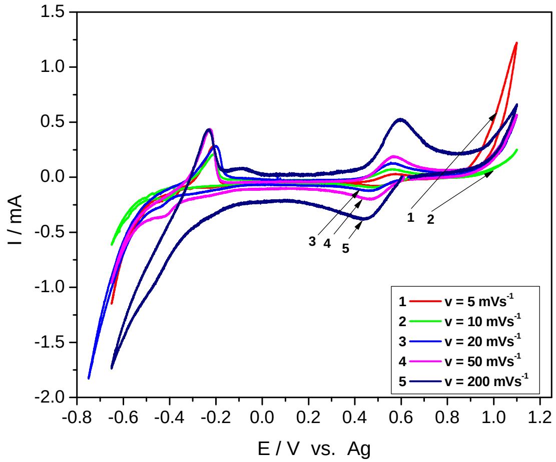

Fig. 7. (a) CV curves on Pt electrode, 60^0C, from ChCl-OxAc + 8 mM $CuCl_2$ ionic liquid

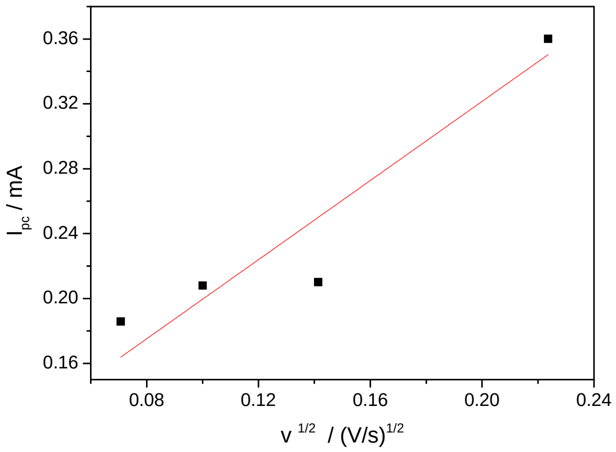

Fig. 7. (b) I_{pc} *vs.* $v^{1/2}$ linear plot for experimental data

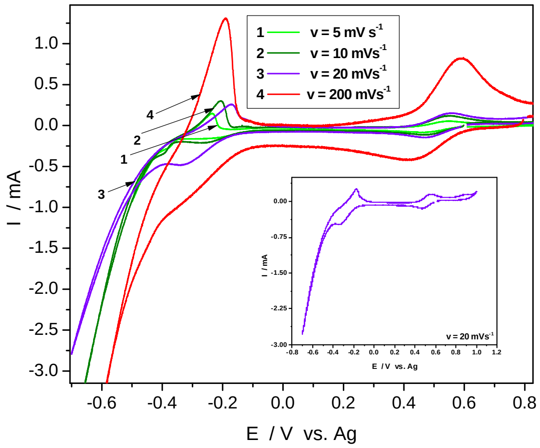

Fig. 8. CV curves on Pt electrode, 60^0C, from ChCl-OxAc + 10 mM $CuCl_2$ ionic liquid
Insert: separate CV curve for 20 mV/s scan rate

Similar shapes of CVs, but with more prominent peaks on both cathodic and anodic branches of voltammograms, were recorded using glassy carbon (GC) electrodes, Fig. 9. Although it is generally accepted that an equilibrium between Cu^{2+} and Cu^{+} ions is established whatever mono- or divalent copper salt is dissolved into electrolyte, we consider that in our experiment the Cu^{2+} concentration is very high compared to Cu^{+} concentration and thus this copper divalent species participates at Faradaic process. The process is quasireversible from electrochemical point of view and is diffusion-controlled. Moreover, in most works we started the potential scanning at more negative values than stationary potential, as can be seen in Fig. 9, in order to avoid Cu^{2+}/Cu^{+} intermediary reduction process. The Cu^{2+}/Cu cathodic process is therefore considered to have n=2 for the transferred electrons.

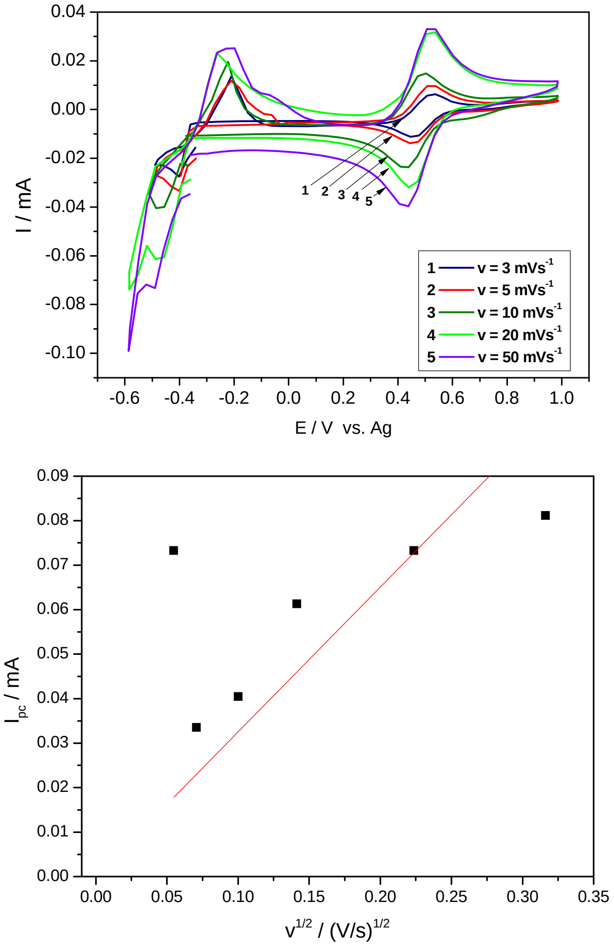

Fig. 9. (a) CV curves on GC electrode, 60^0C, from ChCl-OxAc + 20 mM $CuCl_2$ ionic liquid; (b) I_{pc} *vs.* $v^{1/2}$ linear plot for experimental data

Following the same procedure as in the case of voltammetric analysis for Sb^{3+}/Sb process, we have been able to calculate the diffusion coefficient of Cu^{2+} ion in the ChCl-OxAc ionic liquid media. The averaged values for $D_{Cu}{}^{2+}$ at 60^oC were 1.48 $x10^{-7}$ cm^2/s using Pt electrode and 1.02 $x10^{-7}$ cm^2/s using GC electrode.

These obtained values are in very good agreement with other published values of diffusion coefficient of Cu^{2+} (cm^2/s): 0.741 $x10^{-7}$ at 313 K in ChClglycelyne [26] and 0.139 $x10^{-7}$ at 333 K in ChCl-urea [28], 4.97 $x10^{-7}$ at 323 K in ChCl- ethylene glycol (ChCl-EG) [33] and 1.22 $x10^{-7}$ at 296 K in ChCl- ethylene glycol ChCl-EG [34,35].

Referring to speciation of copper ion into ChCl-OxAc - $CuCl_2$ electrolyte it is also expected to be a mixture between Cu^{2+} free ions, $CuCl_4^{2-}$ complex ions and, of course, Cu^+ free ions (due to mentioned disproportionation reaction). Taking into account the characteristic structure of ChCl-OxAc solvent and experimental conditions, we can suppose that Cu^{2+} free ions exist in a large majority.

4. Conclusions

Families of cyclovoltammograms recorded from ChCl-OxAc ionic liquids with dissolved $SbCl_3$ or $CuCl_2$ exhibited clearly two couples for both Sb^{3+} and Cu^{2+}. However, the supplementary couple in both cases has been not taken into consideration. Our results showed clearly that Sb^{3+} and Cu^{2+} can be reduced to Sb and to Cu in the ionic liquids formed from binary mixtures of choline chloride with oxalic acid. The processes are quasi-reversible but are diffusion controlled.

Using the equation proposed for insoluble products deposited on cathode, we obtained values of the order of 10^{-7} cm^2/s, that are reliable results for diffusion coefficients of Sb^{3+} and Cu^{2+} in ChCl-OxAc containing ionic liquids.

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REFERENCES

1. *M.-H. Yang, I.-W. Sun*, "Electrodeposition of antimony in a water-stable 1-ethyl-3-methylimidazolium chloride tetrafluoroborate room temperature ionic liquid”, J. Appl. Electrochem., vol. 33, 2003, pp. 1077-1084.
2. *M.-H. Yang, M.-C. Yang, I.-W. Sun*, "Electrodeposition of indium antimonide from the water-stable 1-ethyl-3-methylimidazolium chloride/tetrafluoroborate ionic liquid”, J. Electrochem. Soc., vol. 150, no. 8, 2003, pp. C544-C548.
3. *H. Ebe, M. Ueda, T. Ohtsuka*, "Electrodeposition of Sb, Bi, Te, and their alloys in $AlCl_3$–NaCl–KCl molten salt”, Electrochim. Acta, vol. 53, 2007, pp. 100-105.
4. *M. Ueda, Y. Mito, T. Ohtsuka*, "Electrodeposition of Sb-Te alloy in $AlCl_3$-NaCl-KCl molten salt”, Mater. Trans., vol. 49, no. 8, 2008, pp. 1720-1722.
5. *W. Yang, H. Cang, Y. Tang, J. Wang, Y. Shi*, "Electrodeposition of tin and antimony in 1-ethyl-3-methylimidazolium tetrafluoborat ionic liquid", J. Appl. Electrochem., vol. 38, 2008, pp. 537-542.

6. *F.X. Wang, G.B. Pan, Y.D. Liu, Y. Xiao*, "Electrodeposition of Sb on Au(111) from an acidic chloroaluminate ionic liquid: An in situ STM study", J. Phys. Chem. C, vol. 114, 2010, pp. 4576–4579.
7. *H. P. Nguyen, X. Peng, G. Murugan, R. J. Vullers, P. M. Vereecken, J. Fransaer*, "Electrodeposition of antimony, tellurium and their alloys from molten acetamide mixtures", J. Electrochem. Soc., vol. 160, no. 2, 2012, pp. D75-D79.
8. *S. Zein El Abedin, A.Y. Saad, H.K. Farag, N. Borisenko, Q.X. Liu, F. Endres*, "Electrodeposition of selenium, indium and copper in an air- and water-stable ionic liquid at variable temperatures", Electrochim. Acta, vol. 52, 2007, pp. 2746-2754.
9. *T. I. Leong, I. Sun, M. Deng, C. Wu, P. Chen*, "Electrochemical study of copper in 1-ethyl-3-methylimidazolium dicyanamide room temperature ionic liquid", J. Electrochem. Soc., vol. 155, no. 4, 2008, pp. F55-F60.
10. *I. Ben Assaker, M. Dhahbi*, "Electrochemical study and electrodeposition of copper in the hydrophobic tri-n-octylmethylammonium chloride ionic liquid media", J. Molec. Liquids, vol. 161, 2011, pp. 13–18.
11. *S. Zein El Abedin, A. Prowald, F. Endres*, "Fabrication of highly ordered macroporous copper films using template-assisted electrodeposition in an ionic liquid", Electrochem. Commun., vol. 18, 2012, pp. 70-73.
12. *P.Y. Chen, Y.T. Chang*, "Voltammetric study and electrodeposition of copper in 1-butyl-3-methylimidazolium salicylate ionic liquid", Electrochim. Acta,vol. 75, 2012, pp. 339-346.
13. *P. Yang, Y. Zhao, C. Su, K. Yang, B. Yan, M. An*, "Electrodeposition of Cu–Li alloy from room temperature ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate", Electrochim. Acta, vol. 88, 2013, pp. 203-207.
14. *G. Saravanan, S. Mohan*, "Nucleation of copper on mild steel in copper chloride ($CuCl_2.2H_2O$)-1-ethyl-3-methylimidazolium chloride [EMIM]Cl-ethylene glycol (EG) ionic liquid", New J. Chem., vol. 37, no. 8, 2013, pp. 2564-2567.
15. *T. Vainikka, D. Lloyd, L. Murtomaki, J.A. Manzanares, K. Kontturi*, "Electrochemical study of copper chloride complexes in the RTIL 1-butyl-1-methylpyrrolidinium bis (trifluoromethyl sulfonyl)imide", Electrochim. Acta, vol. 87, 2013, pp. 739-748.
16. *T. Liu, R. Vilar, S. Eugenio, J. Grondin, Y. Danten*, "Electrodeposition of nanocrystalline copper thin films from 1-ethyl-3-methylimidazolium ethylsulphate ionic liquid", J. Appl. Electrochem., vol. 44, no. 1, 2014, pp. 189-198.
17. *T. Liu, R. Vilar, S. Eugenio, J. Grondin, Y. Danten*, "Electrodeposition of nanocrystalline copper thin films from 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide", J. Appl. Electrochem., vol. 45, no. 1, 2015, pp. 87-93.
18. *S. Vanderaspoilden, J. Christophe, Th. Doneux, C. Buess-Herman*, "Contrasted electrochemical behaviour of Cu(I) and Cu(II) ions in 1-butyl-3-methylimidazolium dicyanamide", Electrochim. Acta, vol. 162, 2015, pp.156-162.
19. *A. Florea, A. Petica, L. Anicai, T. Visan*, "Preliminary studies of silver coatings formation from choline chloride based ionic liquids", UPB Sci.Bull. Series B, vol. 72, no. 2, 2010, pp. 115-126.
20. *M.L. Mares Badea, A. Cojocaru, L. Anicai*, "Electrode processes in ionic liquid solvents as mixtures of choline chloride with urea, ethylene glycol or malonic acid", UPB Sci. Bull. Series B, vol. 76, no. 3, 2014, pp. 21-32.

21. *F. Golgovici, A. Cojocaru, M. Nedelcu, T.Visan*, "Voltammetric and impedance studies of electrodeposition of Te and its binary compounds with Bi and Sb using choline chloride - urea based electrolyte", *Chalcog. Lett.*, vol. 6, no. 8, 2009, pp. 323-333.
22. *F. Golgovici, A. Cojocaru, C. Agapescu, Y. Jin, M. Nedelcu, W. Wang, T. Visan*, "Electrodeposition of bismuth, tellurium and antimony from ionic liquids based on choline chloride and urea as thermoelectric films", Studia Univ. Babes-Bolyai, Chemia, vol. 54, Spec. Issue 1, 2009, pp. 175-188.
23. *F. Golgovici, A. Cojocaru, M. Nedelcu, T. Visan*, "Cathodic deposition of components in BiSbTe ternary compounds as thermoelectric films using choline-chloride-based ionic liquids", J. Electron. Mater., vol. 39, no. 9, 2010, pp. 2079-2084.
24. *F. Golgovici, A. Cojocaru, L. Anicai, T. Visan*, "Surface characterization of BiSbTe thermoelectric films electrodeposited from chlorides aqueous solutions and choline chloride based ionic liquids", Mater. Chem. Phys., vol. 126, no. 3, 2011, pp. 700-706.
25. *M.L. Mares, F. Golgovici, T. Visan*, "RDE voltammetry and impedance spectroscopy studies of Sb, Te and SbTe electrodeposition from choline chloride – urea ionic liquids", Chalcog. Lett., vol. 10, no. 8, 2013, pp. 259-272.
26. *B.G. Pollet, J.-Y. Hihn, T.J. Mason*, "Sono-electrodeposition (20 and 850 kHz) of copper in aqueous and deep eutectic solvents", Electrochim. Acta, vol. 53, 2008, pp. 4248–4256.
27. *A.P. Abbott, K. El Ttaib, G. Frisch, K.J. McKenzie, K.S. Ryder*, "Electrodeposition of copper composites from deep eutectic solvents based on choline chloride", Phys. Chem. Chem. Phys., vol. 11, no. 21, 2009, pp. 4269-4277.
28. *A.M. Popescu, V. Constantin, A. Cojocaru, M. Olteanu*, "Electrochemical behaviour of copper (II) chloride in choline chloride-urea deep eutectic solvent", Rev. Chim. (Bucharest), vol. 62, no. 2, 2011, pp. 206-211.
29. *A.M. Popescu, V. Constantin, M. Olteanu, O. Demidenko, K. Yanushkevich*, "Obtaining and structural characterization of the electrodeposited metallic copper from ionic liquids", Rev. Chim. (Bucharest), vol. 62, no. 6, 2011, pp. 626-632.
30. *C.D. Gu, Y.H. You, X.L. Wang, J.P. Tu*, "Electrodeposition, structural, and corrosion properties of Cu films from a stable deep eutectics system with additive of ethylene diamine", Surf. Coat. Technol., vol. 209, 2012, pp. 117-123.
31. *A.M. Popescu, A. Cojocaru, C. Donath, V. Constantin*, "Electrochemical study and electrodeposition of copper(I) in ionic liquid-reline", Chem. Res. Chinese Univ. Chem. Res. Chinese Univ., vol. 29, no. 5, 2013, pp. 991-997.
32. *J.C. Malaquias, M. Steichen, M. Thomassey, P.J. Dale*, "Electrodeposition of Cu–In alloys from a choline chloride based deep eutectic solvent for photovoltaic applications", Electrochim. Acta, vol. 103, 2013, pp. 15-22.
33. *A. Mandroyan, M. Mourad-Mahmoud, M.-L. Doche, J.-Y. Hihn,* "Effects of ultrasound and temperature on copper electroreduction in Deep Eutectic Solvents (DES)", Ultrasonics Sonochem., vol. 21, no. 6, 2014, pp. 2010-2019.
34. *S. Ghosh, S. Roy,* "Electrochemical copper deposition from an ethaline-$CuCl_2{\cdot}2H_2O$ DES", Surf. Coat. Technol., vol. 238, 2014, pp. 165-173.
35. *S. Ghosh, K. Ryder, S. Roy*, "Electrochemical and transport properties of ethaline containing copper and tin chloride", Trans. IMF, vol. 92, no. 1, 2014, pp. 41-46.
36. *S. Xing*, *C. Zanella*, *F. Deflorian*, "Effect of pulse current on the electrodeposition of copper from choline chloride-ethylene glycol", J. Solid State Electrochem., vol. 18, no. 6, 2014, pp. 1657-1663.

37. *D.J. Schiffrin*, "Theory of cyclic voltammetry for reversible electrodeposition of insoluble products", J. Electroanal. Chem., vol. 201, 1986, pp. 199-203.

38. *L.A. Avaca*, *S. Kaufmann*, *K. Kontturi*, *L. Murtomaki*, *D.J. Schiffrin*, "Theory of cyclic voltammetry for quasi-reversible electrodeposition reactions with insoluble products", Berichte Bunsenges. Physik. Chemie, vol. 97, no. 1, 1993, pp. 70–76.