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Electrodeposition from Deep Eutectic Solvents

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<http://dx.doi.org/10.5772/64935>

Abstract

Deep eutectic solvents constitute a class of compounds sharing many similarities with properly named ionic liquids. The accepted definition of ionic liquid is a fluid (liquid for $T < 100^\circ\text{C}$) consisting of ions, while DES are eutectic mixtures of Lewis or Brønsted acids and bases. Their most attractive properties are the wide potential windows and the chemical properties largely different from aqueous solutions. In the last few decades, the possibility to electrodeposit decorative and functional coatings employing deep eutectic solvents as electrolytes has been widely investigated. A large number of the deposition procedures described in literature, however, cannot find application in the industrial practice due to competition with existing processes, cost or difficult scalability. From one side, there is the real potential to replace existing plating protocols and to find niche applications for high added-value productions; to the other one, this paves the path towards the electrodeposition of metals and alloys thermodynamically impossible to be obtained via usual aqueous solution processes. The main aim of this chapter is therefore the critical discussion of the applicability of deep eutectic solvents to the electrodeposition of metals and alloys, with a particular attention to the industrial and applicative point of view.

Keywords: electrodeposition, deep eutectic solvents, metals, alloys

1. Introduction

The electrodeposition of metals for industrial surface finishing is nowadays a well-established industrial practice. Many processes are available to obtain a wide variety of coatings on most of

the substrates used in manufacturing. There are however some important limitations, as not all the metal/substrate combinations are possible in the current state of the art. This is connected to the nature of the electrolytes used for the vast majority of the plating processes, which are water based. Water is the most obvious choice to formulate a plating electrolyte, and in the majority of the cases, it is also the most convenient from the point of view of the results obtained. This solvent however presents some limitations: narrow potential window, reactivity towards specific metals, high hydrogen evolution in specific conditions, etc. If metal plating is limited to aqueous solutions, many possibilities are therefore precluded.

A possible way to extend the range of coating/substrate combinations is the use of non-aqueous solvents, characterized by extended potential windows and improved chemical inertness. A notable amount of scientific literature is available on a high number of non-aqueous systems. Deep eutectic solvents (DESs) are a particular class of such systems, and in the last few decades, they are finding application in the electrodeposition of many metals and alloys. This chapter is intended to be a review of the current state of art for electrodeposition from DESs and a critical discussion of the realistic applicability of DESs with particular attention to the industrial point of view.

2. Chemistry of DESs

Despite the fact that the physical properties of DESs are similar to those of other ionic liquids (ILs), their chemical properties exhibit peculiarities, which make them suitable for specific and different applications [1]. Melting point of two components strongly depends upon their reciprocal interaction: when considering a binary mixture of A + B, the difference in the freezing point at the eutectic composition compared to that of a theoretical ideal mixture is directly proportional to the interaction between the two single components A and B. The stronger the interaction, the larger will be the depression of the mixture melting point [1, 2]. This effect is schematically shown in the phase diagram presented in **Figure 1**.

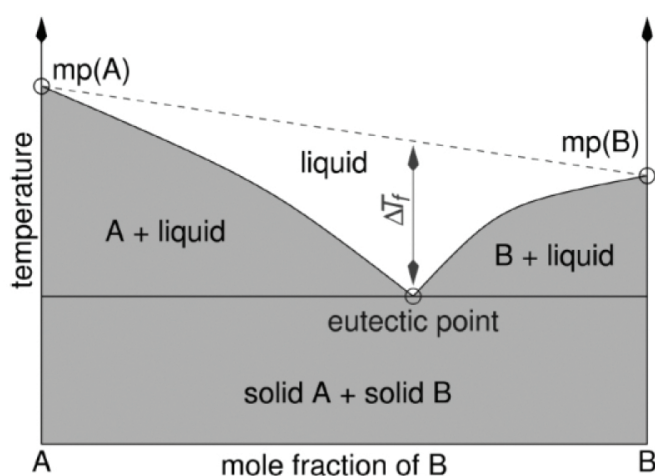


Figure 1. Eutectic formation in a two components phase diagram [1].

The word eutectic comes from a Greek word that means “easily melted” and indicates the temperature where the phases simultaneously crystallize from molten solution [2]. DESs includes a wide range of liquids close to the eutectic composition of the mixtures; differently from ionic liquids, which are formed primarily of one type of discrete anion and cation, they can contain a variety of anionic and cationic species [1]. They are mainly obtained by the complexation of a quaternary ammonium salt with a metal salt or an hydrogen bond donor (HBD) and can be schematically expressed by the general formula $\text{Cat}^+\text{X}^-\text{zY}$, where Cat^+ is in principle any ammonium, phosphonium or sulfonium cation and X^- is a Lewis base, generally a halide anion [1]. The interaction occurs between X^- and z molecules of Y , either a Lewis or Brönsted acid. Depending on the nature of the complexing agent used, four types of DESs can be categorized [1]. Such classification is presented in **Table 1**.

Type	General formula	Examples of terms
Type I	$\text{Cat}^+\text{X}^-\text{zMCl}_x$	$\text{M} = \text{Zn, Sn, Fe, Al, Ga, In}$
Type II	$\text{Cat}^+\text{X}^-\text{zMCl}_{x/y}\text{H}_2\text{O}$	$\text{M} = \text{Cr, Co, Cu, Ni, Fe}$
Type III	$\text{Cat}^+\text{X}^-\text{zRZ}$	$\text{Z} = \text{CONH}_2, \text{COOH, OH}$
Type IV	$\text{MCl}_x + \text{RZ} = \text{MCl}_{x-1}^+ \cdot \text{RZ} + \text{MCl}_{x+1}^-$	$\text{M} = \text{Al, Zn and Z} = \text{CONH}_2, \text{OH}$

Table 1. Classification of DESs and examples [1].

Up to now, the most widely Cat^+ species studied have been based on pyridinium, imidazolium and quaternary ammonium species [2]. As in traditional ionic liquid systems, the strongest depression of the freezing point is encountered when imidazolium-based DESs are used, due the intense interaction between the anion and the complexing agent. The simple handling and manufacture of DESs is one reason for their success. Mixing the two components, a mild endothermic reaction occurs, requiring only a gentle heating and stirring [2]. Moreover, they are water insensitive, which make it unnecessary to work in a glovebox with a controlled atmosphere.

2.1. Type I eutectics

Type I DESs formed from MCl_x and quaternary ammonium salt are the analogues of the well-studied metal halide/imidazolium salt systems [1]. Despite the fact they include a wide range of eutectic mixtures, from famous chloroaluminate/imidazolium to less common EMIC with different metal halides (FeCl_2 , AgCl , CuCl , LiCl , CdCl_2 , CuCl_2 , SnCl_2 , ZnCl_2 , LaCl_3 , YCl_3 , SnCl_4 , etc. [3]), the number of non-hydrated metal halides with a suitable low melting point is limited. Among them, the only ones which form ionic liquids with pyridinium, imidazolium and quaternary ammonium halides are FeCl_3 , ZnCl_2 , SnCl_2 , CuCl , InCl_3 , CdCl_2 , AuCl_3 [2]. ZnCl_2 -based DESs have been studied deeper in detail with respect to other systems: it was found that ZnCl_3^- , Zn_2Cl_5^- and Zn_3Cl_7^- species are present in the liquid, with proportions depending on the ionic liquid composition [2, 5]. They differ in dimensions and charge density one from the other and thus have peculiar electrostatic interactions with the cation. For

example, since ZnCl_3 ions are smaller and have stronger electrostatic interactions, the freezing point increases [2]. It is difficult to model the potential energy between the ions due to the complex nature of the anion and the non-centrosymmetric charge distribution on the cation. However, considering simultaneously the freezing point difference between the quaternary ammonium salts and the complexed metal salt and the potential energy, a correlation can be found: the variation of interionic potential energy and of the freezing temperature are indeed strictly related [2]. It was found that is possible to extrapolate the phase behaviour from simple ionic size considerations and that the symmetry has a minimum effect on the depression of the freezing point. Endres et al. show that the cation has a little effect on the freezing point of the eutectic-based ionic liquids: smaller cations depress the freezing point more because the correspondent halide salts have a higher freezing point [2]. Considering different cation dimensions, the two effects are to some extent compensated and the freezing point does not almost change. The ions size strictly influences both the conductivity and the viscosity of the type I eutectics: anhydrous zinc and iron salts based on DESs show lower conductivity and higher viscosity with respect to corresponding aluminium ionic liquids because of the larger ion size. In general, imidazolium-based liquids have lower viscosity and higher conductivity than the pyridinium or quaternary ammonium eutectics formed under the analogous conditions.

2.2. Type II eutectics

The number of metals that can be incorporated into an ionic liquid can be increased by using hydrated metal halides and choline chloride (ChCl) [1]. The presence of water decreases the melting point since the lattice energy is decreased too. Therefore, hydrated salts are more prone to form mixtures with quaternary ammonium salts that are liquid at ambient temperature with respect to anhydrous salts [2]. Examples of metal salts mixed with ChCl are $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{LaCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ [1]. Studies on the first mixture showed how the main charge carrying species are $[\text{Choline}]^+$ and $[\text{Cl}_3\text{H}_2\text{O}]^-$: this is consistent with the highest conductivity of these liquid compared to anhydrous salt mixtures [1]. The addition of Li^+ ions from LiCl does not cause the expected increase of the conductivity, probably due to the high ion solvation or to its high association with the anion. These systems are more temperature sensitive with respect to anhydrous metal salts. Although different metal salts can be theoretically deposited from these type of eutectic mixtures, up to now only Cr and Co have been deposited. Since hydrated systems are being considered, the deposition of Al and other low reduction potential metals is not possible due to the limited potential window [2].

2.3. Type III eutectics

These eutectics are formed from choline chloride and hydrogen bond donors [1]. They are able to solvate different metal species, including chlorides and oxides. Since the number of hydrogen bond donors is high, they constitute a group of easily tuneable liquids, adjustable for specific peculiar applications. Hydrogen bond donors (HBDs) include amides, carboxylic acids and alcohols [1]. These eutectic mixtures are easy to prepare and handle, as they are almost unreactive with water and biodegradable. For some of these eutectics, depression of

the freezing point is extremely high, even higher than 200°C for the oxalic acid-zinc chloride system [6].

2.4. Type IV eutectics

A metal chloride hydrate and a hydrogen bond donor mainly form these eutectic mixtures. Type IV eutectics are very interesting due to the production of cationic metal complexes, guaranteeing a high metal ion concentration close to the electrode surface [7]. A noteworthy example is ZnCl_2 , which forms eutectic compounds with different substances such as urea, acetamide, ethylene glycol and 1,6-hexanediol [1].

3. Physical properties of DESs

3.1. Viscosity

Viscosity is one of the most important properties of DESs due to its practical and industrial relevance. Although numerous works are present in scientific literature, there is a lack of information on DESs' behaviour at pressures different from ambient one and for related applications [8]. Typical DESs viscosity ranges from tens to hundreds of mPa s at temperatures around ambient one or slightly higher [1, 2, 8]. Some exceptions occur, for example, in the case of compounds containing $\text{ChCl} + \text{ZnCl}_2$ in a 1:2 molar ratio, which can give rise to viscosity of 85,000 mPa s at room temperature [9]. The most remarkable DESs for practical purposes are in general those with low viscosities, close to the widely used organic solvents or water-based solutions. It is important to note that differences in experimental methods, sample preparation and impurities can affect significantly the measure obtained [8].

The presence of impurities is the variable that more deeply affects the rheological behaviour of these systems. Moreover, some of DESs are non-Newtonian fluids: this feature can influence the viscosity analysis methods for this kind of system. The hygroscopic nature of many DESs strongly influences their viscosity, which can change of even two orders of magnitude from dehydrated to hydrated eutectics [8]. An example is that of ChCl and oxalic acid equimolar mixtures, whose viscosity passes from 5363 to 44.49 mPa s when water is absorbed [9]: water addition could be an easy method for tuning the viscosity and it is indeed applied in different cases. However, because water may compete with CO_2 in absorption sites occupation in systems tailored for CO_2 absorption, the efficiency could be depressed affecting the obtained result [10, 11]. Moreover, the presence of water could be detrimental for some electrodeposition procedures [1, 2, 8].

The temperature-viscosity dependence has been deeply investigated in literature following Arrhenius equation or Vogel-Fulcher-Tammann one [7]. As intuitively predictable, viscosity decreases with increasing temperature. In particular, using an approach based on a temperature-viscosity fitting through an Arrhenius model, it is possible to calculate the activation energy E_a and therefore the strength of intermolecular forces in DESs [2, 12, 13]. Low-viscosity DESs have low E_a values, whereas more viscous systems show higher activation energies.

Abbot and co-workers [8], following the same approach used to relate melting temperature and activation energy of molten salts, found out an almost linear relationship also for DESs: larger melting points are indeed associated with larger E_a (and subsequently larger viscosity) (Figure 2).

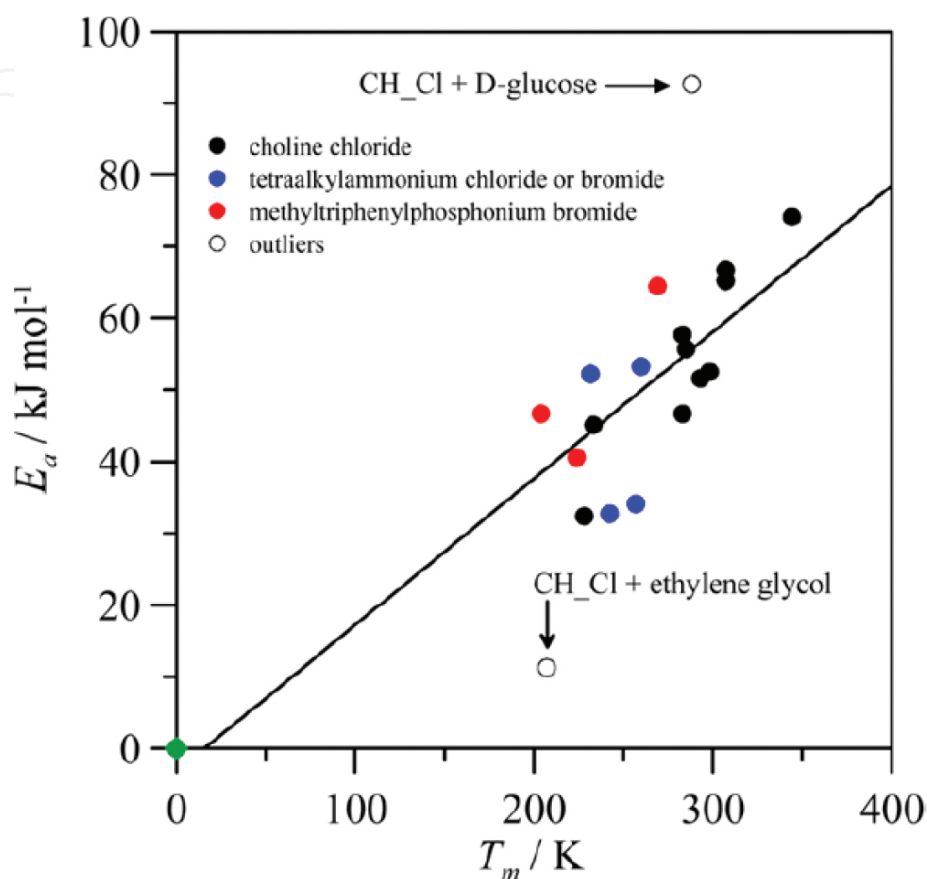


Figure 2. The almost linear relationship between activation energy and temperature [13].

In the case of DESs, ions have a relatively large size if compared with the voids between the ions themselves. Such voids represent the free space between the different moieties that constitute the DES and are generally called holes. Relating viscosity data in the light of hole-theory approach [14–16], for which viscosity and electrical conductivity are correlated with availability of holes in the fluid, it is possible to evince that DESs with larger holes lead to less viscous fluids. Deviation from this general trend is shown when very viscous systems are taken into account.

3.2. Conductivity

Conductivity cannot be considered separately from viscosity, since the two are strictly related. Generally, a low viscosity is usually associated with a high conductivity and vice versa [8]. Low viscosity DESs have conductivity in the order of even tens of mS cm⁻¹ [16], while for most common high density DESs an order of magnitude lower is usually observed. A theoretical

approach for determining conductivity can be followed using the hole-theory approach [15, 16]. Because of both holes availability and kind of bonds between ions and HBDs have to be taken into account, achievement of a univocal trend in all the analysed systems is difficult to obtain. During conductivity modelling, many aspects from chemical to hydrodynamic ones have to be taken into account. The typical trend implies an increase in conductivity when higher quantities of salts are used [16], but this is not always true, since both the type of salt and HBD and their interaction have to be considered. Some DESs indeed manifest deviation from the general trend: for example, CHCl_3 :ethylene glycol-based DESs show a maximum in conductivity, which then decreases after a certain salt concentration [8]. The conductivity dependence on temperature is well described by an Arrhenius model, through which analogous computation to those used for viscosity can lead to activation energy evaluation [8].

Viscosity and conductivity are usually plotted together in the so-called Walden plot, where molar conductivity and the inverse of viscosity, that is fluidity, are represented in a logarithmic scale [8]. The obtained data are compared with an ideal line passing through the origin for a potassium chloride solution. The deviation from ideality is higher in the case of DESs with respect to common ILs, since in the first case ions and HBDs complexes have to be considered [16]. An example of Walden plot is reported in **Figure 3** [8].

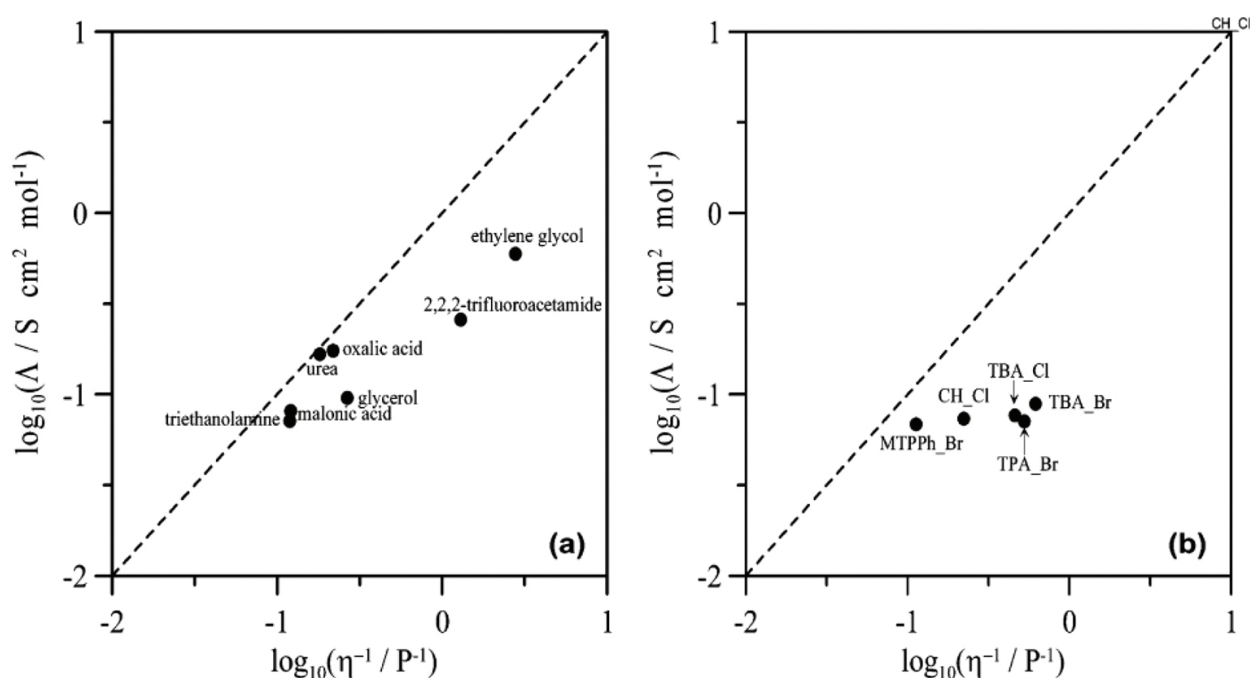


Figure 3. Walden plots for a series of DESs [13].

The deviation from the ideal line is associated with the systems ionicity: low viscous liquids have lower ionicity i.e. high deviation, whereas high DESs show the opposite behavior [15]. Ionicity is influenced by both salt nature and interaction between ions and different HBDs [8, 15]. Nowadays, although good correlation between effective experimentally measured conductivity and theoretically predicted one has been proved with some models for a set of

DESs, a unique broadly applicable method for conductivity is still not available or, at least, not reliable [8]. An important factor which governs both viscosity and conductivity is the diffusion coefficient of molecules present in ILs [17, 18] influenced by both hole size distribution and intermolecular forces [8].

3.3. Electrochemical reactions

Due to their practical application, DESs electrochemical properties are very important: they are evaluated by means of cyclic voltammetries and electrochemical impedance spectroscopy [19]. The material used as working electrode has obviously a relevant influence, and peculiarities are revealed for each material selected. Many studies have been performed on mixtures, revealing some differences with respect to high-temperature molten salts [4]: the differential capacitance indeed increases with temperature for all the electrodes studied with the exception of Au [1]. For example, when different HBDs are used for the same ChCl system, specificities are encountered related to the HBD type: it has indeed an influence on the negative limit of polarization [1]. Moreover, an increase in temperature of DESs results in narrower electrochemical windows and in larger capacitance currents [1]. Although the electrochemical window is generally smaller than pure ILs one, it is suitable for a wide range of electrochemical purposes [1, 8]. In the cathodic part of CV curves, again for ChCl-based DESs, a layer of HBDs molecules adheres to the electrode surface, while choline cations are in contact with the electrolyte [1]. When passing to less negative potentials, the absorption of anions occurs replacing partially positive choline ions [1]. The Helmholtz type layer model of the double layer at large negative potential is validated from very similar results obtained by replacing choline with other cations, such as acetylcholine [1]. Because of DESs ionic character is dependent on their chemical-physical properties, the comprehension of metal ions behaviour in the liquid is really important. Many efforts have been made by Abbott's group to determine, through equilibrium electrochemical measurements, the activity coefficients for metal salts in DESs and how they vary with concentration [16]. Understanding the activity of a solute in solution is indeed fundamental for using the full potential of a reactive species. Comparing the redox potentials of metal couples in an established DES mixture with those in an aqueous medium allows understanding the potentialities of a system for electrodeposition purposes and other applications. However, since there is plenty of factors influencing them, a univocally valid model cannot be found.

4. Electrodeposition of metals from DESs

Due to their good properties as electrolytes, electrodeposition is an obvious possible application for DESs. Nowadays, this technique is one of the most used surface finishing methods in industrial applications. It consists mainly in the formation of a solid metal coating on the electrode surface starting from metal cations dispersed in the electrolyte, reduced on the cathode under an electrical potential. This electrochemical process is used to functionalize surface to obtain required properties, for example hardness, corrosion and wear resistances, abrasion, brightness, magnetism, electrocatalysis [20]. Although electrodeposition can be

carried out using several solvents, due to the well-known baths chemistry and handling, electrodeposition of metals and alloys is performed usually from aqueous solutions. The number of metallic coatings obtaining from aqueous baths is strictly related to those having redox potential higher than the water one: this narrow potential window entails gas evolution with subsequent hydrogen embrittlement phenomena and the formation of insoluble oxides and/or hydroxides on the electrode surface (passivation) which hinder the deposition of thick metallic coatings. Moreover, many of the traditional aqueous solutions are based on toxic components and show low current efficiency [e.g. Cr(VI) plating]. For these reasons and especially for the possibility to electrodeposit metals having Nernst potential well below water decomposition one, for example titanium, aluminium, tungsten suitable for many industrial applications (e.g. anti-corrosion, batteries) that cannot be plated starting from aqueous solutions, electrodeposition based on deep eutectic solvents (DESs) could be the alternative [21]. DESs show high solubility for metal and metal oxides and hydroxides allowing the possibility to avoid passivation phenomena during electrodeposition or electropolishing, to plate thicker metal layers and to use them in electrochemical processes such as metal recovery and metal separation. Furthermore, the wider potential window, the absence of water (no embrittlement phenomena), the relatively high conductivity compared to other non-aqueous solvents, the relatively low cost, simply preparation and biodegradability make them suitable for industrial electrodeposition processes, although these are not economically competitive with respect to the existing ones. However, the instability of DES baths, while the electrodeposition proceeds, has to be solved prior to a possible industrial transfer [2]. Electrodeposition from DESs could be the way to easy circumvent legislative restriction related to aqueous precursor toxicity used in current technological electroplating systems (Ni, Cr, Co) known to be carcinogenic and the related high disposal costs [1, 21]. In case of DESs deposition, morphology and adhesion of the growing metal coatings are dependent on applied current density, DES composition and presence of additive. As in case of aqueous-based baths, the plating process can be carried out under constant current or constant voltage regimes [2]. In this dissertation, electrodeposition of the most popular metallic coatings starting from DESs made of ChCl and either ethylene glycol or glycerol or urea are shown.

4.1. Nickel

Nickel metal coatings can be successfully obtained by dissolving nickel chloride dehydrate salts both in ChCl:urea and ChCl:ethylene glycol [16, 22]: coatings morphology obtained from DESs baths is completely different compared to the aqueous plated Ni, due to the different thermodynamics and kinetics of the two processes [23]. Recent works demonstrate that the addition of different components into DESs-based electrolyte can induce changes in terms of microstructure, morphology and redox behavior of the Ni(II) ion. Let us consider the case of nicotinic acid [23] and ethylenediamine [24], whose addition in a ChCl: urea bath affects the morphology and the microstructure of the metal coatings and allows obtaining high uniform and shiny deposits. The effect of these species on the electrodeposition process can be ascribed to the formation of Ni(II) complexes and their subsequent absorption on the electrode surface. These phenomena decrease the nickel deposition current and its nucleation lowering the particles size. The effect of process temperature on the coating quality was investigated by Gu

et al. [25] performing electrodeposition at ambient temperature and at 90°C using a ChCl:ethylene glycol bath on a brass foil. This work demonstrates that the surface roughness increases with temperature due to the formation of nanosheets with a thickness of 10–20 nm and grains size of about 10–50 nm. This phenomenon is related to a decrease of DES viscosity causing an increase of ion species mobility, enhancing in this way the deposition process and the nucleation of Ni. The obtained coating shows also low corrosion potential. Abbott et al. [22] have also studied the Ni electrodeposition starting from the ChCl:ethylene glycol DES bath, obtaining a dark grey deposit: the addition of ethylenediamine and acetylacetamide in this kind of electrolyte induces the suppression of the Ni underpotential deposition. Due to the growing industrial interest on composite materials, several studies have been done in order to develop electrodeposition process starting from DESs. Using Ni as matrix, compact Ni-multiwalled carbon nanotubes (MWCNTs) were deposited on copper substrate. In order to have a high efficient deposition process, a homogeneous dispersion of MWCNTs into the electrolyte has to be guaranteed. This has been obtained dispersing MWCNTs into ChCl:urea DES before the addition of soluble Ni chloride salt. Morphology, crystallinity and roughness of Ni coating were affected by the presence of MWCNTs [26].

4.2. Chromium

For several decades, hard chromium plating has been the most used metallic coating employed for several applications, especially to protect components operating in high wear and corrosion environment. This was due to its high hardness and its natural ability to inhibit corrosion. Due to its significant use in the industry, chromium electroplating based on Cr(VI) aqueous electrolyte is the highest optimized process. However, a series of issues, with most important the extremely negative environmental impact of the hard chromium plating process, due to the use of the carcinogenic hexavalent chromium, has led to a number of directives and legislation related to the restriction of this method [27]. This favours the necessity of finding less hazardous method replacing the present one. Up to now, some Cr(III) processes are on the market, but the obtained results are not repeatable. As demonstrated by recent scientific studies, the Cr electrodeposition from DESs could be the way to achieve metallic coatings having same properties of Cr(VI) ones. In particular, Abbott et al. have reported DESs obtained mixing ChCl with trivalent chromium chloride salts [28, 29]: in this electrolyte, electrodeposition process with a very high current efficiency (>90%) leads to a formation of a very thick and adherent chromium layer. Modifying the Cr(III)-based electrolyte is possible to plate coatings with different morphologies: soft but not microcracked (dull black), hard chromium (hardness > 700 HV, increased up to 1500 HV after thermal treatment) and very thin layer with a mirror appearance. The same research group demonstrated that the addition of LiCl into the bath promotes the formation of nanocrystalline crack-free black chromium deposit, suitable for decorative applications, with good corrosion resistance [30].

4.3. Zinc

Due to its peculiar features such as low cost and protection against corrosion, zinc has a paramount importance into the metal finishing industry. Because of Zn electrodeposition from

aqueous solution is inexpensive and produces very good coatings, the study of electroplating from DESs is mostly used for Zn alloys production [1]. However, several studies have been done in order to understand the Zn deposition process using different DESs, in particular ChCl:urea [31] and ChCl:ethylene glycol [32]. Compared to aqueous electrodeposited Zn having a dendritic structure, those ones plated with DES shows very different morphologies. Using ChCl:ethylene glycol bath, deposited Zn shows very thin platelets with the planar face perpendicular to the electrode surface, according to progressive nucleation mechanism. In case of ChCl:urea, zinc coating has a rice-grain morphology, consistent with a rapid nucleation mechanism. The effects induced by the addition of some chelating agents such as acetonitrile, ammonia and ethylenediamine on the electrochemical process were studied [31]: these additives act as brightener but at the same time affect the electrodeposition process and lead to the formation of macro-crystalline deposit like in water. This phenomenon can be ascribed to the adsorption inhibition of chloride on the electrode surface induced by the presence of ammonia and ethylenediamine. Because of the addition of complexing agent to ChCl:urea and ChCl:ethyleneglycole baths does not change the metal species present in the baths ($[\text{ZnCl}_4]^{2-}$), it is possible to deduce that the morphology variation after their addition is caused by the chemical processes taking place in the diffusion layer or on the cathodic surface rather than in the bulk [16, 33]. Another important study was performed by Bakkar et al., in which the electrodeposition of Zn using ChCl based electrolytes on magnesium substrates [34]. Mg and its alloys are difficult to be electroplated and so cannot be used as substrate in aqueous solution due to their water-sensitiveness, their tendency to form MgO and/or $\text{Mg}(\text{OH})_2$ film inhibiting adhesion of the electrodeposited coating and their high reactivity inducing formation of loose immersion layers on the surface by replacement that stops the following electrodeposition. Furthermore, magnesium suffers of microgalvanic deterioration if it is in contact with cathodic metals in a wet environment: this means that Mg is subjected to strong corrosion attack by aqueous electrolytes. Developing an electrodeposition process based on DESs could be an important turning point for a successful application of protective coatings on magnesium largely used in automobiles, aerospace and electronics industries. The authors have compared the efficiency of several ChCl-based DESs, in particular 1 ChCl:2 urea, 1 ChCl:2 ethylene glycol, 1 ChCl:1 malonic acid, 1 ChCl:2 glycerol and 1 ChCl:2 ZnCl_2 . From this study, it is possible to evince that Mg has the lowest corrosion rate in 1 ChCl:2 urea, the most feasible mixture for successful Zn electrodeposition, whereas the other mixtures produce powdery deposits or Mg corrosion. In particular, in case of 1 ChCl:2 glycerol pitting phenomena on Mg surface occur. The application of pulsed cathodic current during the electroplating process helps for the production of smooth, uniform and corrosion-resistant Zn coating, similar to that of pure zinc [34].

4.4. Aluminium

Aluminium is one of the metals that cannot be plated in aqueous media because of its Nernst potential, well below the water decomposition one. Moreover, the high stability of aluminium oxide makes it high resistant to corrosion, but unfortunately this means that it cannot be electroplated from aqueous electrolytes [21]. In any case, aluminium electrodeposition is an important technological target due to its application in electronic, energy storage and anti-

corrosion fields. During the last years, many efforts have been put on aluminium electrodeposition from pure ionic liquids (ILs). However, the high hygroscopic nature of AlCl_3 -based ILs obligates to prepare and handle them under inert gas atmosphere, delaying progresses in this kind of process [35]. Several kinds of electroplating processes for Al deposition have been developed starting from DESs, both I type and IV type. Although the anodic reaction of this process is still low and the deposition rate has to be increased, the simple addition of acetamide to AlCl_3 allows obtaining an electrolyte suitable for Al electrodeposition, relatively insensitive to water. Electrolytes characterization has shown that both cationic and anionic aluminium species, namely $[\text{AlCl}_2]^+$ and $[\text{AlCl}_4]^-$, are present [1].

4.5. Copper

Since Cu electrodeposition is very common in surface finishing industry, many studies involving DESs copper plating have been done. In particular, Popescu et al. have studied Cu electrodeposition from ChCl combined with urea, malonic acid, oxalic acid and ethylene glycol, using as CuCl as copper source [36]. From those studies, it is possible to evince that the better deposit can be obtained from ChCl:oxalic acid and ChCl:ethylene glycol: the coating was fine, homogeneous and adherent. Furthermore, Abbott et al. have produced different kind of Cu deposits depending on Cu concentration into ChCl:ethylene glycol DES: bright nanostructured deposit corresponding to progressive nucleation of Cu was obtained for concentrations 0.01–0.1 M; for concentration lower than 0.01 M, black deposit was formed corresponding to a spontaneous nucleation of Cu [37]. Using chronoamperometry, impedance spectroscopy and cyclic voltammetry (CV) analyses into ChCl:ethylene glycol DES, Murtomaki et al. have studied the electron transfer kinetics of $\text{Cu}^+/\text{Cu}^{2+}$: the reaction was found to be quasi reversible and the [38]. In some cases electrodeposition from DESs not containing chloride ions can be advantageous. This is valid in general when a metallic layer is deposited on thin layers of metals sensitive to chloride corrosion, like nickel or iron. In the case of copper, deposition from a chloride free DES was studied for instance by Bernasconi et al [39] using a choline chloride dihydrogencitrate:ethylene glycol mixture with anhydrous copper sulfate as metal source. Abbott et al. have studied the electrodeposition of composite Cu coating with SiC and Al_2O_3 . The addition of these particles does not affect the morphology and the size of Cu particles. The amount of particles dispersed into the DESs is directly related to the composition of the composite materials [37].

4.6. Silver and other metals

Silver electrodeposition from ChCl:ethylene glycol DES was performed using Cu as substrate: Ag not only oxidizes the copper substrate, but it is deposited on the electrode surface on the same time, forming a very shiny nanocrystalline coating. Gomez et al. have evaluated the chloride anion function during the electrodeposition process in 2 urea: choline chloride DES by means of voltammetric and chronoamperometric analyses [40]. The work reveals that Ag deposition takes place as 3D nucleation and growth process under diffusion control. The best hypothesis is that chloride induces the formation of rounded grains at short deposition times hindering uncontrolled directional growth. Adding SiC and Al_2O_3 particles to ChCl:ethylene

glycol DES, the Ag coating morphology is not affected by the particles presence. The most important point is that the hardness of the Ag coating from DESs after the incorporation of the particles is higher with respect to the same deposit obtained from aqueous electrolytes. Moreover, this value is not dependent on the reinforcing particles size. Al_2O_3 reinforced coatings show a low friction coefficient. Because of the lithium salts modify the mechanism of metal nucleation, LiF was added during the Ag deposition, inducing higher hardness leaving the structure unchanged [41, 42]. Magnesium metal can be plated using dimethylformamide and magnesium chloride hexahydrate-based DES. Cyclic voltammetry analyses indicate that the deposition of this metal is irreversible whereas from X-ray diffraction analyses, it is possible to evince that the plated coatings are Mg_2Cu and MgO , revealing that an alloy with Cu substrate is formed [43]. Rahman et al. have studied indium electrodeposition starting from 1ChCl: 2urea DES at which indium sulphate is added [44]. The electrodeposition was performed on Au and Mo. To determine the type of nucleation, the current-time transients were normalized and compared to the theoretical dimensionless current-time transients obtained from Scharifker-Hills model. The work reveals that indium electrodeposition on molybdenum electrode proceeds via instantaneous nucleation with diffusion-controlled growth, whereas on the Au electrode, the deposition proceeds via progressive nucleation. The surface roughness decreases at higher current density [44].

5. Electrodeposition of alloys from DESs

A significant amount of scientific work is present on the electrodeposition of pure metals from DESs. The interest in such systems is even greater considering the electrodeposition of alloys; the use of aprotic liquids (e.g. DES) avoids the limited potential window and hydrogen evolution issues of aqueous solutions [1, 45]. Thus, the number of possible metallic elements combination is largely increased. The study on systems already affirmed in the galvanic industry increases the amount of useful information on DES without claiming new possible industrial solution. On the contrary, for example, the possibility to deposit alloys containing rare earth elements with relatively ease may represent a unique and valid solution also outside academics [1, 45].

5.1. Corrosion resistant alloys

The demand of corrosion resistant coating is one of the highest in the surface finishing market, consequently great efforts are put in finding new solutions to improve nowadays processes. DES may avoid problems related to bath toxicity of existing process or for improving process efficiency [1, 43]. One example is the electrodeposition of Zn alloy, largely employed in the galvanic industry, for example ZnNi, ZnFe, ZnMn. The main advantage over the aqueous solutions is related to the reduction of hydrogen evolution, causing substrate embrittlement and poor deposit quality [45]. In addition, the relatively high redox potential difference between Zn and the correspondent alloying element complicates the deposition process, and anomalous deposition is observed. Employing DES system, chlorometallate ions are formed in the solution shifting the redox potential; higher compositional control of the deposits is

obtained. Fashu et al. show a significant dependence of composition and surface morphology of ZnNi deposits, obtained from choline chloride-urea solution, on electrolyte concentration, temperature and voltage applied; alloy composition can thus be tuned significantly with different process parameters [46]. Abbot et al. reported the electrodeposition of ZnSn alloys, candidates for replacing Cd, from ethylene glycol-based solution; ChCl:urea and ChCl:ethylene glycol DESs containing 0.5 M ZnCl₂:0.05 M SnCl₂ are studied in terms of deposit composition and morphology [47]. In view of corrosion resistance coatings, different alloys have been reported in literature.

You et al. carried out a study on NiCo alloys from ChCl:ethylene glycol; Ni-rich alloys with 4–40 wt.% Co showed an important improvement with respect to pure Ni deposit in the corrosion potential [48]. In a similar DES system, Saravanan et al. replace Ni with Cr evaluating both microstructure and potentiodynamic polarization behaviour in the composition interval 65–81 wt.% Co of CoCr deposits [49]. The same research group obtained NiFeCr deposits containing approximately 53–61% Fe, 34–41% Ni and 4–15% Cr from ChCl:ethylene glycol [50]. Zhang et al. successfully deposited CrP coating from a Cr(III) solution by adding ammonium hypophosphite (NH₄H₂PO₂) to a ChCl:ethylene glycol deep eutectic solvent containing CoCl₂ salts [51]. Employing the same system, You et al. firstly deposited NiP alloy coatings at room temperature; deposits with 8 wt.% P have been evaluated from the corrosion point of view [48].

5.2. Magnetic alloys

With progressive improvements and miniaturization in the microelectronic industries, the ability to obtain functional thin films is fundamental. Magnetic alloys have assumed a crucial role in a huge number of microelectromechanical system (MEMS), for example actuators, sensors [52]. In addition, the huge potential in biomedical applications of wirelessly controlled microrobots has attracted the attention of many researchers [53]. Nowadays, electrodeposition from aqueous solution is largely employed for the fabrication of magnetic films, for example FeCo, FeCoNi and CoPt, while few studies are present employing DES solvent. In the field of MEMS application, Guillamat et al. successfully obtain hard-magnetic CoPt without the need of subsequent heat treatments [54], avoiding a critical fabrication step for microelectromechanical system with layered and complex architecture. Yanai et al. showed the suitability of ChCl:ethylene glycol-based DES for FeNi alloys where deposits composition has shown to be easily controlled varying the reagent in the bath [55].

On the other hand, complex systems are commercially available for high performances magnets: SmCo, AlNiCo and NeFeB alloys. The correspondent metallic products are mainly fabricated through sintering or casting; the presence of rare earth metals or elements having high negative reduction potential limits the suitability of electrodeposition processes. Gomez, Cojocar and co-workers firstly succeeded in the electrodeposition of SmCo alloys employing a choline chloride–urea solution [40, 56]; the relative ease, low cost and precision of this process may represent an alternative to the metallurgical ones.

5.3. Semiconductors and photovoltaic alloys

With the emerging field of thin films solar cells, electrodeposition process started to gain importance also in the photovoltaic field. Unlike common vacuum techniques employed in the semiconductors industries, electrodeposition is a low-temperature atmospheric process allowing the fabrication of small features with high precision and control [57]. Among the active materials, CdTe is the most extensively studied chalcogenide material in the field of electrodeposition; the process is affirmed, and efforts are paid to bring the process to high volume production. On the other hand, Cu(In,Ga)Se₂ (CIGS) is the material having the best absorbing properties [56]. Studies on aqueous solution show the difficulties in controlling the composition, for example non-linearity between the metal concentration in solution and in the deposit; moreover, the process is characterized by very low faradaic efficiency (5%) due to Ga low reduction potential [58]. Malaquias et al. proposed a Mo/Cu/InGa metal stack subsequently selenized to obtain CIGS [58]; InGa deposition has been successfully carried out from 1ChCl:1Urea system [59]. Steichen et al. proposed a similar route for the fabrication of CuGaSe₂(CGS) active material; controlled electrodeposition of CuGa alloy is proposed using the same DES solution [60].

5.4. Alloys for electrocatalysis

Electrocatalytic processes are largely employed in the industry in different area of interest such as hydrogen production, energy conversion/production, electroplating. The employment of a catalyst is in fact a fundamental pillar of all the electrochemical processes. For example, nickel alloys have assumed an important role in water electrolysis process, both for the hydrogen and oxygen evolution reaction [61]. Vijayakumar et al. successfully deposited NiCoSn alloy from 1ChCl:2EG system and evaluated the improvement with respect to NiSn and CoSn alloys, obtained from the same solution, in terms of catalytic activity in 1 M KOH alkaline solution [59]. PtCo alloys are characterized by high electrocatalytic activities as well, and Guillaumat et al. successfully electrodeposited alloys with different composition between 54 and 90% wt. Pt [54].

6. Industrial applicability and implemented processes

A series of concerns must be considered when evaluating the realistic applicability of DESs electrodeposition in the industry. The main driving force for the development of new surface finishing processes is of course the need to improve existing industrial processes or to introduce brand new ones. For this reason, also electrodeposition from deep eutectic solvents must open new possibilities with respect to the current state of the art in order to be implemented as an industrial finishing process. Almost all the plating technologies used nowadays in the galvanic field use aqueous-based solutions. Each new DES-based process is therefore in competition with its homologous water-based counterpart, and possible advantages and disadvantages of its substitution must be carefully weighted. Aqueous solutions are widely used, the know-how for their employment is well established and in most cases their cost is

highly competitive. For this reason, in order to be accepted as realistic alternatives for water-based treatments, DESs must present significant advantages. This part of the chapter is intended to be an analysis of the realistic possibility to see large-scale applications for DES-based electroplating in the next few decades, as anticipated by some existing reviews [35]. Some pilot projects, already used on smaller scales, are presented as well to give a perspective and to demonstrate that, if the application is well calibrated, DESs can find application in industry.

6.1. Industrial applicability of metal deposition from DESs

As reported previously in this chapter, in principle DESs can be used to electrodeposit the main commodities metals: copper, nickel and zinc. From the practical point of view, however, their application to the deposition of coatings on most of the metals used in the industry (iron, copper, brass, nickel and their alloys) to produce functional parts is not realistic. These substrates are in general easy to plate after suitable pretreatments, and a wide variety of aqueous-based solutions is available for the most common metals [20]. A good example is copper, which can be deposited from alkaline, nearly neutral or acidic solutions reaching high thicknesses, excellent surface finishing and cathodic efficiencies [62]. The same is true also for nickel or zinc [62]. Moreover, deposits from DES-based solutions present in general a lower quality with respect to the ones from aqueous solutions. This is not always true, as Abbott et al. demonstrated in the case of nickel [63]. In this case, however the comparison is done between non-additive aqueous nickel baths and a choline chloride-based DES, while in industrial practice, solutions are most of the times modified with suitable additives to improve properties of the deposit (hardness, ...) or surface finishing.

There are however some applications where plating commodities metals from a non-aqueous solution are preferable, like in the case of substrates that are not easy to metalize (e.g. aluminium and magnesium). These metals are widely used, in general as alloys, for their low weight and good mechanical properties. The application of metallic layers on their surface is not trivial, since they tend to quickly passivate (or corrode, according to the pH of the electrolyte) upon exposure to the plating solution [64–66]. As already previously exposed, Mg alloys are in particular the most difficult due to their tendency to form MgO and/or Mg(OH)₂ film inhibiting adhesion of the electrodeposited coating and their high reactivity inducing formation of loose immersion layers on the surface by replacement that stop the successive electrodeposition. Furthermore, Mg is subjected to strong corrosion attack by aqueous electrolytes. The use of DES-based electrolytes can allow the deposition on aluminium or magnesium without specific pretreatments. This was demonstrated by Abbott et al. [22], Florea et al. [67] and Bernasconi et al. [68] in the case of nickel on aluminum and by Bakkar et al. [34] in the case of zinc on magnesium. Compact metallic layers can be applied on Al 1100 alloys and Mg-RE alloys by using a 1:2 mixture of choline chloride and urea additivated with metal ions and, in the case of nickel, a suitable complexing agent (ethylenediamine). The resulting coatings present good adhesion and corrosion behaviour. Other metals, such as chromium, can be plated on the resulting nickel if it is used as adhesion layer, producing thus multilayers [68].

A notable case in which it may be preferable to use DESs on an easy to plate substrate like steel is zinc deposition. Zinc is efficiently deposited from aqueous solutions, but, in this case, a considerable amount of the current supplied is lost for hydrogen evolution. Besides the low cathodic efficiency, the hydrogen produced can cause many problems to high-strength steels, inducing an embrittlement of the material [45, 69]. It can be thus beneficial to use DES-based electrolytes to plate zinc due to their low hydrogen evolution.



Figure 4. A chrome plating pilot plant part of the IONMET consortium activities [80].

Another possible application is the electrodeposition of some metals that are difficult or costly to electrodeposit from aqueous solutions. These may include highly reactive metals like samarium [40, 56] or inert metals such as indium [44]. In addition, the electrodeposition of metals which reduction potential falls outside the electrochemical window of water, like Al [70], can be in principle achieved. Their plating however must be performed in inert atmosphere with anhydrous solutions and a coating quality lower than imidazolium-based ionic liquids is in general achieved [71, 72]. For this reason, DESs do not offer real advantages with respect to other ionic liquids. Silver and other precious metals, characterized by high reduction potentials, can present some advantages when electrodeposited from DESs. Typically, these metals require strongly complexed electrolytes or the presence of intermediate plating steps to avoid undesired displacement deposition (resulting in poor adhesion) [62]. DESs strongly complex metallic ions, and for this reason, their use can result in good quality layers. Examples may include Ag [73] and Pd [74].

A particular case is represented by chromium plating. Functional chromium coatings are usually obtained from Cr(VI) containing solutions, but Cr(VI) is a recognized carcinogenic and environmentally hazardous chemical [75]. For this reason, it will be progressively banned from the industrial practice. EU is currently eliminating Cr(VI) as a chromium source in the case of decorative coatings, since Cr(III)-based aqueous solutions constitute a good alternative [76].

This is unfortunately not true in the case of functional hard chromium and aqueous solutions are not able nowadays to provide properties comparable to those coming from Cr(VI)-based electrolytes. DES-based Cr(III) solutions on the contrary showed promising results. In particular, cracked and crack-free thick coatings have been obtained from CrCl₃/choline chloride mixtures with cathodic current efficiencies higher than Cr(VI)-based electrolytes [29, 30, 45].

Not many examples of plants using DES-based electrodeposition processes are available nowadays, and all of them are pilot or semi-industrial projects. The Abbott group [77] at the University of Leicester is the most active in the industrialization of DES-based processes with its collaboration in the IONMET consortium [78], created under the 6th EU Framework Programme of Research. IONMET, in collaboration with Scionix [79], realized the ionic liquid demonstrator (ILD), which is a multi-application pilot plant facility to showcase the application of ionic liquids. Industrial electroplating of chromium and nickel was demonstrated at ILD. The IONMET consortium itself is scaling up many laboratory processes [78, 80], the most interesting one being hard chromium plating from DESs. Scionix is the largest world manufacturer of ionic liquids for industrial applications and of DESs in particular (**Figure 4**) [79]. Some patents are available as well for general metal deposition [81] or for specific applications: Ag [82], Au [83], superhydrophobic Ni layers [84], Fe [85], Zn and Ni [86] and Ga [87].

Some patents are available as well for general metal deposition [78] or for specific applications: Ag [79], Au [80], superhydrophobic Ni layers [81], Fe [82], Zn and Ni [83] and Ga [84].

6.2. Industrial applicability of alloys deposition from DESs

The considerations exposed in the case of metals deposition can be adapted to the plating of alloys. In particular, many different alloys are difficult to electrodeposit from aqueous solutions. The reasons are mainly correlated to the properties of some metals, which present high reactivity or refractoriness in water.

ZnMn alloys are difficult to plate in aqueous mediums due to the low reduction potential of manganese and to its reactivity [88]. These alloys, useful for corrosion protection, can be however obtained from choline chloride/urea mixtures [89] with good coating properties. On the contrary, Mo-based alloys are difficult to obtain in a wide composition range due to the inertness of molybdenum. The use of DES to obtain these alloys, also in this case promising for corrosion protection, can extend the compositional range with respect to water solutions (like in the case of NiMo and CoMo [90]). Always in the field of Zn-based materials, ZnSn is a particular case of alloy that can be deposited in water but present some advantages when plated in DESs. This material, a good option to replace cadmium in anticorrosion coatings, is plated from aqueous solutions [47], but composition control is easier when the deposition is performed in strongly complexing electrolytes like DESs [47]. Plating with DESs also avoids excessive hydrogen evolution, which may result in embrittlement of the coating. Similar considerations can be done for ZnNi and ZnFe.

Due to their negative standard reduction potential and high reactivity, almost all the rare earth-based alloys are not easy to plate in water-based solutions. Many of these alloys, like SmCo,

present however interesting properties, suitable for magnetic recording devices. The use of DESs for their electrochemical deposition can remove many obstacles with respect to aqueous plating. This was demonstrated by Gomez et al. [40, 56], which obtained high coercivity layers from a choline chloride/urea DES.

From the applicative point of view, for alloys the IONMET consortium is currently scaling up laboratory scale ZnSn deposition to perform barrel plate on industrial scale [78]. This is so far the only notable example of industrial application for alloys plating from DESs. Also in the case of alloys deposition, like in the case of pure metals, some patents for industrial processes are available: CrNi [91], CIGS [92] and AuSn [93].

6.3. Industrial applicability of electroless and displacement deposition from DESs

In this part are treated some processes not strictly related to electrodeposition but of some industrial interest. In the case of electroless and displacement deposition, few processes are available and almost none of them can be applied in current industrial practice. Some notable exceptions are the displacement deposition of some noble metals for PCB technology.

Water-based solutions for immersion plating of PCB contacts are currently used for corrosion protection of electrical contact, but some critical issues have been reported from their use [35]. Novel DES-based processes have been developed in the case of silver application on copper [45, 94] or copper application on aluminium [78]. **Figure 5** represents a PCB treated with immersion silver deposition.

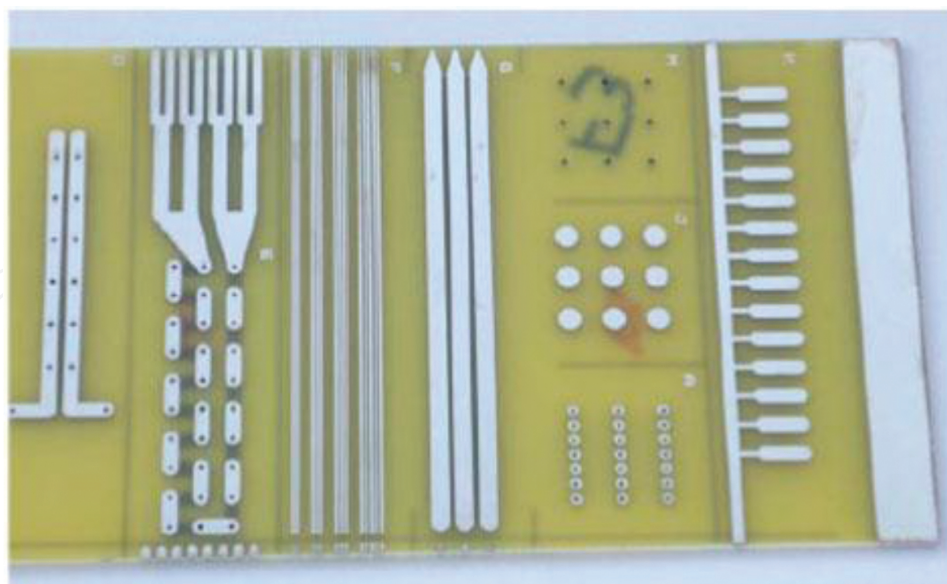


Figure 5. A PCB presenting copper tracks immersion plated with Ag from DESs [79].

ENIG-like processes have been developed as well, with gold deposited on nickel-plated contacts [94, 95]. The neutral nature of the DES can help avoiding the “black pads” effect,

induced by an excessive corrosion of Ni in the Au electrolyte. This advantage can increase the industrial attractiveness of such processes.

7. Conclusions

Deep eutectic solvents have the real potential to widen the panorama of modern galvanic techniques. Their application on large-scale production is however subordinated to the challenge of competing with well-established technologies and industrial systems not always easy to adapt to new techniques. As demonstrated by the examples presented, deep eutectic solvents are slowly leaving the laboratories to approach a real usage in plating plants. The next few decades will be the reference timeframe to understand whether these electrolytes have the possibility to be accepted as complements to existing water-based processes.

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