Original Research

Anodic dissolution of metals in ionic liquids

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Abstract

The anodic dissolution of metals is an important topic for battery design, material finishing and metal digestion. Ionic liquids are being used in all of these areas but the research on the anodic dissolution is relatively few in these media. This study investigates the behaviour of 9 metals in an ionic liquid [C$_4$mim][Cl] and a deep eutectic solvent, Ethaline, which is a 1:2 mol ratio mixture of choline chloride and ethylene glycol. It is shown that for the majority of metals studied a quasi-passivation of the metal surface occurs, primarily due to the formation of insoluble films on the electrode surface. The behaviour of most metals is different in [C$_4$mim][Cl] to that in Ethaline due in part to the differences in viscosity. The formation of passivating salt films can be decreased with stirring or by increasing the electrolyte temperature, thereby increasing ligand transport to the electrode surface.

1. Introduction

Anodic dissolution reactions are one of the cornerstones of metal processing and energy production in batteries. They are used for metal digestion, electropolishing, anisotropic etching, batteries and anodising. And they are also intrinsically linked with cathodic processes, such as electrodeposition. In aqueous solutions, passive film formation is a common issue, and for metal deposition a dimensionally stable anode is used, such that the anodic reaction is the decomposition of water, which is generally faster than the electrodeposition process and is in general ignored.

Recently, significant attention has been given to the use of ionic liquids as electrolytes for metal processing, secondary batteries and photoelectric devices [1–4]. Relatively little is known about anodic reactions in ionic liquids and very little data has been published on anodic dissolution efficiencies. Unlike aqueous solutions, the decomposition of the ionic

liquid is not usually a desirable option for a counter electrode reaction, due to the production cost of the liquid and the often complex products produced [5]. The high ionic strength and lack of water in most ionic liquid systems means that oxide and hydroxide films are less likely to form on electrode surfaces. Metals which would usually passivate in aqueous solutions, such as Cr and Al, can be readily oxidised in ionic liquids, and have been used as soluble anodes [6]. That is, however, not to say that insoluble layers do not form at the electrode surface and super-saturation can occur from the lack of suitable ligands to solvate the dissolving metal ion. With a few exceptions [7], the formation of passivating layers is poorly understood in ionic liquids.

To fully understand metal dissolution processes, it is often informative to look at the differences in metal speciation between aqueous solutions and ionic media. If a metal, M, is oxidised, the produced cation, M^{x+}, will interact with one or more types of ligand, L^{y-}, in solution to form a complex of the form [ML$_z$]$^{x++zy-}$. The solubility of the complex will depend upon the solvation and the overall charge of the complex species, where the latter can vary for a particular ion-ligand-combination depending on the coordination number z. In polar

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or ionic solvents, the complex usually requires an overall charge in order to be soluble. In water, L can be H_2O, OH^-, O^{2-} or the anion from the solute, all of which can affect the overall charge of the complex. The speciation and, hence solubility, of a metal complex in solution is strongly affected by pH, ligand concentration, and the coordinating ability of potential ligands. For example, in dilute basic media, metals such as zinc and chromium form the insoluble precipitates [Zn $(OH)_2 \cdot 4H_2O$] and [$Cr(OH)_3 \cdot 3H_2O$]. These are amphoteric, i.e. can be dissolved in acid, forming [$Zn(H_2O)_6$]$^{2+}$ and [Cr $(H_2O)_6$]$^{3+}$, whereas in strongly alkaline solution they are solubilised as [$Zn(OH)_4$]$^{2-}$ and [$Cr(OH)_6$]$^{3-}$. By using ligand acceptors, the dissolution and re-deposition of metals can be altered. For the example of iron acetylacetonate (acac) systems, the addition of Li ions hinders re-oxidation of electrodeposited metal by binding to the acac ligands, resulting in a more positive oxidation potential [8]. Similar effects can be observed in ionic liquids, where Lewis-acidic, Lewis-basic, cationic and anionic metal species can be observed, depending on solvent composition [9–11].

In an ionic liquid in most cases the anion of the ionic liquid will be the dominant ligand. This could be a poorly coordinating ligand, such as BF_4^- or [$(CF_3CSO_2)_2N$]$^-$, or it may be a more strongly coordinating ligand, such as Cl^- or SCN^-. The rate of the anodic process will depend upon the activity of the ligand and, in most cases, the viscosity of the ionic liquid. In many cases the counter electrode reaction is slow due to these issues, and at a fixed potential the current density and hence the overall process rate can be limited by the anodic reaction. An example of this is the electrodeposition of aluminium from chloroaluminate ionic liquids. Aluminium can only be electrodeposited from Lewis acidic compositions, i.e. where $AlCl_3$: [$C_x$mim][Cl] > 1:1. Under these conditions the liquid contains $Al_2Cl_7^-$, and it is known that aluminium cannot be electrodeposited from $AlCl_4^-$ at ambient conditions [12–14]. Considering that the only practical anodic reaction is the electrodissolution of aluminium, this introduces the issue of what the ligand for the reaction is. In Lewis acidic liquids the activity of free chloride will be insignificant, indicating that the necessary ligands will have to come from $AlCl_4^-$, a minor aluminium-containing component. Therefore, the anodic reaction becomes

$$Al + 7AlCl_4^- \rightarrow 4Al_2Cl_7^- + 3e^-$$
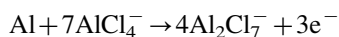
The cathodic reaction is faster and the anodic reaction is slower as the liquid becomes more Lewis acidic. In addition, this liquid becomes more viscous as the composition moves away from 2:1 to 1:1 $AlCl_3$:[$C_x$mim][Cl]. Diluents, such as toluene, are thought to modify the deposition rate and morphology at fixed potential by increasing mass transport and speeding up the anodic reaction [12].

The largest application of anodic processes in ionic liquids has been for electropolishing. This has been applied to both stainless steel and nickel based superalloys [15–17]. In both systems, polishing is thought to occur due to the formation of viscous layers close to the dissolving electrode surface. It has been found that the mild steel and a variety of other nickel

alloys can also be electropolished in deep eutectic solvents. As will be discussed below other metals, such as silver, copper and lead, do not electropolish, but pit instead.

Several plating processes to date have been scaled up using ionic liquids and DESs but most have used dimensionally stable anodes because soluble anodes often limit the current density that can be applied to the cell. The optimum process would ideally involve the use of soluble anodes, as the overpotential required to drive the deposition process will be small. This is especially important with ionic liquids because the ohmic loss across the cell can be significant. However little is known about the dissolution processes of metals in ionic liquids. The aim of this study is to investigate the behaviour of a selection of 9 commonly electroplated metals in two electrolytes with chloride as the anion: Ethaline, a 1:2 mixture of choline chloride and ethylene glycol, and 1-butyl-3-methylimidazolium chloride [C_4mim][Cl]. The data obtained here will help to explain some of observations made about metal dissolution and electropolishing, and in particular, aid in the understanding of the factors affecting dissolution rates.

2. Material and methods

2.1. Reagents and working electrodes

Ethaline was prepared from a 1:2 M ratio mixture of choline chloride, [$(CH_3)_3NC_2 H_4OH$]Cl, (ChCl) (Sigma-Aldrich, > 99%) and ethylene glycol (Sigma-Aldrich, ≥ 99.5%). This was heated and stirred at around 60 °C in a beaker until a homogeneous and colourless liquid had formed. 1-Butyl-3-methylimidazolium chloride, [C_4mim][Cl], (Sigma-Aldrich, > 99%) was dried under vacuum before use but had a water content of *c.a.* 0.1 wt% (Thermogravimetric Analysis, Mettler Toledo TGA/DSC1 STARe system) which enabled it to be liquid at 70 °C. The working disc electrodes used in these experiments were made in-house by sealing the following wires in glass with an epoxy resin: Ag (Alfa Aesar, ≥ 99.9%), Au (Goodfellow, ≥ 99.99%), Fe (Goodfellow, ≥ 99.9%), Co (Alfa Aesar, ≥ 99.995%), Cu (Alfa Aesar, 99.9%), Ni (Alfa Aesar, 99.98), Pb (Alfa Aesar, 99.9), Sn (Alfa Aesar, 99.998) and Zn (Alfa Aesar, ≥ 99.95%). All had a diameter of 1 mm except for Au which was 0.5 mm. Prior to electrochemical measurements, each electrode was polished mechanically using alumina (1 μm). Anodic products were observed on 1 cm^2 sheets by polarisation at constant potential for 10 min.

2.2. Electrochemical measurements

All electrochemical measurements were conducted using a three electrode system, with a platinum flag counter electrode, Ag^+/Ag (0.1 M AgCl in either Ethaline or [C_4mim][Cl], depending on the ionic liquid) reference electrode, using the working electrodes described above.

Anodic linear sweep voltammetry (LSV) experiments were performed at both 20 and 70 °C, using an Autolab/PGSTAT12 potentiostat controlled with PGES2 software. Electrochemical impedance spectra were collected using an Autolab/
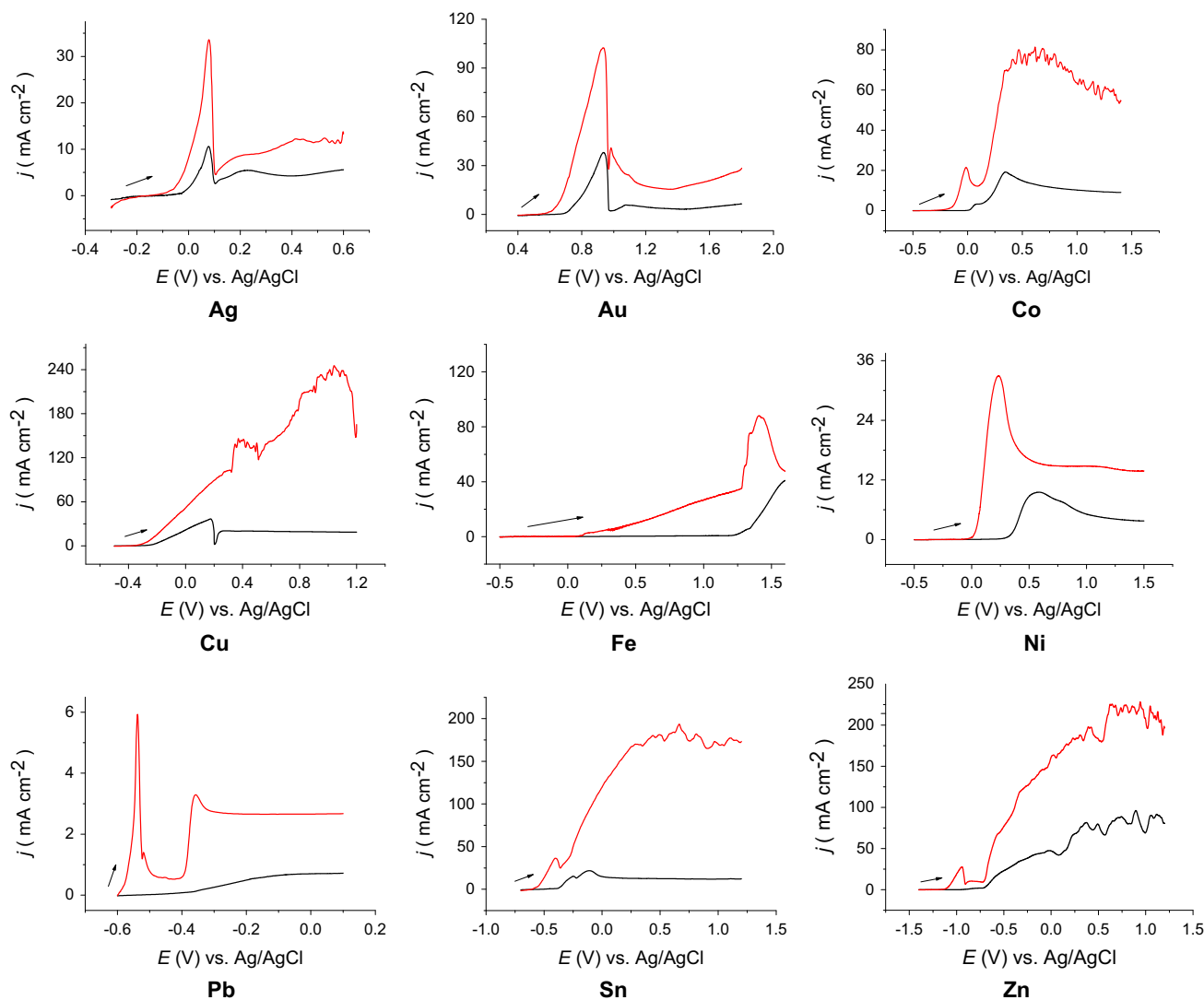
Fig. 1. LSVs of (from top left) Ag, Au, Co, Cu, Fe, Ni, Pb, Sn and Zn in Ethaline at 20 (black line) and 70 °C (red line). The sweep rate was 5 mV s^{-1}.
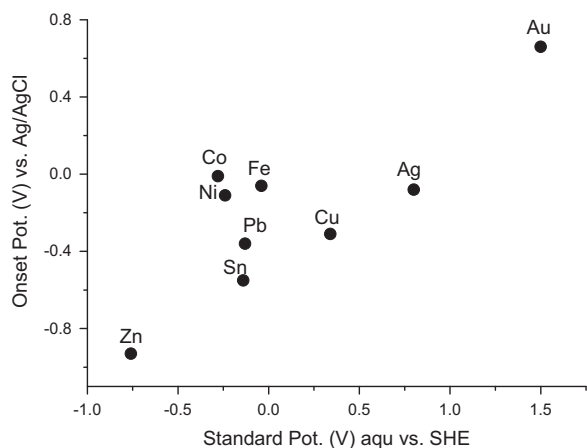

Fig. 2. Onset potential of metals in Ethaline vs. corresponding standard potential in aqueous solution [19].

PGSTAT12 potentiostat fitted with an FRA impedance module using GPES software. Frequency spectra acquisition were obtained in the range 1–65000 Hz and the amplitude of the a.c. signal was 10 mV. All LSVs and impedance spectra were made on freshly polished surfaces.

Three dimensional optical images were conducted using a Zeta optical profiler.

3. Results and discussion

3.1. Anodic linear sweep voltammetry (LSV)

Fig. 1 shows the LSVs for the 9 investigated metals in Ethaline at 20 and 70 °C. All of the metals studied here can be electrochemically oxidised in this medium, including gold. There is naturally a significant difference in the onset potentials but oxidation does not occur in the order that would be expected from aqueous standard potentials.

Electrode potentials for some of the redox couples in Ethaline have previously been reported [18]. The differences of the aqueous standard potentials have been rationalised in terms of metal speciation. Fig. 2 shows the general relationships between the oxidation onset potentials in Ethaline vs. the

E^0 values for aqueous solutions. Whilst the absolute values are not comparable, it is apparent that in the ionic liquid, the relative potentials and sometimes even the order in which the metals are oxidised are different from the aqueous solution. As a general trend, the metals such as gold, silver and copper, which form stable complexes with chloride, are particularly easy to oxidise in the chloride containing electrolyte.

The chloride salts of these metals generally have high solubility in Ethaline, with copper and zinc being soluble in excess of 0.5 mol dm^{-3}. It is therefore counter-intuitive that the voltammograms display pseudo-passivation behaviour in some cases and diffusion controlled responses in others. However, in some cases where oxidation involves the formation of an intermediate state such as Cu^I, the dissolution rate may be limited by the solubility of this intermediate species.

3.2. Characterisations of copper dissolution

3.2.1. Linear sweep voltammetry

Fig. 3 shows a series of LSVs of a copper disk electrode in Ethaline at a variety of sweep rates. The sudden decrease in current following the peak is characteristic of a passivation
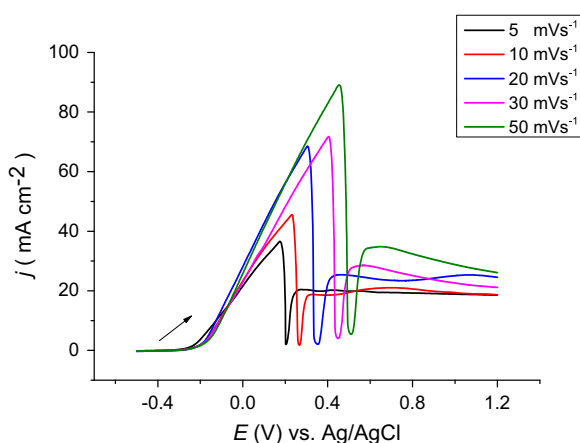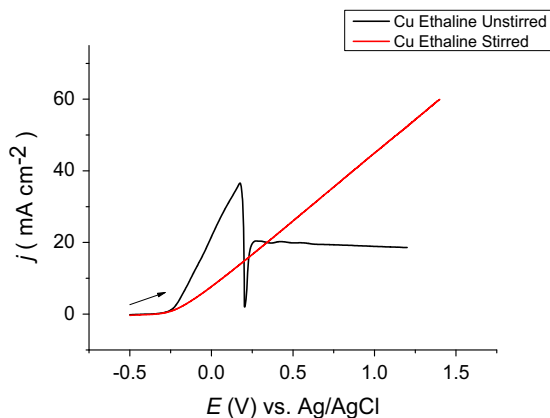

Fig. 3. LSVs of a Cu disc electrode in Ethaline at 20 °C at a range of different sweep rates.

(surface blocking) process [20–22], and appears at more positive potentials with an increasing scan rate. The current then increases slightly and levels off, suggesting that at least a part of the blocking layer remains on the electrode surface.

The initial rising part of the linear sweep is most likely due to the formation of a Cu^I species, e.g. [CuCl$_2$]$^-$ [23]. As the layer of ionic liquid at the electrode surface becomes enriched in Cu^I species, which has a low solubility compared to Cu^{II} in these solvents, a layer of crystalline material precipitates onto the electrode surface, resulting in the sharp drop in current density [24]. Shortly afterwards, the system returns to a diffusion controlled steady state.

In Ethaline, the Cu$^{II/I}$ redox couple appears at $+0.45$ V [18], with respect to the 0.1 M AgCl/Ag reference electrode, however this is not clearly observable in Fig. 3. The precipitation and re-dissolution processes would probably be slow, which may explain the sweep rate dependency observed in Fig. 3.

The dissolution of copper in aqueous solutions containing varying concentrations of chloride has been investigated by several authors. At high chloride concentrations, a two stage mechanism occured for the dissolution corresponding to the changeover of Cu^I to Cu^{II} but no quasi-passivation was observed [25–27]. It was however found that the rate of dissolution is diffusion controlled, i.e. limited by the diffusion of the anion to the electrode surface [28].

3.2.2. Electrochemical impedance spectroscopy of copper (EIS)

Fig. 4 shows the EIS of copper in Ethaline at different d.c. potentials. At negative d.c. potentials there is a single semi-circle with a diffusion limited electron transfer process. At $+0.2$ V a second semi-circle developed and at higher positive over-potentials this dominated, indicating that an insulating layer formed on the electrode surface.

The data in Fig. 4 were fitted to an equivalent circuit containing a two Randle's circuits in series with a Warburg impedance using the in-built GPES software. For the data an applied voltage of $+0.8$ V the capacitance of the film was
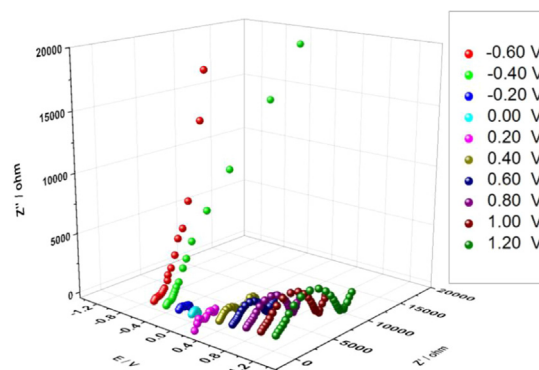

Fig. 4. Anodic LSV of Cu disc in Ethaline vs. Ag/Ag$^+$, at a scan rate of 5 mV s (black) and the same electrode rotated at 3000 rpm (red) (left) and electrochemical impedance spectra at various potentials with a.c. amplitude of 10 mV in the frequency range of 1–65000 Hz (right).
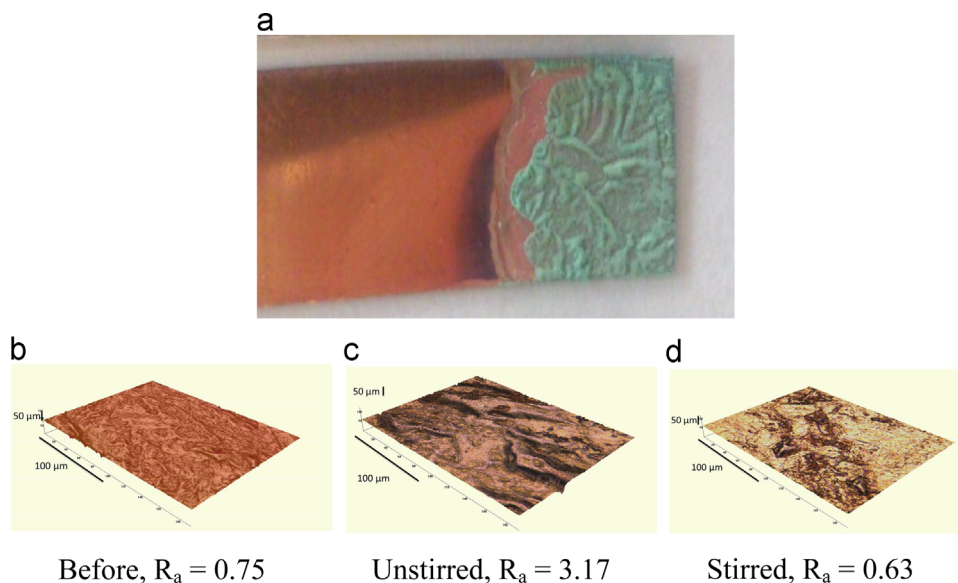
Fig. 5. (a) Copper electrode after being held at +0.18 V for 10 min (b) copper rotating disc electrode before cycling (c) after polarisation from -0.5 to + 1.5 in Ethaline at 5 mV s^{-1} without rotation and (d) as (c) but with rotation at 3000 rpm.

found to be 4.9×10^{-6} F cm^{-2}. Assuming a dielectric constant of 8.0 the thickness of the film was calculated to be 1.4 μm [29]. When the copper electrode was held at +0.18 V for 10 min the surface initially darkened and a green film slowly formed on the electrode surface (Fig. 5). At this potential, the most likely precipitate is CuCl, which is only moderately soluble in Ethaline. The light green colour indicates that some further oxidation of Cu^{II} occurs, however, given the applied electrode potential, the oxidation is probably caused by dissolved oxygen.

If the film is washed off the electrode then the metal is seen to darken quite considerably due to surface roughening. To determine the role of mass transport on morphology the experiment was repeated using a rotating disc electrode. The morphology of the surface before and after anodic polarisation can be seen in Fig. 5 for a copper electrode with and without stirring. During the anodic sweep it can be seen that the average surface roughness value, R_a, of the electrode prior to anodic polarisation was 0.75 μm, whereas the value after polarisation was 3.75 μm. When the electrode was rotated at 3000 rpm, the R_a was 0.63 μm. If the liquid is stirred (by rotating the electrode at 3000 rpm) then no film forms at the electrode surface and the solution becomes green in colour. The nature of the film that forms is strongly dependent on the applied potential and current density. At lower over-potentials the film was smoother, and pitting was less severe, presumably due to fact that the passivating layer was produced at a lower rate and forms a more uniform barrier.

The electropolishing of copper in ionic liquids has previously been studied by Lebedeva et al. who found that copper which already had an oxide film on it could be electropolished in water saturated [C$_4$mim][Tf$_2$N] [30]. It was found that the water played an important role in the polishing process, as it maintained an oxide layer through which the electrode was polished.

3.3. Characterisations of cobalt dissolution

The electrochemistry of iron, cobalt and nickel is dissimilar to the other metals in Fig. 1, in that they do not reversibly electrodeposit on a Pt electrode from an Ethaline solution of their salts. This irreversibility is important in the anodic behaviour and has previously been ascribed to the formation of poorly soluble films at the anode-solution interface [16]. Previous work has characterised the speciation of metal salts in a selection of DESs and ionic liquids with discrete anions. It was found that many monovalent transition metal salts, e.g. AgCl, formed complexes of the form [MX$_2$]$^-$ whereas most divalent metals formed complexes of the form [MX$_4$]$^{2-}$ [23]. As one notable exception, nickel was observed to form complexes with the hydrogen bond donor of the DESs, instead of the anticipated chloro-complexes, as was observed for the corresponding cobalt and iron salts. When FeCl$_3$ is dissolved in Ethaline it initially forms [FeCl$_4$]$^-$ [31], however a brown precipitate is observed to form over time, the exact nature of which is unknown. When iron dissolves either under potential control or through open circuit corrosion, a brown precipitate forms at the electrode surface, most likely an oxide/hydroxide complex.

3.3.1. Electrochemical impedance spectroscopy (EIS)

LSV and a.c. impedance spectroscopy of cobalt in Ethaline produces very different responses to those observed for copper, but similar to those of nickel and iron. It can be seen from Fig. 6 that the oxidative current decreases less abruptly than was the case with copper (Fig. 4). It can also be seen that the magnitude of the impedance semi-circle is significantly larger for cobalt than for copper. At an applied voltage of +0.9 V the capacitance of the film was found to be 8.83×10^{-6} F cm^{-2} (Fig. 6). The dielectric constant for cobalt chloride is unknown, but given that most similar transition metal halides are in the
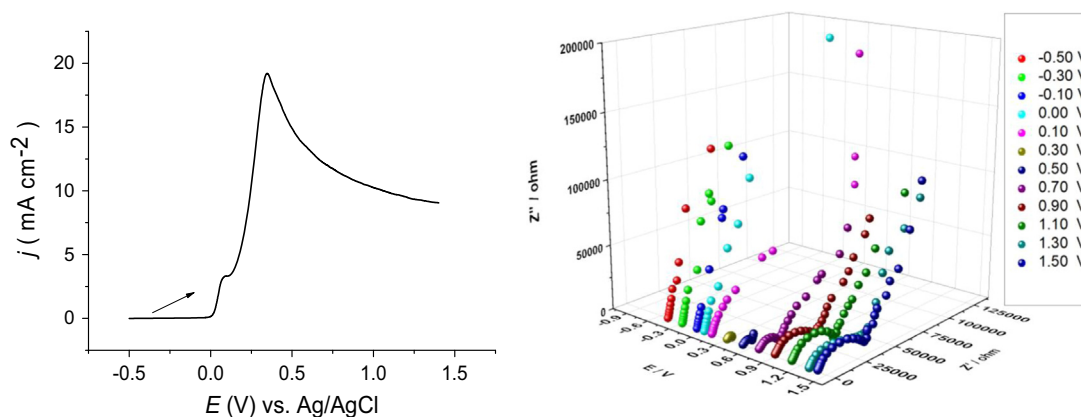
Fig. 6. Anodic LSV of Co disc (dia. 1 mm) in Ethaline at a scan rate of 5 mV s (left) and electrochemical impedance spectra at various potentials with a.c. amplitude signal of 10 mV in the frequency range of 1–65000 Hz (right).

range 5.3–11.2 [32] the film forming on the cobalt surface can be calculated to be in the range 6–12 μm. This suggests that the film formed on the electrode surface is very different to that formed on copper.

Holding the anodic potential of a cobalt sheet at $+0.34$ V resulted in cobalt dissolution but without the surface roughening observed for copper. Prior to anodic polarisation the R_a was 0.23 μm, whereas the value after polarisation was 1.0 μm. This shows that uniform metal dissolution occurs when crystalline layers do not form on the electrode surface.

3.4. Effect of temperature

Since the diffusivity in solution will be higher at elevated temperatures due to lower viscosities, it was anticipated that the anodic LSVs would display the presence of a reduced passivating salt film. Fig. 1 also shows the LSVs for the 9 metals at 70 °C and compares them to those obtained at 20 °C.

The anodic current is significantly higher at 70 °C than at 20 °C, in many cases an order of magnitude larger. For the majority of the metals studied, there are still signs that film formation continues to occur at 70 °C, although in most cases it is either reduced or occurs at a different potential. This could be due to an increased solubility of the metal salts at higher temperatures, the formation of different solid phases or the increased diffusion of the ligand due to the reduced viscosity of the liquid.

For some metals with a low dissolution potential, e.g. Sn, Pb and Zn, significant passivation effects are still observed. This might possibly be due to a double layer effect; at potentials negative of the potential of zero charge (pzc) the layer close to the electrode surface is dominated by quaternary ammonium cations, and there will be insufficient chloride to enable the formation of a charged oxidation product [33]. As the electrode is polarised to positive potentials, the double layer switches to being anion dominated and the oxidation product becomes negatively charged and hence soluble. Work by Costa et al. has characterised the double layer properties of DESs and found that the pzc is in the region of -0.2 to -0.4 V vs. Ag [33].

Endres et al. have shown that multi-layer films form at the electrode-ionic liquid interface, and these are proposed to affect electrode processes [34]. This ties in well with what is proposed here and adds another layer of complexity to the picture of double layer behaviour in these electrolyte systems.

It should however be noted that these results are only qualitative for the purposes of comparison, as the anodic dissolution processes are dependent upon the presence (or lack thereof) of residual films (oxide/hydroxide or halide). These surface films vary with the number of sweeps made previously, along with whether the system is stirred or not.

3.5. Comparison of ionic liquids vs. deep eutectic solvents

Fig. 7 shows the LSVs of 9 electrodes in Ethaline and [C$_4$mim][Cl] both at 70 °C. For the majority of these metals, the onset potentials between the two solvents are similar. This could reasonably be expected, given that the metal species are in most cases similar, if not the same, in both solvents, i.e. chloro-complexes.

The dissolution current in Ethaline is larger than that for [C$_4$mim][Cl], which is almost certainly due to the difference in viscosity (Ethaline$=16$ cP and [C$_4$mim][Cl]$=142$ cP, both at 70 °C) [35]. During the anodic sweep of each electrode, the discolouration of the electrode surface can be seen with [C$_4$mim][Cl]. Interestingly only nickel displayed an anodic response with a similar shape and oxidation onset potential in both liquids. At room temperature, the speciation of Ni^{II} is known to be different in imidazolium chloride-based ionic liquids compared to Ethaline, e.g. [Ni(EG)$_3$]$^{2+}$ in Ethaline, and [NiCl$_4$]$^{2-}$ in [C$_6$mim][Cl] [23]. However, the speciation in Ethaline has been observed to change with increasing temperature to the tetrachloronickelate species [36,37]. At 70 °C a significant proportion of the dissolved nickel in Ethaline should form the tetrachloro species, however this does not explain why the other metals do not also show similar behaviour between the two solvents. However, only room temperature speciation is known for many of the samples used here.
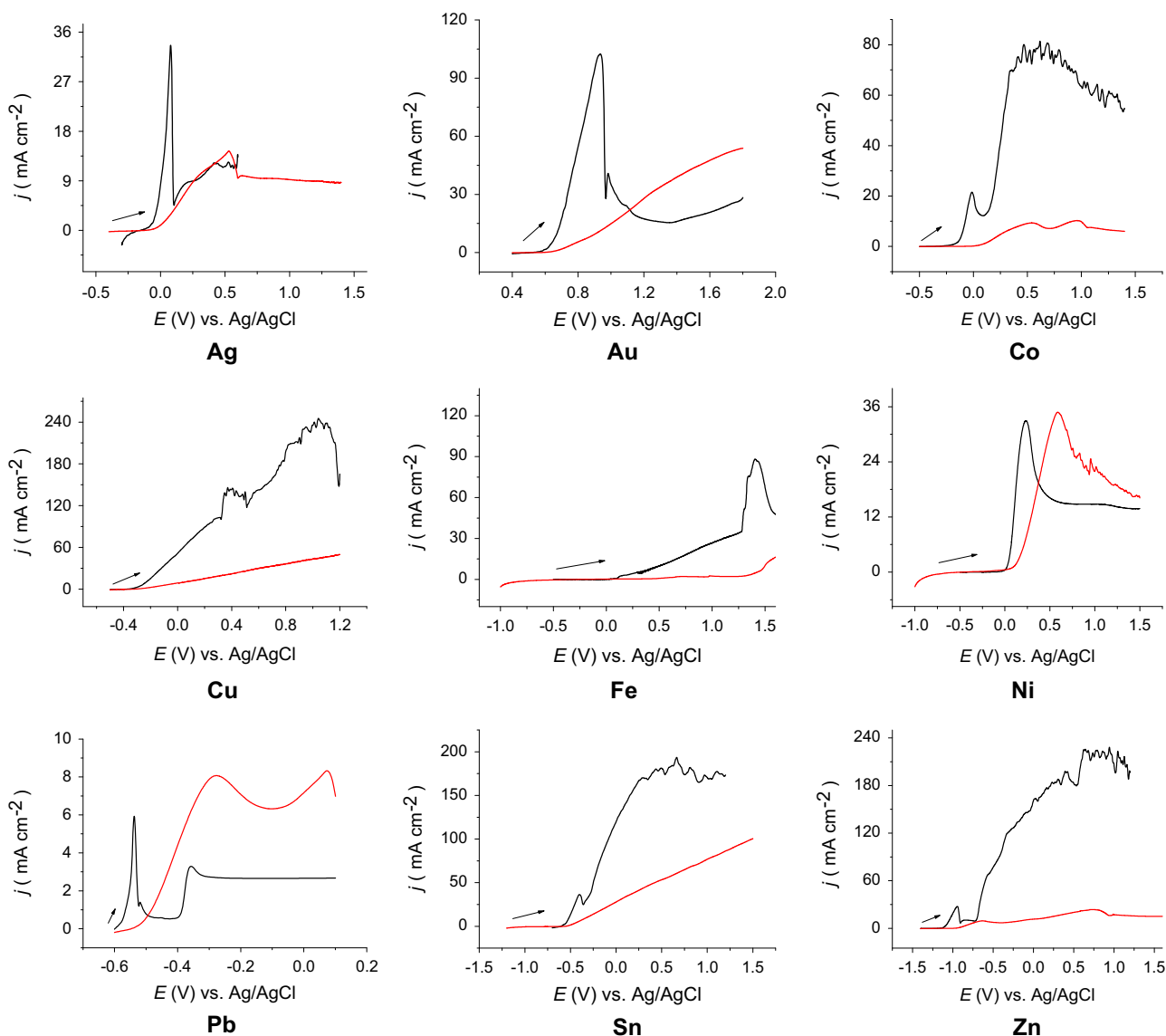
Fig. 7. LSVs of (from top left) Ag, Au, Co, Cu, Fe, Ni, Pb, Sn and Zn in in Ethaline (black line) and [C$_4$mim][Cl] (red line) at 70 °C. The sweep rate was 5 mV s^{-1}.

The responses for metals such as gold, copper and tin in [C$_4$mim][Cl] suggest that there is no film formation during dissolution under the conditions of the experiment. This is supported by the observation that only one charge-transfer semi-circle is observed in the EIS at high over-potentials. The large semi-circle for copper above $+0.4$ V in Ethaline (Fig. 4) is absent in [C$_4$mim][Cl], which is surprising, given that the speciation should be similar in both cases. The same is also the case with cobalt, despite the LSV reaching a limiting current there is no film formation observable in the EIS. An additional level of complexity could arise from the structure of the double layer and the availability of sufficient ligands to complex the metal. In Ethaline, the chloride anion will interact with ethylene glycol and could have a greater interaction with the cation, potentially reducing the availability of chloride to complex with the metal cation.

4. Conclusions

From this preliminary investigation into selected simple examples, it can be seen that the anodic oxidation of metals from their elemental state in an ionic liquid environment is a complex issue which is strongly dependent upon speciation, mass transport and solubility. The anodic dissolution behaviour of metals is a very complex subject that should be investigated in greater depth. It is, however, observable from this study that the type of ligand alone is not the sole factor controlling the solubility of a metal complex in an ionic liquid. The structure of the double layer and the availability of the ligand may also play a significant role. To fully understand electrodeposition and dissolution in ionic media, both the anodic and cathodic processes need to be studied in the same depth. It is shown that increasing the temperature reduces the

formation of a salt film on anodically dissolved metals. For certain metals, such as gold, copper and tin, a salt film is observed when dissolved in Ethaline, but not in [C$_4$mim][Cl]. Oxidation onset potentials between the two ionic solvents are generally similar, as would be expected for similar dissolved species, but are significantly different from aqueous solutions.

This study shows that even for metals where the halide salt is generally soluble, film formation can block the electrode surface, leading to a decrease in anodic current and hence affecting the even dissolution of metal. This is more prevalent in unstirred solutions, where ligand transport to the electrode surface is diffusion limited, highlighting the need for optimisation of fluid flow throughout the whole cell where ionic liquids are used for electrochemical applications. This, together with speciation and viscosity effects, could also be one of the reasons that such a large temperature dependence has been observed for deposition and dissolution processes in ionic liquids.

Acknowledgements

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