Copper electrodeposition from a chloride free deep eutectic solvent

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1. Introduction

Nowadays copper is largely used in the electronic industry to manu-facture semiconductor based products. This is related to the recent replacement of Al with Cu in microelectronic interconnections produc-tion, which increased the performances in terms of lower electrical resistance, higher thermal conductivity and lower cost [1,2]. As a side effect, the need of developing economically affordable and reliable pro-cesses to plate copper having the required features became a priority. Copper electroplating is commercially carried out using aqueous solu-tions [3–5] due to the high solubility of the corresponding metal salts resulting in high conductivity of the electrolytes and consequent good throwing power. Nonetheless some issues such as their toxicity, corrosivity (pH ≪ 1) and environmental impact leaded to the investiga-tion of less dangerous electrolytes, like ionic liquids [6]. The use of these novel solvents is a promising way to solve the cited issues, as evidenced by the significant number of research publications on the topic in the last decades (especially on the deposition of metals that cannot be reduced in aqueous solutions due to the limited potential window of water) [7–11]. In different research fields electrodeposition of copper has been performed from various ionic liquids, and the chloroaluminate based were considered the first generation of ILs to fulfil this purpose [12–14]. Some limitations related to these solvents such as reactivity towards air and water forced the researchers to focus on alternative ILs having less reactive anions compared to haloaluminate ionic liquids [15–17]. Among the air and water stable ILs, deep eutectic solvents (DESs) based on quaternary ammonium salts have been selected recently due to their moisture stability, low price, biodegradability, non-toxicity, and ease of synthesis and handling. The synthesis of these solvents can be done simply by mixing quaternary ammonium salts with hydrogen bond donors (such as amines or carboxylic acids) [18,19], and the most studied electrolytes belonging to this category are based on choline chloride (ChCl) as ammonium compound [20, 21]. Copper electroreduction, its electrochemical characteristics [8, 22–26] and the relative speciation [27] in these electrolytes has been fully characterized, and the plating has been achieved successfully [26,28].

The present work investigates for the first time the influence of the physical properties of electrolytes based on choline dihydrogencitrate (CDHC) mixed in different ratios with a hydrogen bond donor such as ethylene glycol (EG) on the deposition of copper on a nickel substrate. In particular the relation between chemistry, viscosity, conductivity of the solutions and the quality of the Cu layer obtained is evidenced. The actual possibility of good quality metal deposition from the new electrolytes is demonstrated as well. Chloride free quaternary ammonium salts are used in this work instead of choline chloride, and by doing this the intention is to remove the chloride ion from the electrolyte and study the properties of solutions prepared using a choline chloride homologue (CDHC). A possible reason to remove Cl^- can be found in its aggressiveness towards reactive metals like Al and Mg, or in its low compatibility with the plating on thin films of metals sensitive to the presence of Cl^- (Fe, Ni). Another advantage connected with the use of a chloride free homologue of ChCl is the reduced hygroscopicity of the resulting DES, as ChCl is characterized by a high affinity towards

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atmospheric moisture. If compared to choline chloride based ILs the two organic mixtures present different interactions between the components, resulting in different physical properties. In particular the ratio between the quaternary ammonium salt and the hydrogen bond donor suitable to achieve the eutectic composition, that is 1:2 molar for ChCl/EG, is expected to change. For this reason different ratios CDHC/EG were tested to achieve ideal complexation of the DHC^- ion. The starting point of the experimentation was the determination of the physical properties of the pure electrolytes, including ChCl/EG for comparison. This was done measuring viscosity and conductivity for the pure electrolytes. To test the possibility of Cu deposition a metal salt was added, and the resulting solutions were characterized from the electrochemical point of view using cyclic voltammetry. Copper sulphate was selected as source of metal to avoid the presence of Cl^-. Finally copper was deposited from the resulting plating baths, including ChCl/EG + $CuSO_4$ for comparison, on nickel substrates. To support the work, the morphological characterization of the copper layers through analysis like SEM, microprofilometry and XRD are provided.

2. Experimental methods and materials

2.1 Electrolytes preparation, physical characterization and electrochemical investigation

Two different types of organic mixtures were formulated using the following chemicals: choline chloride (ChCl), ethylene glycol (EG) and choline dihydrogencitrate (CDHC). All chemicals were purchased from Sigma-Aldrich and used as received. The solutions were formed by combination of two components in the following molar ratios: 1:2 for ChCl/EG, 1:2–1:3–1:4 for CDHC/EG. In ChCl/EG 1:2 and CDHC/EG 1:4, $CuSO_4$ (200 mM) was added. An additional plating test was performed using a 600 mM $CuSO_4$ CDHC/EG 1:4 solution. Cyclic voltammetries were performed using a Solartron Modulab potentiostat/galvanostat. For the electrochemical characterization of pure electrolytes glassy carbon, platinum and graphite were used as working, reference and counter electrode respectively. In particular as working electrodes were used PEEK encapsulated glassy carbon tips of the E3 RDE series by Pine Research Instrumentation, suitable to work at 80 °C. Platinum was used as pseudo-reference [29] due to the high temperatures of the baths. For the electrochemical investigation of the copper electrolytes glassy carbon, platinum and copper were used as working, reference and counter electrode respectively. All the electrochemical tests were carried out at 80 °C and no stirring was applied. The conductivity measurements were done using a parallel Pt plates Amel 160 conductivimeter. Prior to measurement process, the ILs were heated at 90 °C and then cooled to examine their conductivity at different temperatures. The viscosity was measured using a Viscotester VT5L/R equipped with a low viscosity adapter. The samples were heated at 90 °C for the first measure and then cooled until 60 °C, controlling the rate with a thermocouple to obtain results at different temperatures.

2.2 Copper electrodeposition

The electrodeposition of copper was carried out in a cell using two electrodes and a Solartron Modulab potentiostat/galvanostat. The anode and the cathode were copper and 316 stainless steel plates respectively. Ni plating was performed on the 316 stainless steel prior to copper deposition. A sulfamate solution including 200 g/L Ni sulfamate, 10 g/L Ni chloride, 30 g/L boric acid and 2 g/L saccharine was used. The plating was done at 30 °C for 10 min using as current density 10 mA/cm^2. The copper electrodeposition process was fulfilled for each copper electrolyte with current density 5 mA/cm^2 and stirring rate of the bath (obtained via magnetic stirrer) 300 rpm at $T = 80$ °C for different times. Such low current density (5 mA/cm^2) was employed to compare the quality of the layers in low growth rate conditions. After each deposition, the samples were washed with water and dried under nitrogen flow. Efficiency was calculated comparing the weight of the samples before and after the deposition. The surface morphology of copper layers was analyzed by mean of a Zeiss EVO 50 scanning electron microscope. XRD analysis was performed using a Philips PW 1830 in Bragg–Brentano configuration. The instrument used to determine the thickness of copper deposits was a Fischerscope X-RAY XAN and the roughness measurements were performed using a Ubm Microfocus laser profilometer. Microhardness was measured on the sections of the samples using a Fischerscope HCU microindenter in Vickers configuration and applying a 50 mN load. The sections of the samples were observed using a Leica DMLM in direct illumination mode.

3. Results and discussion

3.1 Appearance and chemistry of the electrolytes

ChCl/EG is well characterized in the existing literature in its pure form as well as mixed with copper chloride [28] to give a typically orange-brown colored solution. This color is due to the characteristic radiation absorption at 400 nm (blue light) of the tetrachloride $[CuCl_4]^{2-}$ complex [27,30], and is typical not only of Cu^{2+} containing ChCl/EG but also of $[CuCl_4]^{2-}$ in aqueous solutions rich in Cl^- ions [31]. The appearance of the electrolyte obtained in the present work using $CuSO_4$ as copper source was identical to equivalent 0.2 M $CuCl_2$ ChCl/EG solutions [28], presenting the same absorption wavelength. CDHC/EG, composed of a quaternary ammonium salt and a hydrogen bond donor, is a properly named DES like ChCl/EG. The dihydrogencitrate moiety is therefore at some extent complexed by EG. CDHC/EG + $CuSO_4$ presented a dark blue color, similar to what observed for aqueous solutions.

A complete speciation description is beyond the goals of the present work, but a preliminary analysis of the possible species present in the three electrolytes can be extrapolated from their behavior and their appearance. From the literature on copper ions dissolved in ChCl/EG is possible to associate the orange-brown color of the solution described in the present work with the presence of the $[CuCl_4]^{2-}$ specie. The tetrachloro complex is the most probable electroactive specie present in the melt formed using anhydrous copper sulphate. For CDHC/EG + $CuSO_4$ is reasonable to state that Cu^{2+} ions are complexed by citrate, giving species of the kind $[Cu(H_2Cit)_m]^{2-m}$. This is supported by the consideration that starting CDHC was anhydrous and no water was added, making possible to minimize water influence. Moreover, the negligible solubility of anhydrous $CuSO_4$ in EG excludes the possibility that the dissolution of the salt is not due to a citrate complex formation.

3.2 Ionic conductivity

The first property of interest was electrical conductivity of the pure solutions, since current efficiency of these electrolytes is related to their ionic conductivity. Fig. 1 represents the behavior of the ChCl/EG and CDHC/EG solutions at constant compositional ratio.

As shown in Fig. 1, the conductivity of the CDHC based electrolyte is lower than the conductivity of the ChCl based (which is consistent with values present in the literature [32]). This phenomenon can be de-scribed by taking into account the fact that a larger sterical size of the ions (comparing Cl^- and DHC^-) decrease their mobility in an electro-lyte exposed to an electrical field. In addition, the influence of tempera-ture on the conductivity of ionic liquids can be clearly observed: a higher temperature increases ion mobility, in agreement with the Vogel–Fulcher–Tamman equation [33].

Another factor that affects the electrical conductivity of ionic liquids is the concentration of the hydrogen bond donor (HBD) and this effect was examined by adding more EG to CDHC/EG 1:2. The results obtained are described by Fig. 2.

The addition of more HBD (EG) separate cations and anions and reduce the interaction between them, helping therefore ions to move easily and increasing the ionic conductivity. Furthermore it decreases the

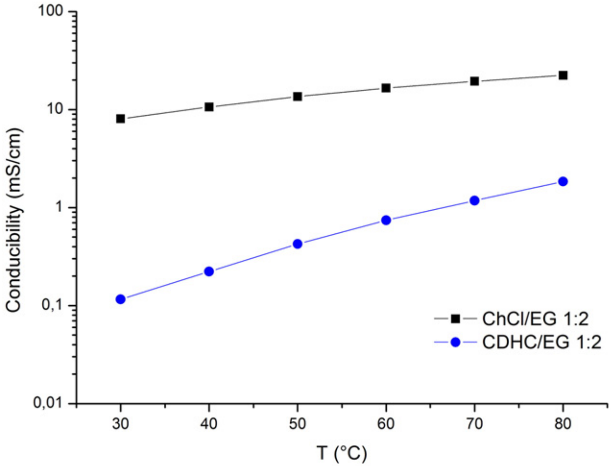

Fig. 1. Conductivity of ChCl/EG and CDHC/EG at 1:2 ratio vs. T.

viscosity of the electrolyte, increasing consequently ions mobility. Ionic conductivity was measured also after the addition of copper sulphate, and Table 1 reports the results obtained.

The plating temperature of 80 °C was selected and two different amounts of $CuSO_4$ were tested in the case of CDHC/EG. CDHC/EG 1:4 was selected between the different ratios for its high conductivity, which is poorly increased by the presence of $CuSO_4$. Also after the addition of $CuSO_4$ the conductivity reaches values one order of magnitude lower than ChCl/EG at equivalent metal salt content.

3.3 Viscosity measurements

Electrochemical processes are more influenced by viscosity in ILs than in water based solutions. This physical property was therefore con-sidered in this work, and Fig. 3 shows the viscosity vs. temperature for the different DESs. For comparison, viscosity of water is 0.355 mPa·s at 80 °C.

The viscosity of the organic mixtures considered did not change by varying shear rate in the mentioned temperature range, and for this reason these fluids are all Newtonian. As observed in the graph, the viscosity values of the ChCl based electrolyte are in good agreement with the literature [34]. The influence of HBD content on the viscosity of CDHC/EG is also studied in Fig. 3. It is evident from the graph that the viscosity of CDHC/EG strongly depends on the ratio between the two chemicals. In the 1:2 molar ratio of this mixture, the viscosity has values ten times higher than ChCl/EG. This feature can be attributed to the sterical size of dihydrogencitrate, that is far larger than Cl^- in ChCl/EG. The experimental values agree with an Arrhenius relation of the kind:

Table 1
Comparison of the copper plating baths conductivity (σ) with the pure electrolytes (at 80 °C).

DES	$CuSO_4$ added	Pure (mS/cm)	Cu bath (mS/cm)	$\Delta\sigma$ (%)
ChCl/EG	200 mM	22.31	26.84	+20.3
CDHC/EG 1:4	200 mM	4.15	4.19	+0.96
CDHC/EG 1:4	600 mM	4.15	4.28	+3.13

$$\eta_i = \eta_0 e^{\left(\frac{E_a}{RT}\right)}$$

where η_0 is the hypothetical viscosity at infinite temperature and E_a the activation energy for viscous flow [34]. The values obtained from the mathematical fitting (Fig. 2(b)) are in agreement with what was observed measuring the viscosity: higher viscosities are related to higher threshold energy values to have viscous flow. Fig. 4 reports the activation energies for the four electrolytes considered.

The reference ChCl/EG value of 25.43 kJ/mol [34] is similar to the observed one and the quality of the fitting is acceptable ($r \gg 0.995$). The values of η_0 are reported as well: 4.87×10^{-3} mPa·s for ChCl 1:2, 9.21×10^{-6} mPa·s for CDHC 1:2, 3.62×10^{-5} mPa·s for CDHC 1:3, 7.11×10^{-5} mPa·s for CDHC 1:4. No significative effects were observed on the viscosity after the addition of $CuSO_4$.

3.4 Electrochemical behavior

In order to investigate the electrochemical behavior of pure electro-lytes, cyclic voltammetry was performed. Fig. 5 shows the cyclic voltam-mogram of pure ChCl/EG 1:2 at the scan rate of 20 mV/s. The potential window can be determined between −2 V and 1.25 V, and such range corresponds to what was observed in previous literature for the same electrolyte [25]. Fig. 5 makes also possible to estimate the potential win-dow of the pure CDHC/EG 1:4 ionic liquid between −1 V and 1 V. The significantly higher lower limit of the CDHC/EG potential window with respect to ChCl/EG is probably related to the reduction of H^+ ions coming from the DHC^+ cation to elemental hydrogen or from mois-ture contamination.

The cyclic voltammograms of 200 mM $CuSO_4$ in ChCl/EG 1:2, shown in Fig. 6, reveal that there are two Cu reduction peaks on the cathodic branch of the diagram. In particular, at 10 mV/s, the $Cu^{2+} + e^- \rightarrow Cu^+$ peak is seen around 0.2 V (R_{Cu1}) while the $Cu^+ + e^- \rightarrow Cu^0$ is observed around − 0.75 V (R_{Cu2}). Copper electroreduction proceed thus following the well-known two step

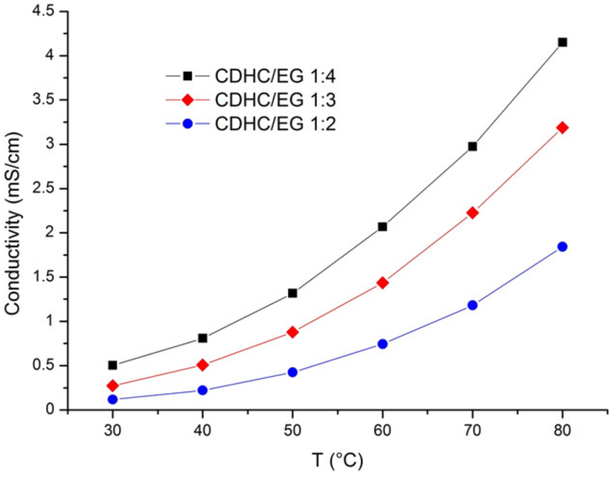

Fig. 2. Conductivity of ChCl/EG and CDHC/EG at 1:2 ratio vs. T.

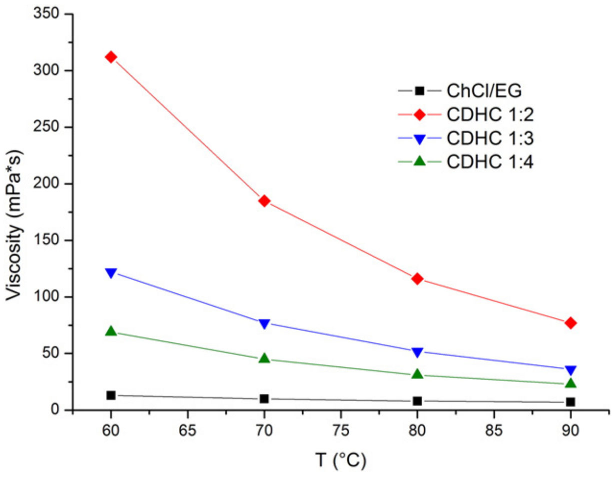

Fig. 3. Viscosity vs. T in ChCl/EG, CHDHC/EG.

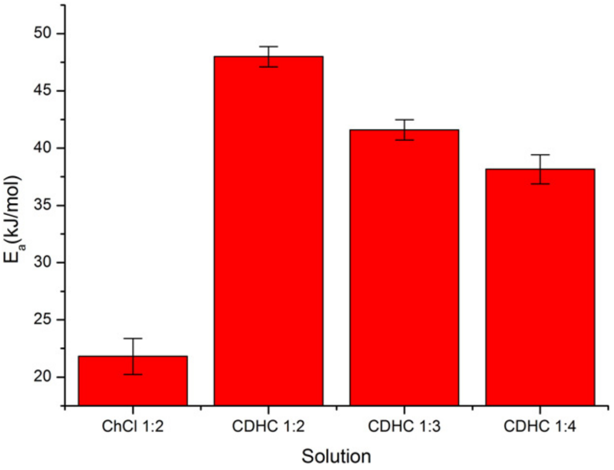

Fig. 4. Activation energies for the viscous flow for ChCl/EG 1:2 and CDHC/EG at various ratios.

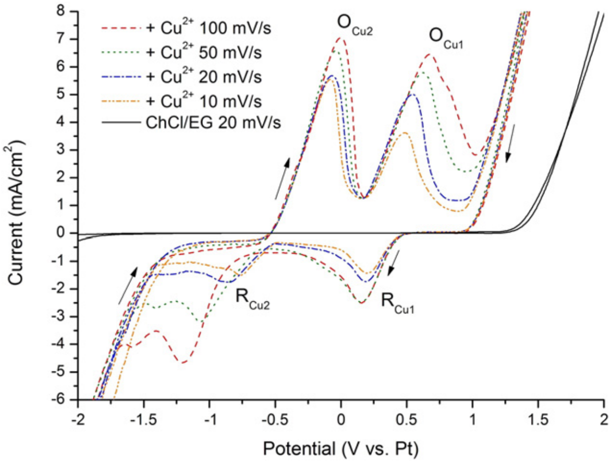

Fig. 6. Cyclic voltammograms of ChCl/EG + 200 mM $CuSO_4$ at different scan rates.

reduction process Cu(II)/Cu(I) + Cu(I)/Cu(0) already observed in the case of $CuCl_2$ in choline chloride and urea mixtures [25]. The presence of a Cu(II)/Cu(I) peak is a consequence of the Cu(I) stabilization operated by the Cl^- ion present in the bath. This phenomenon is well documented also in the case of aqueous solutions [35].

The corresponding oxidation reactions (O_{Cu2} and O_{Cu1}) are visible in the anodic zone at 0 V and 0.5 V, depending on the scan speed. In this experiment, the increase of scanning rate shifted the reduction peaks to lower potentials and the oxidation peaks to higher potentials. This can be indicative of slow charge transfer rate in reactions occurring on the surface and it is evident in particular for the R_{Cu2} peak. The peak shift observed is also a consequence of the high solution resistance, as observed by Popescu et al. [25], which introduce an IR ohmic drop in the ionic liquid. A mass transfer control in the zone located after the R_{Cu1} reduction peak can be hypotized observing the plateau between -0.1 V/-0.8 V. The behavior of the system appears quasi-reversible, with copper electroreduction occurring from the well-known two step mechanism [25]. Different voltammetric cycles overlap in a good way, as observed by Popescu et al. [25].

Fig. 7 shows the cathodic and anodic processes related to CDHC/EG 1:4 + 600 mM $CuSO_4$. In the cathodic part of the diagram, at 10 mV/s, a peak associated with the reduction of Cu^{2+} is present at -0.6 V (R_{Cu}). Comparing with the graph of the pure DES, is possible to include the zone in the potential window and associate this feature to the reduction to Cu^0. At higher scan speeds the same feature is visible as a change in slope of the curve. No peaks related to the $Cu^{2+} + e^- \rightarrow Cu^+$ reaction can be observed. This fact is a consequence of the absence of Cl^- ions, the chemical specie that stabilizes the Cu(I) in the case of the ChCl/EG DES. On the anodic branch only one oxidation peak at 20 mV/s can be seen around 1 V. The position of the anodic peaks is considerably altered by the scan rate adopted for the test and this is indicative of a slow charge transfer rate. This is true also in the case of the cathodic feature R_{Cu}, which position and intensity were evaluated as a function of scan speed (Fig. 8). To determine its position, the zone where the concavity of the curve changed was considered, allowing to estimate the displacement also in the absence of a well-defined peak.

The current intensity of the peak is correlated to different parameters of the electrochemical reaction by [36]:

$$\frac{i}{A} = j = \left(2.69 \times 10^5\right) n^{3/2} {D_{Cu}}^{1/2} C_{Cu} v^{1/2} = Bv^{1/2}$$

i/A is the current density, n is the number of electrons transferred during the reaction, D_{Cu} is the diffusion coefficient of the Cu ions, C_{Cu} is the concentration of copper and v is the scan speed. Operating a linear fitting on the experimental points is possible to estimate a value of 0.15 for B, slope of the linearized relationship. Considering the concentration of copper ions C_{Cu} equal to 0.6 M and the number of transferred electrons equal to 2 a diffusion coefficient of 1.08×10^{-9} cm^2 s^{-1} can be estimated. This value is one order of magnitude lower than the typical value observed (1.39×10^{-8} cm^2 s^{-1}) in the case of ChCl/EG mixtures containing copper ions [25] and is indicative of a strongly diffusion controlled deposition process.

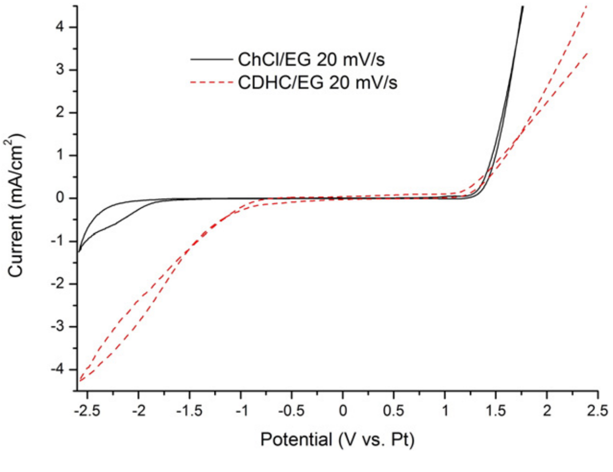

Fig. 5. Cyclic voltammograms of the pure DESs.

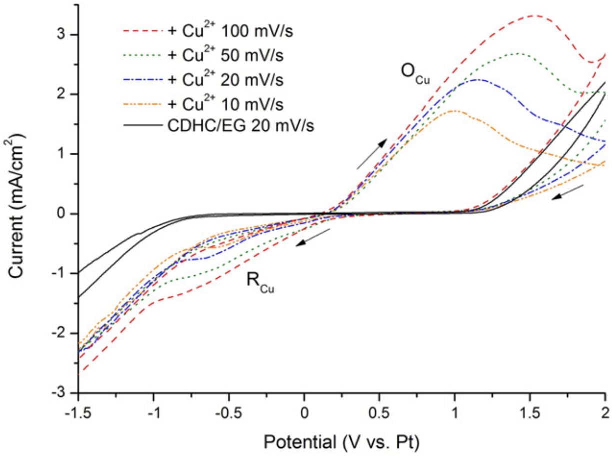

Fig. 7. Cyclic voltammograms of CDHC/EG + 600 mM $CuSO_4$ at different scan rates.

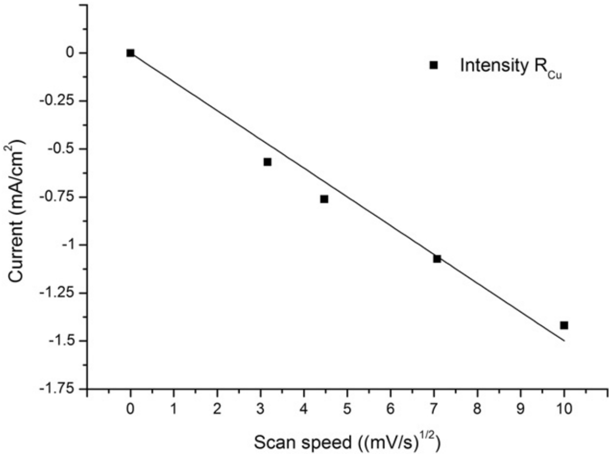

Fig. 8. R_{Cu} peak intensity as a function of scan speed square root.

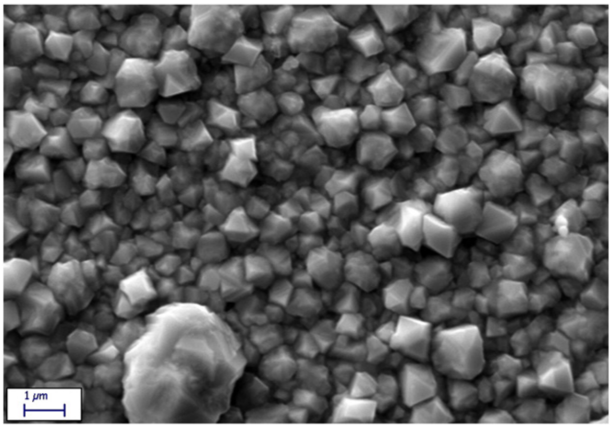

Fig. 9. SEM micrograph of the copper deposit obtained at 5 mA/cm², 20 min of deposition time and stirring rate 300 rpm at T = 80 °C from ChCl/EG 1:2 + 200 mM $CuSO_4$ (25,000×; high vacuum; secondary electrons).

3.5 Copper deposition from the two electrolytes

As one of the main goals of this work was the investigation of the possibility of metal deposition from the two formulated electrolytes, different electroplating tests were performed to verify the possibility of Cu deposition and to compare the resulting coatings with the ones obtained from well-known ILs (the ChCl based DES). The operating parameters were kept constant to favor the comparison. The cathodic efficiency (η), thickness and roughness (R_t and R_a) of the samples obtained using the three different electrolytes together with working conditions are reported in Table 2. Ni electroplating on stainless steel had an important role, providing a reproducible surface for copper deposition.

As visible in Fig. 9, a uniform and compact deposit was achieved from ChCl/EG + $CuSO_4$ at 5 mA/cm². The surface presents a morphology similar to the one obtained from ChCl/EG when using $CuCl_2$ as copper source [28]. Copper was deposited also from CDHC/EG. CDHC/EG in both 1:2 and 1:3 ratios was characterized by a high viscosity and this caused porous and dark deposits in comparison with deposits obtained from ChCl/EG + $CuSO_4$. The same working conditions as those for deposition from the previous electrolyte were applied to the 1:4 CDHC/EG solutions. Fig. 10 present the sample obtained observed with SEM.

In Fig. 10 a considerably rough and porous deposit is visible, probably induced by a combination of high viscosity of the solution and low metal ion concentration. The exterior appearance of the sample is characterized by a dull red layer of copper.

Since the reduction reaction is strongly diffusion limited, as evidenced by the voltammetric study, a possible method to improve the deposition can be the increase of the metal ion concentration in the electrolyte. More ions reaching the surface were thus obtained bringing the $CuSO_4$ concentration from 200 mM to 600 mM. The result obtained from the deposition performed using the same parameters as the other samples is reported in Fig. 11.

As demonstrated in the pictures there is a significant difference in terms of quality and compactness between the samples obtained from CDHC/EG 1:4 + 200 mM $CuSO_4$ and the ones obtained from CDHC/EG 1:4 + 600 mM $CuSO_4$. A better quality is seen in the second case due to a higher amount of metal ions present in the solution. The exterior appearance of the film switch from a dull red to a semi-bright pink. The obtained result demonstrates that the CDHC electrolyte can be optimized to obtain good quality copper layers.

From the efficiency point of view, the novel electrolytes present a lower efficiency with respect to ChCL/EG. The roughness values for the different samples are comparable, except for the deposit from the CDHC/EG 1:4 + 200 mM $CuSO_4$ solution. This sample presents the highest values of R_t and R_a, which is consistent with the structure seen using the SEM. The low hardness level of the CDHC/EG 1:4 + 200 mM $CuSO_4$ is a direct consequence of its porous structure.

3.6 XRD analysis

The XRD diffractograms of the samples obtained from the two different solutions (ChCl/EG 1:2, CDHC/EG 1:4 + 600 mM $CuSO_4$) are presented in Fig. 12. The data are normalized with respect to the Cu (111) peak.

As shown in Fig. 12, the two samples present the three typical crystallographic orientations of copper (JCPDS 04-0836) in the range of $40° < 2\theta < 80°$. The intensity of the Cu (111) peak reveals that this orientation is the preferential one in all the samples. The CDHC/EG sample shows a slightly different distribution of the crystallographic phases with respect to the sample from ChCl/EG, as observed comparing the ratio between (220) peaks. The mean crystallite size calculated according to Scherrer's law is approximately 39 nm for all the samples if measured using the FWHM of the (111) peak. The reflections of the other two peaks provide lower values of crystal size (approximately 26 nm for both).

4. Conclusions

The electrochemical/physical properties of a ChCl/EG homologue characterized by an ionic specie larger than Cl^- (DHC^-) was determined. Considering the physical properties of the new electrolytes, viscosity of CDHC/EG is greatly influenced by the amount of EG (HBD). This property is however of several orders of magnitude higher than water or well established DESs like ChCl/EG. Conductivity measurements confirmed what was observed with viscosity. In the case of CDHC/EG

Table 2
Cathodic efficiency (η), thickness and roughness (R_t and R_a) of the samples obtained using 5 mA/cm², 20 min of deposition time and stirring rate 300 rpm at T = 80 °C.

Solution	η (%)	Thickness (μm)	R_t (μm)	R_a (μm)	Microhardness (HV)
ChCl/EG + 200 mM $CuSO_4$	56	3.28	3.07	0.274	231.49
CDHC/EG 1:4 + 200 mM $CuSO_4$	40	2.34	4.13	0.339	85.82
CDHC/EG 1:4 + 600 mM $CuSO_4$	47	2.79	3.24	0.278	202.48

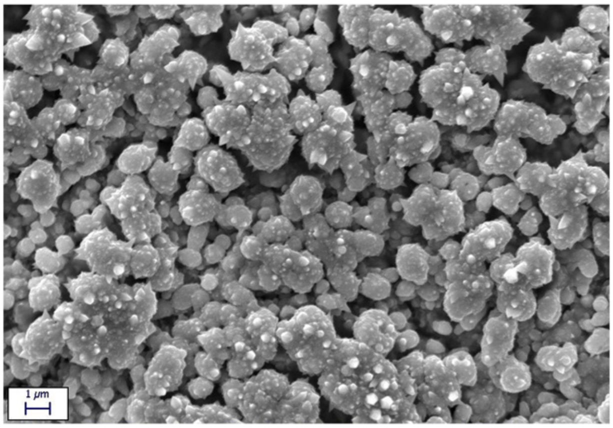

Fig. 10. SEM micrograph of the copper deposit obtained at 5 mA/cm^2, 20 min of deposition time and stirring rate 300 rpm at T = 80 °C from CDHC/EG 1:4 + 200 mM $CuSO_4$ (15,000×; high vacuum; secondary electrons).

the ionic conductivity increases significantly with CHCD/EG ratio due to the increase of complexation. After the addition of copper, all the resulting solutions showed at least one reduction peak $Cu^{n+} + ne^- \rightarrow Cu^0$ in the cyclic voltammograms. Copper layers made by the CDHC/EG solution in 1:2 and 1:3 ratios were not found to be acceptable since the obtained coatings are characterized by dark color and poor quality, and this is valid also for the ratio 1:4 at 200 mM $CuSO_4$. The reason for this phenomenon can be related to the high viscosity of the DES and, for the latter, to a not optimal concentration of Cu ions. On the contrary deposition from CDHC/EG 1:4 + 600 mM $CuSO_4$ proved to be able to provide good quality coatings. Comparison of the conductivity measurements with the results of the layers characterization indicates that viscosity has a greater effect on the final quality of the deposited copper than conductivity, which on the contrary shows less influence on the resulting deposition. Of particular interest is the fact that adding high concentrations of copper ions to CDHC/EG is possible to compensate the high viscosity, balancing the limited ionic mobility with a suitable concentration of the electroactive specie. This is evident also from the voltammetry performed on the solution, where a strongly diffusion limited reduction reaction can be observed. CDHC/EG 1:4 is suitable for copper deposition, as the coatings produced present comparable quality with respect to their equivalents from ChCl/EG. This demonstrates the possibility of metal electrodeposition in chloride free organic mixtures for applications presenting critical issues towards aggressive baths.

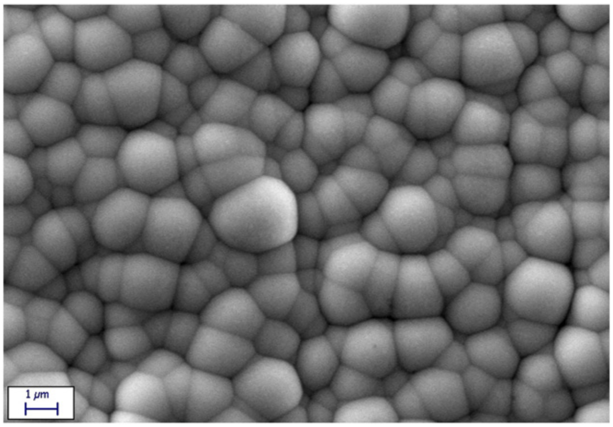

Fig. 11. SEM micrograph of the copper deposit obtained at 5 mA/cm^2, 20 min of deposition time and stirring rate 300 rpm at T = 80 °C from CDHC/EG 1:4 + 600 mM $CuSO_4$ (20,000×; high vacuum; secondary electrons).

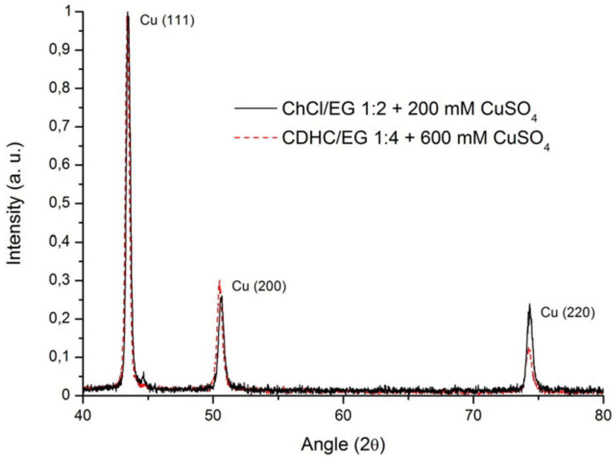

Fig. 12. XRD diffractograms of two different Cu layers.

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