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Ionic Liquids as Electrodeposition Additives and Corrosion Inhibitors

Zhang Qibo and Hua Yixin

Abstract

Ionic liquids (ILs) are molten salts with a melting point of 100°C or below and solely consist of cations and anions. As a kind of novel green solvent, ILs have been obtained broad and deep investigations, and enormous progresses in various fields have been made during the recent 20 years. Despite the fact that the application studies of ILs have been proposed in various fields, no processes have yet been developed to an industrial scale. However, the main interests are still focused on their industrial applications. In this chapter, two perspective applications of ILs in electrochemical fields including additives for metal electrodeposition and inhibitors for metal anti-corrosion were introduced.

Keywords: ionic liquids, additives, metal electrodeposition, corrosion inhibitors, adsorption

1. Introduction

Additives are widely used in electrodeposition of metals and alloys due to their special functions in the deposition process. These additives are found to affect both the deposition and crystal-building processes through their adsorbates at the electrode surface [1]. Traditional colloidal and some organic additives have gained wide industrial use and achieved good additive effect, even though they can be decomposed easily and are not environmentally friendly due to their disadvantages, such as thermal stability, bad chemical and high toxicity. Consequently, there is a continuing search for better additives that combine good stability, high efficiency and environmentally friendliness. The effect of corrosion inhibitors is similar to that of electrodeposition additives to some extent, as their excellent corrosion resistance performance on metals is attributed to their adsorption on the metal surface, which protects the metal from attack by the acidic solutions [2]. However, most commercially available

picking inhibitors are toxic compounds that should be replaced by new environmentally-friendly ones. Research studies in the field of 'green' corrosion inhibitors have been aimed at using cheap, effective molecules with low or 'zero' environmental impact [3].

Ionic liquids (ILs) are organic salts that are liquids at ambient temperature and comprised entirely of organic cations and organic/inorganic anions. Due to the unique structure characteristics, ILs have many attractive properties and attract a great deal of interest in various fields [4–17]. Some of the most important prosperities of ILs are their thermal stability and avirulence, which make them potential additives for metal electrodeposition and green inhibitors for metal anti-corrosion. In our previous studies, alkylimidazolium, alkylpyridinium and quaternary ammonium-based ionic liquids were observed to be an excellent levelling agent in zinc [18–22] and copper [23–25] electrodeposition and showed favourable corrosion resistant on metals such as aluminium [26], copper [27] and mild steel [2].

2. Why use ILs as electrodeposition additives and corrosion inhibitors?

As mentioned above, the effect mechanism of electrodeposition additives and corrosion inhibitors is quite similar. Both are dependent on their surface adsorbability to achieve the expected additive effect. The main difference from each other could be the use of additives is under electric field and their electrode surface adsorption behaviour will be influenced by the electric field distribution, while the corrosion inhibitors are used without galvanization and their adsorption mainly depends on certain physico-chemical properties of the inhibitor group, such as electron density at the donor atom, π-orbital character and the electronic structure of the molecule [28].

ILs are composed entirely of organic cations and organic/inorganic anions that are liquid at low temperature. Their relatively high cationic configuration makes them readily adsorb on the cathode surface under the electric field. In addition, some functional groups such as –C=N– group and electronegative nitrogen in the molecule of imidazolium ILs enables them spontaneous adsorption on the metal surface due to the specific interaction between these functional groups and the metal surface [2]. Furthermore, the high thermal stability, negligible vapour pressure and environmentally benign characteristics of ILs allow them to be considered as very promising replacements for the traditional volatile organic solvents. Therefore, it is hopeful to overcome these defects of traditional additives and toxic organic corrosion inhibitors, and help to realize additives with good stability and inhibitors with avirulence by using ILs as metal electrodeposition additives and corrosion inhibitors, respectively.

The application studies of ILs have been proposed varying from precious metal processing [29–40] to mineral leaching [41–44]; however, very few have come to practical fruition although several are at a pilot scale [45–47]. Except some technical difficulties that are hard to solve at our present state of knowledge [48], the relatively prohibitive high cost of ILs is also a main reason for delaying their industrial application [44]. In comparing to the use ILs as electrolytes for metal electrodeposition and rechargeable batteries, where the

reproducible operation in these ILs requires either a strictly controlled inert gas atmosphere with extremely low water concentration or at least closed vessel conditions with limited contamination [49], the applications of ILs in electrodeposition additives and corrosion inhibitors are not only cost accepted with the trace amount of consumption, but also have more practical operability.

On the basis of these discussions, it is accepted that the applications of ILs as additives for metal electrodeposition and corrosion inhibitors are with favourable industrial application prospect, as in our opinion they are very likely to initiatively realize the zero breakthrough of industrial applications of ILs.

3. Additives for metal electrodeposition

In modern electrodeposition and electrowinning practice, it is well known that the introduction of one or more inorganic or organic additives in the electrolyte leads to produce smooth, free of voids and compacted metallic deposits at the cathode. The quantity of additives required is always considerably small, but their action is often specific [50]. Although the number of these additives studied in electrodeposition is very high, their action mechanism can be divided into two main categories, which are levelling additive and brightening additive. Levelling additive [51] has been defined as the additive with the ability to produce deposit relatively thinner on small protrusions and then decrease in depth on height of the small surface irregularities. While brightening additive [52] can be defined as the ability to obtain fine deposits with the crystallites smaller than the wavelengths of visible light. In this section, we reported the use of a series of novel 1-alkyl-3-methylimidazolium hydrosulphate ILs, namely, [BMIM]HSO$_4$, [HMIM]HSO$_4$ and [OMIM]HSO$_4$ as additives in zinc electrodeposition from the acidic sulphate electrolyte. Furthermore, effects of ILs on copper electrodeposition from acidic sulphate electrolyte were also introduced.

3.1. Additives for zinc electrodeposition

Zinc electrodeposition is very sensitive when it comes into contact with some types of impurities in augmenting simultaneous evolution of hydrogen during zinc ion electroreduction from aqueous solutions. Apart from occluding hydrogen into the zinc deposit, hydrogen evolution will increase specific electric energy consumption and decrease current efficiency (CE), bringing about an increment in the level of internal stress to produce pitted deposits [19]. To counteract the harmful effect of metallic impurities, achieve high CE and produce a smooth, levelled and dense cathodic deposit, additives such as glue and gum arabic are most often used. In addition, enormous organic additives [53–62] have been proposed for use as additives and some authorities have reported them to work better than glue or gum arabic. We have reported that 1-alkyl-3-methylimidazolium hydrosulphate ILs ([BMIM]HSO$_4$ [18], [HMIM]HSO$_4$ and [OMIM] HSO$_4$ [19]) had a pronounced inhibiting effect on Zn^{2+} electroreduction and all were efficient as levelling agents for zinc electrodeposition.

Figure 1(a) shows the effect of [BMIM]HSO$_4$ on the CE during zinc electrodeposition. The CE increases with the initial addition of [BMIM]HSO$_4$ and steadily decreases at higher concentrations. Without additives, the CE is ~89%, whereas at 5 mg dm^{-3} [BMIM]HSO$_4$ the CE was ~92.7% and then fell to 87.8% at 50 mg dm^{-3}. The trend observed in CE with increasing [HMIM]HSO$_4$ and [OMIM]HSO$_4$ concentration is similar to that for [BMIM]HSO$_4$, where we obtained a CE of 92.9–92.2% with the addition of 2 mg·dm^{-3} [HMIM]HSO$_4$ and 1 mg dm^{-3} [OMIM]HSO$_4$, respectively, but at higher concentrations there is a reduction. The CE decreases with increasing additive concentrations in the order [OMIM]HSO$_4$ > [HMIM]HSO$_4$ > [BMIM]HSO$_4$, which reflects increasing absorbability at the electrode surface with increasing molecular size and hence molecular mass [62, 63].

The cyclic voltammograms recorded for zinc electrodeposition from acidic sulphate solution in the absence and presence of ILs additive [BMIM]HSO$_4$ are presented in **Figure 1(b)**. The voltammograms were initiated at point '*A*' (−0.70 V versus SCE), scanned in the negative direction and reversed at −1.30 V in the positive direction. The nucleation overpotential (NOP) for zinc deposition on an aluminium substrate is defined as the potential difference between the electroreduction potential of zinc ions at '*B*' and the crossover potential at '*D*', which is regarded as an indicator of the extent of polarization of a cathode [64]. It is clear that the addition of additives has a significant effect on the zinc electrocrystallization process as shown in **Figures 1(b)** and **2–4**, where the NOP values increase substantially, along with the reduction of the cathodic process area. The strong adsorption of the additives on the electrode surface is usually held to be responsible for this. The extent of absorption appears to be in the order [OMIM]HSO$_4$ > [HMIM]HSO$_4$ > [BMIM]HSO$_4$, which shows the adsorbability of the studied additives and reflects their effect on the process of deposition. The analysis of the kinetic parameters [18, 19] indicates that the presence of ILs does not have any significant effect on the Tafel slopes and transfer coefficients, suggesting that they do not change the zinc electrodeposition mechanism in the absence of additives.
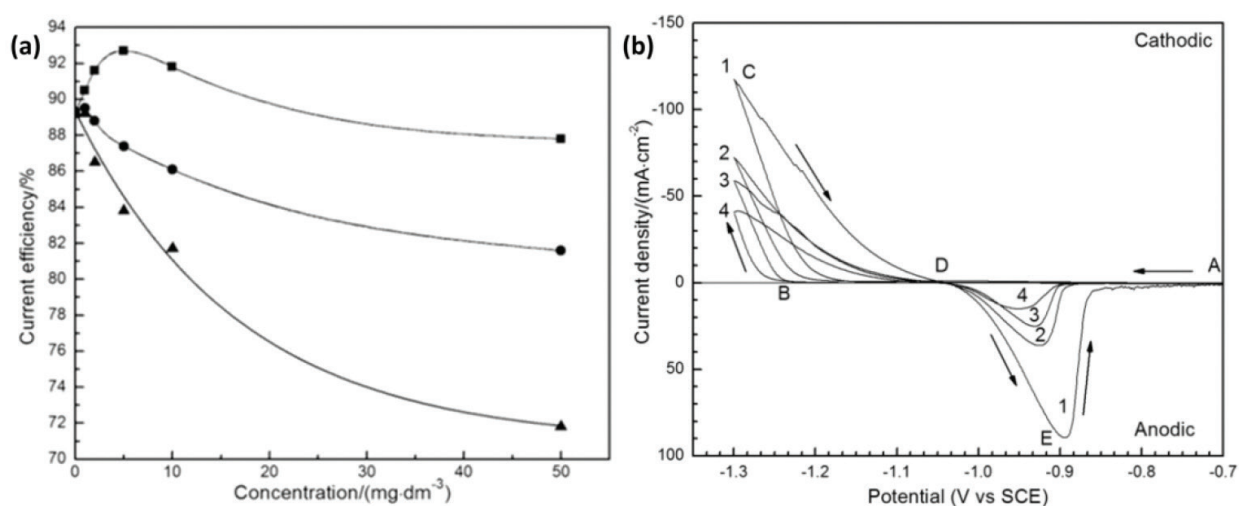

Figure 1. (a) Effect of additives on current efficiency during zinc electrodeposition. (■) [BMIM]HSO$_4$, (●) [HMIM]HSO$_4$ and (▲) [OMIM]HSO$_4$. (b) Cyclic voltammograms of acidic zinc sulphate solutions in the absence and presence of 5 mg dm^{-3} different additives. (1) Blank, (2) [BMIM]HSO$_4$, (3) [HMIM]HSO$_4$ and (4) [OMIM]HSO$_4$ [18, 19].

The investigated additives significantly changed the morphology of the zinc deposits as compared with those obtained from solutions without additives, as shown in **Figure 2**. The zinc deposit obtained from addition-free electrolyte is bright but not smooth and consists of hexagonal platelets of moderate size (**Figure 2a**). Introducing the additives into the solution did not affect the shape of the crystals but improved the quality of deposits by reducing the platelet sizes and giving smooth and compact deposits (**Figure 2b** and **d**) with changing the preferred crystal orientations [18, 19].

Moreover, the addition of [BMIM]HSO$_4$ was observed to relieve the harmful effect of impurities, such as copper, iron, cobalt, nickel and lead, to some extent and led to a reduc-tion of the impurity content in the zinc deposits and improved the CE and the quality of the cathodic deposits [65]. Considering the anodic reaction, [BMIM]HSO$_4$ was also found to have a catalytic effect on oxygen evolution by stimulating the reaction rate constant. Introduction of 5 mg dm^{-3} [BMIM]HSO$_4$ can markedly reduce the oxygen evolution charge transfer resistance by at least 50% [66]. [BMIM]HSO$_4$ manifested superior chemical and thermal stabilities compared with traditional industrial additives, gelatine and gum ara-bic. The inhibition effects of gelatine and gum arabic on the zinc electrocrystallization weakened significantly under observation because of their partial degradation after 12-h long-time successive electrolysis and high temperature (90°C) treatments. In contrast, 24-h long-term successive electrolysis and high-temperature treatments have no effect on the activity of [BMIM]HSO$_4$ [67].
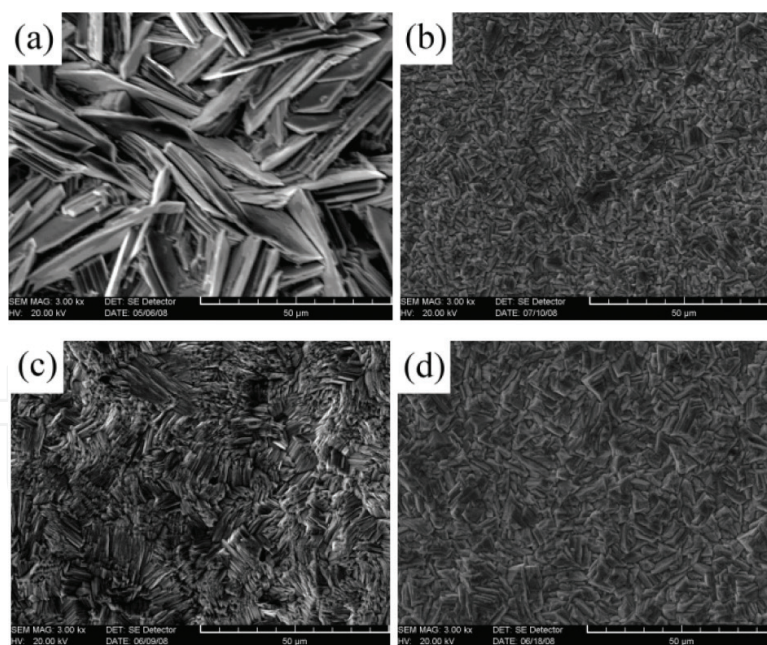

Figure 2. Scanning electron micrographs of zinc deposits in the presence of different additives. (a) Blank, (b) [BMIM] HSO$_4$–5 mg·dm^{-3}, (c) [HMIM]HSO$_4$ –10 mg·dm^{-3} and (d) [OMIM]HSO$_4$ –10 mg·dm^{-3} [18, 19].

The inhibition effect of [BMIM]HSO$_4$ for zinc electrodeposition was also found in a typical plating solution (0.1 M ZnSO$_4$ + 0.5 M Na$_2$SO$_4$) [22], in which [BMIM]HSO$_4$ can induce the for-mation of finer-grained deposits by the adsorption of additive in the first stages of deposition

(**Figure 3a** and **d**). The corrosion behaviour of Q235 steel with coating by a thin layer of zinc in the presence of [BMIM]HSO$_4$ exhibited more excellent protection of the base metal in comparison to the additive-free one in 3.5% NaCl solution (**Figure 3e**).
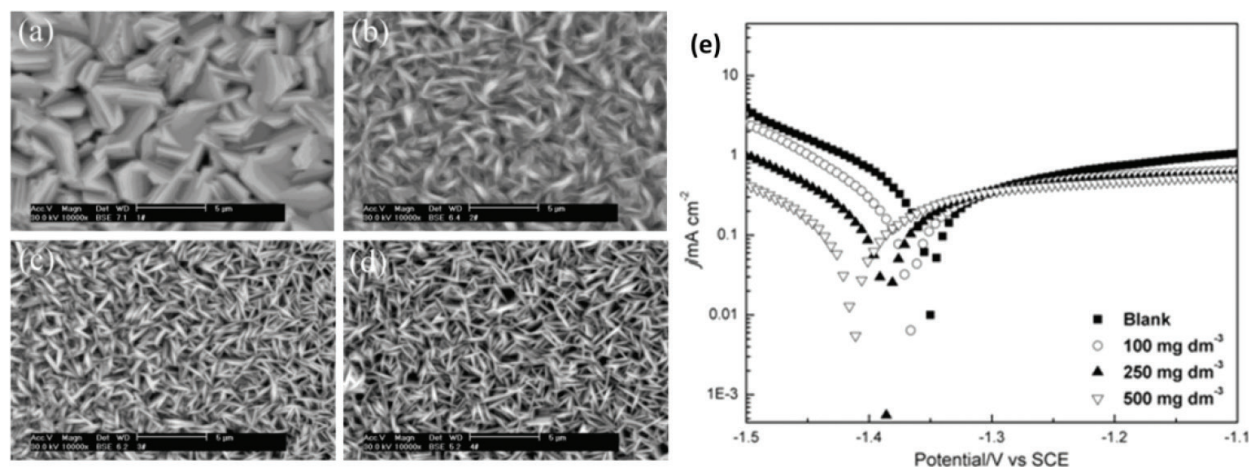

Figure 3. SEM micrographs of zinc electrodeposits produced on GC electrode from solution 0.1 M ZnSO$_4$ + 0.5 M NaSO$_4$, pH 2.6 in the absence and presence of [BMIM]HSO$_4$. (a) Blank, (b) 100 mg dm^{-3}, (c) 250 mg dm^{-3} and (d) 500 mg dm^{-3}. The deposition potential was −1.30 V and Q = 1.00 ± 0.01 C (e). Potentiodynamic polarization curves of Q235 steel substrate free and coated by a thin layer of zinc from the baths in the presence of different concentrations of [BMIM]HSO$_4$ in 3.5% NaCl solutions. The deposition charges, Qd, were approximately 1.00 ± 0.01 C [22].
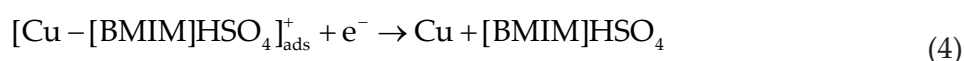
3.2. Additives for copper electrodeposition

Copper electrodeposition from acidic sulphate electrolyte with different small amounts of certain additives has been investigated extensively and it is well known that they lead to significant changes in the properties and orientation of the deposit [68]. Appropriate amounts of additives are necessary for the formation of fine-grained, smooth and compact deposits. Additives, such as thiourea [69–71], gelatine [72, 73] and animal glue [74], are commonly used as levelling and brightening agents in copper electrodeposition and electrowinning in order to produce smooth, free of voids and porosity copper deposits. Although advances have been made, in many cases the use of these additives is still carried out in an empirical way, and there are still many unknown aspects concerning the mechanism of action of additives.

Recently, we have investigated the effect of [BMIM]HSO$_4$ on copper electrodeposition [21]. Its effects on the morphology of cathodic deposits and the kinetic parameters of the cathodic process were deeply studied. Similar to the case for zinc electrodeposition, the addition of [BMIM]HSO$_4$ was found to have a strong inhibiting effect on the electroreduction process, and the effect is more pronounced at higher additive concentrations.

The kinetic parameters obtained show that the presence of [BMIM]HSO$_4$ has an inhibiting effect on the kinetics of the copper discharge process with slight changes in the copper electrodeposition reaction pathway, indicated by the changes in Tafel slopes and the corresponding charge transfer coefficient [21]. A possible mechanism of the action of this additive may

be explained as follows: cathodic surface can effectively adsorb [BMIM]HSO$_4$. When we add [BMIM]HSO$_4$ in the electrolyte, the additive molecules adsorb at the cathodic surface and interact with the Cu$^+$ ions produced from Eq. (1) to form a copper-[BMIM]HSO$_4$ complex Eq. (3) by these equations:

$$Cu^{2+} + e^- \rightarrow Cu^+ \tag{1}$$

$$Cu^+ + e^- \leftrightarrow Cu \tag{2}$$

$$Cu^+ + [BMIM]HSO_4 \leftrightarrow [Cu - [BMIM]HSO_4]^+_{ads} \tag{3}$$

$$[Cu - [BMIM]HSO_4]^+_{ads} + e^- \rightarrow Cu + [BMIM]HSO_4 \tag{4}$$

We attribute the inhibition effect of [BMIM]HSO$_4$ on the process of copper electroreduction to the adsorption of the complex at active sites, where it may receive an electron from the cathode and discharge copper atoms which are embedded at the active sites (Eq. (4)). The [BMIM]HSO$_4$ will be released and can then become a complex.

The effect of [BMIM]HSO$_4$ on the complex-plane impedance diagrams is illustrated in **Figure 4**. The complex-plane impedance spectra obtained from the additive-free solution exhibit two capacitive features at high frequencies followed by an inductive loop at low-frequency values (**Figure 4a**). On the other hand, two intermediate-frequency capacitive features, far more separated at high concentration of additive (**Figure 4b** and **c**) in the presence of [BMIM]HSO$_4$, are obtained; that implies that two adsorbed species play a role in the process of copper electrodeposition and the addition of [BMIM]HSO$_4$ brought about a change in the copper electrodeposition mechanism.
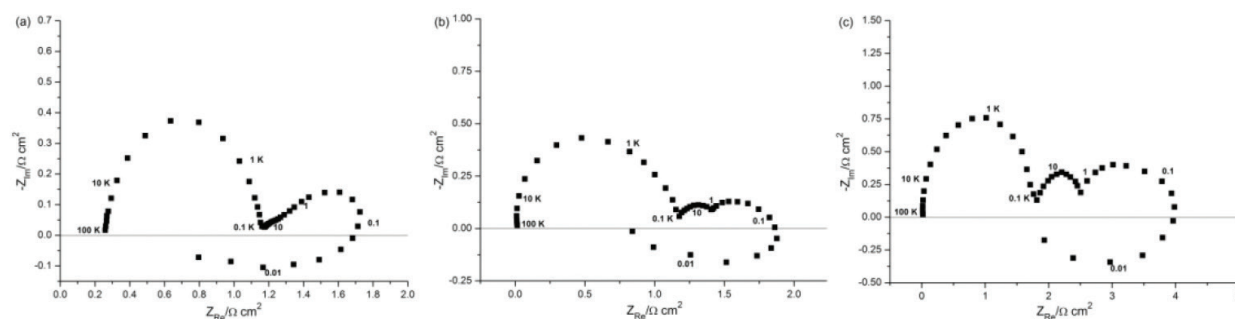

Figure 4. Impedance plots for copper electrodeposition at E= −0.15 V in the absence (a) and presence of [BMIM]HSO$_4$ (b) 10 mg·dm^{-3}, (c) 50 mg·dm^{-3} [21].

Figure 5 shows the SEM images of copper deposits obtained by small-scale electrolysis from the sulphate electrolyte in the absence and presence of [BMIM]HSO$_4$. As it can be seen from **Figure 5(b** and **c)**, introducing [BMIM]HSO$_4$ has brought a notable effect on the surface quality of the copper deposits as compared with those gained from the additive-free bath

(**Figure 5a**) consisting of comparatively large, coarse grains. The size of the copper grain is smaller and continuously decreases with increasing additive concentrations in the presence of [BMIM]HSO$_4$ (**Figure 5b** and **c**). The fact that there was a blockage of the electrocrystallization process is indicated by the results. Blockage of the crystal growth process is the action of [BMIM]HSO$_4$, which induces a relative improvement in the process of nucleation. This results in a finer grained deposit. It is also noteworthy that the copper deposits' morphology remains essentially unchanged, irrespective of the additive concentration. The influence of [BMIM]HSO$_4$ on the crystallographic structure of the deposits is presented in **Figure 5(d)**. The copper deposit consists of (111), (200), (220), (311) and (222) crystal orientations without additives. The addition of 10 mg·dm^{-3} [BMIM]HSO$_4$ inhibited the growth in the direction of the (111), (311), (222) planes and promoted the growth of the (220) plane.
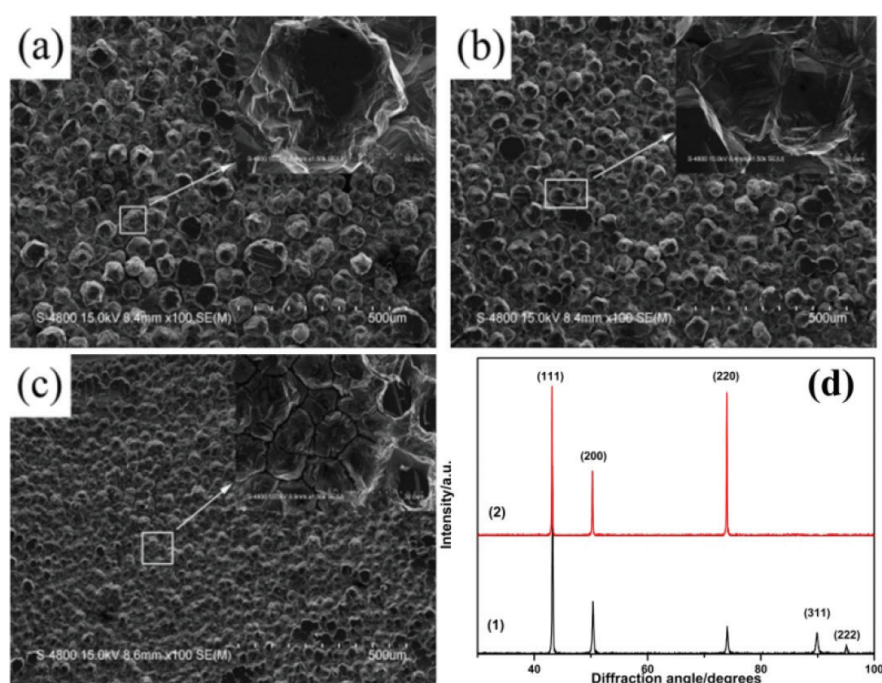

Figure 5. Scanning electron micrographs of copper deposits in the absence and presence of [BMIM]HSO$_4$. (a) Blank, (b) 10 mg·dm^{-3} and (c) 50 mg·dm^{-3}. (Insets: local magnified graphs). (d) XRD patterns for the copper deposits in the absence and presence of [BMIM]HSO$_4$ (1) Blank, (2) 10 mg·dm^{-3} [21].

Pyridinium-based ionic liquids were also found to be readily adsorbed on the metallic surface similar to that of imidazolium-based ILs [21], which provide a larger potential group to be researched as novel metal electrodeposition additives. We have previously studied the effects of two alkylpyridiniumILs (py-iLs), including N-butylpyridinium hydrogen sulphate (BpyHSO$_4$) and N-hexylpyridinium hydrogen sulphate (HpyHSO$_4$), on copper electrodeposition from acidic sulphate electrolyte [22]. BpyHSO$_4$ and HpyHSO$_4$ both turn out to be efficient levelling additives in copper electrodeposition, which leads to more levelled and fine-grained cathodic deposits. Copper electrodeposition is associated with the growth process and a nucleation. The addition of py-iLs has a blocking effect on copper electrodeposition, which causes a blockage of the nuclei growth process and some improvement in the process of nucleation. Both additives increase the cathodic polarization of copper through their adsorption on the

cathodic surface and block the kinetics of the Cu^{2+} reduction process. A higher inhibition effect is offered by $HpyHSO_4$ than by $BpyHSO_4$, which may be due to $HpyHSO_4$'s stronger adsorbability and complexation in comparison with $BpyHSO_4$.

For further nucleation investigation [23], the initial stages of the process of copper electrodeposition take place through a three-dimensional instantaneous nucleation with diffusion-controlled growth of the nuclei. We changed the practically instantaneous nucleation mechanism observed in the additive-free solution to become more progressive for the additives in the solution. The blocking effect of alklpyridinium hydrosulphate-based ILs on the copper electrocrystallization process through its cathodic adsorption on the active sites of the electrode surface brought about this change in the nucleation mechanism and, as a consequence, caused a decrease in the nucleation and growth rate of these nuclei and induced the formation of levelled and finer grained copper electrodeposits.

To be distinguished from alkylimidazolium and alkylpyridinium-based ILs, for which their additive effects were found to come from surface adsorption together with complexing action, quaternary ammonium-based ILs feature their action simply through specific adsorption [25]. The typically feasible cathodic adsorption of quaternary ammonium-based ILs, including tetraethylammonium hydrogen sulphate (NEt_4HSO_4, **Figure 6a**) and tetrabutyl-ammonium hydrogen sulphate (NBu_4HSO_4, **Figure 6b**), may have been caused by electrostatic attractive forces between dissolved quaternary ammonium cations and the electrically charged surface of the cathode, which can be schematically described in **Figure 6(c)**. Furthermore, the possible difference applied during the process of electrodeposition makes the charge on the cathode surface more negative and enhances the adsorption of positively charged quaternary ammonium ions. At a lower additive concentration, the alkyl chain of these quaternary ammonium cations may be oriented in the direction of the electrolyte. Nevertheless, a horizontal arrangement to the cathode can also be made of them. As there is an increment in the concentration of added ILs, the alkyl chain may trend for a vertical arrangement to improve absorption [75].
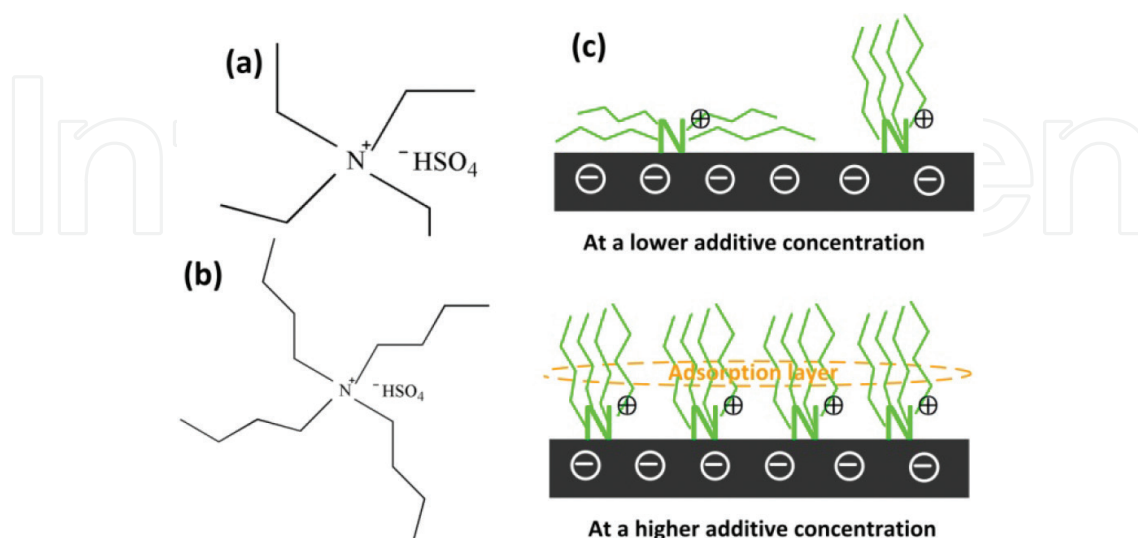

Figure 6. Structures of quaternary ammonium-based ILs used. (a) NEt_4HSO_4, (b) NBu_4HSO_4 and (c) the proposed surface adsorption of NBu_{4+} at different additive concentrations on the cathode [25].

In this manner, more quaternary ammonium cations can adsorb at the cathode surface and act together to form a layer above the head group; this will block the cathode surface and bring about an increment in the inhibition effect on the approach of the Cu^{2+} species and the resulting electroreduction reaction. Longer alkyl chain will result in greater surface adsorbability of the ILs cations because of the alkyl group's electron releasing ability [76], which is found to improve with any increment in the alkyl chain. Therefore, NBu_4HSO_4 provides a higher inhibition effect than NEt_4HSO_4.

4. Corrosion inhibitors

Because of the general aggressiveness of acid solutions, inhibitors are commonly used to reduce the corrosive attack on metallic materials. Numerous possible inhibitors have been investigated. Amongst them there are inorganic inhibitors [77], but in much greater numbers there are organic compounds. Most of the effective organic inhibitors used contain hetero-atoms such as oxygen, nitrogen, sulphur, phosphorous and multiple bonds in the organic compound molecules through which they can adsorbed on the metals surface [78–83]. The adsorption behaviour could include two main modes [1]. They are chemisorption (involving chemical combination between the metal and the adsorbate where electrons are shared and/or transferred, usually leading to the formation of covalent bonds) and physisorption (involving physical force such as van der Waals and pure electrostatic attraction between the charged metal and the charged inhibitor molecules). The former may occur if the inhibitor contains lone pairs of electrons, multiple bonds or conjugated p-type bond system. And there is no electron transfer and no electron sharing in the later adsorption mode. In this section, we reported the effect of some alkylimidazolium ILs on the corrosion inhibition of metals such as mild steel, aluminium and copper in acid solution.

4.1. Mild steel

Acid solutions are widely used in industry, such as acid pickling, industrial acid cleaning, acid descaling and oil well acidizing. However, due to their general aggressively, inhibitors are generally used in these processes to control metal dissolution. There are various organic inhibitors that tend to decrease the corrosion rate of steel and iron in acidic solutions [28, 83–86]. ILs with imidazolium [87–92] and pyridinium cations [93, 94] have showed excellent corrosion inhibition performance on mild steel in an acidic environment. We have first investigated the acid corrosion inhibition process of mild steel [2] in 1 M HCl by 1-butyl-3-methyl-imidazolium chlorides (BMIC) and 1-butyl-3-methyl-imidazolium hydrogen sulphate ([BMIM]HSO$_4$) and found that the studied inhibitors are mixed type inhibitors. For both inhibitors, the inhibition efficiency increased with an increase in the concentration of the inhibitor and the effectiveness of the two inhibitors are in the order [BMIM]HSO$_4$ > BMIC.

Figure 7 shows the Nyquist plot diagram for mild steel in 1 M HCl solution in the absence and presence of BMIC and [BMIM]HSO$_4$. It is clear from these figures that the impedance spectra obtained yield a semi-circular shape, suggesting that the corrosion of the mild steel in 1 M HCl solution is mainly controlled by a charge transfer process [95, 96]. A similar profile

of the Nyquist plots observed in the absence and presence of the inhibitors indicates that the addition of inhibitors does not change the mechanism for the dissolution of mild steel in HCl.
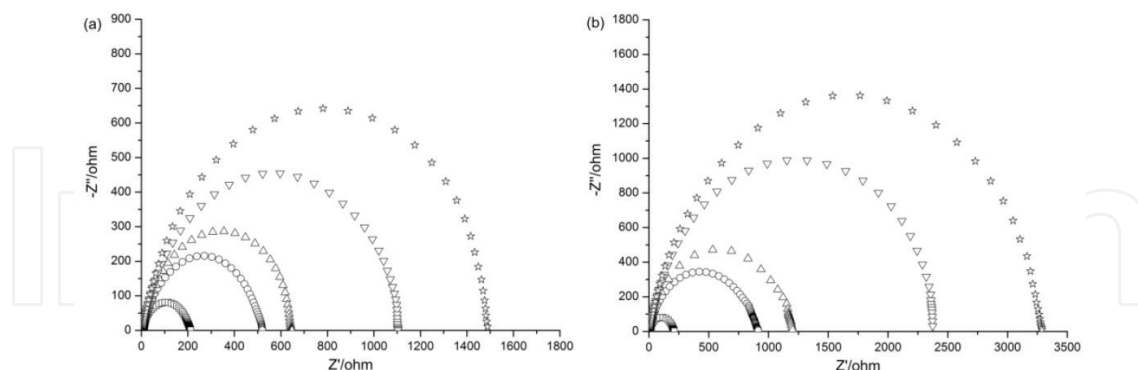

Figure 7. Nyquist plots for mild steel in 1 M HCl solution in the absence (□) and presence of 5×10^{-4} (○), 1×10^{-3} (△), 5×10^{-3} (▽) and 1×10^{-2} M (⇔) inhibitor at 303 K: (a) BMIC, (b) [BMIM]HSO$_4$ [2].

The corrosion mechanism of iron in hydrochloric acid was proposed [97, 98] as follows. We assume that columbic attraction first adsorbed Cl$^-$ anion is onto the positively charged metal surface. Then the inhibitor molecules can be adsorbed via electrostatic interactions between the negatively charged metal surface and the positively charged molecules. These adsorbed inhibitor molecules come together with (FeCl$^-$)$_{ads}$ species to form monomolecular layers (by forming a complex) on the surface of the steel; it protects the surface of the steel from attack by chloride ions and prevents the oxidation reaction of (FeCl$^-$)$_{ads}$ as seen in steps (b→d). In contrast, in competition with hydrogen ions reducing hydrogen evolution (e→g), the protonated imidazolium molecules are also adsorbed at cathodic sites.

These are the steps followed by the anodic dissolution of iron:

a. $Fe + Cl^- \leftrightarrow (FeCl^-)_{ads}$

b. $(FeCl^-)_{ads} \leftrightarrow (FeCl)_{ads} + e^-$

c. $(FeCl)_{ads} \rightarrow (FeCl^+) + e^-$

d. $(FeCl^+) \leftrightarrow Fe^{2+} + Cl^-$

The cathodic hydrogen evolution follows the steps:

e. $Fe + H^+ \leftrightarrow (FeH^+)_{ads}$

f. $(FeH^+)_{ads} + e^- \rightarrow (FeH)_{ads}$

g. $(FeH)_{ads} + H^+ + e^- \rightarrow Fe + H_2$

Meanwhile, the presence of the electron-donating groups on the imidazolium base structure, such as Cl and S, increases the electron density on the nitrogen of the –C=N– group due to their ability of offer free electrons. In particular, the ability of S atom is more excellent than that of Cl [99]. Therefore, [BMIM]HSO$_4$ is more effective than BMIC in inhibiting the corrosion of mild steel in HCl.
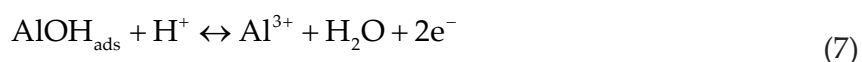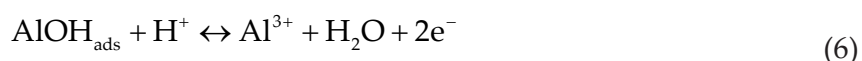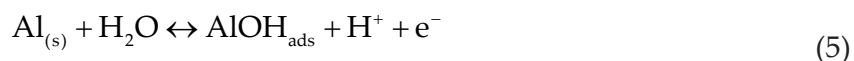
The characteristics of adsorption of the imidazolium base inhibitors on the mild steel in 1.0 M HCl solution follow Langmuir's adsorption isotherm. The analysis of thermodynamic parameters [2] such as equilibrium constant and standard free energy indicate that the inhibitors are physically adsorbed on the metal surface and the adsorption of inhibitor molecule with the corroding mild steel surface is a spontaneous and exothermic process [100].

4.2. Aluminium

A rapidly formed compact, strongly adherent and continuous oxide film may be responsible for the resistance of aluminium against corrosion in aqueous media [101, 102]. Consequently, many industries, such as reaction vessels, pipes, machinery and chemical batteries, have come to rely heavily on aluminium and its alloys. Hydrochloric acid solutions are employed for pickling, chemical and electrochemical etching of aluminium [103]. Having aggressive ions such as chloride, however, creates a huge localized attack [104]. The corrosion inhibition of aluminium in an acid medium has been reported while using hydrazone [105], anionic surfactants [106] and amino acid [107] as inhibitors. We have studied the corrosion inhibition performance of three alkylimidazolium ILs namely 1-butyl-3-methylimidazolium chlorides, 1-hexyl-3-methylimidazolium chlorides (HMIC) and 1-octyl-3-methyl-imidazolium chlorides (OMIC) on the corrosion of aluminium in 1.0 M HCl [22]. All the inhibitors studied could be classified as mixed type inhibitors with the obvious inhibition effect on both cathodic and anodic reactions of the corrosion process. The inhibition efficiency increased with an increase in the concentration of inhibitor and the effectiveness of these inhibitors was in the order of OMIC > HMIC > BMIC. Similar to the adsorption behaviour of imidazolium base inhibitors on the mild steel, the adsorption of these inhibitors on the aluminium surface also obeyed Langmuir adsorption isotherm and had a physical mechanism involving a spontaneous and exothermic process.

The Nyquist plots (**Figure 8**) for aluminium in 1.0 M HCl solution showed that the impedance spectra are made up of a large capacitive loop at high frequencies, which is followed by a small inductive one at low-frequency values. There is a relationship between the high-frequency capacitive loop and the charge transfer of the corrosion process and the double layer behaviour, and the inductive loop could be interpreted in terms of the relaxation processes in the oxide film covering the electrode surface [108] or attributed to the stabilization of the layer by the adsorbed intermediate products of the corrosion reaction on the electrode surface involving inhibitor molecules as well as reactive products [109].

A general mechanism for the dissolution of aluminium in the presence of chloride ions would be similar to that reported in the literature [110, 111].

$$Al_{(s)} + H_2O \leftrightarrow AlOH_{ads} + H^+ + e^-$$

(5)

$$AlOH_{ads} + H^+ \leftrightarrow Al^{3+} + H_2O + 2e^-$$

(6)

$$AlOH_{ads} + H^+ \leftrightarrow Al^{3+} + H_2O + 2e^-$$

(7)

$$[AlOH]^{2+} + Cl^- \rightarrow [AlOHCl]^+ \tag{8}$$

The water molecules originally adsorbed on the surface are partly displaced by the adsorption of imidazolium compounds on the aluminium surface; this blocks the formation of $AlOH_{ads}$ (Eq. (5)). Thus, we can prevent both the oxidation reaction of $AlOH_{ads}$ to Al^{3+} as shown by step (Eq. (6)) and the complexation reaction between the hydrated cation $[AlOH]^{2+}$ species that are formed in step (Eq. (7)) and chloride ions (Eq. (8)). Moreover, these protonated molecules also compete with the hydrogen ions, which will curtail the evolution of hydrogen. The presence of the electron-donating group (Cl) on the imidazolium base structure is observed to increase the electron density on the nitrogen of the –C=N– group and to result in high inhibition efficiency. In particular, this effect appears more pronounced with the increase in the chain length of the alkyl connecting with $N_{(3)}$ of the imidazolium ring. Therefore, the effectiveness of these inhibitors with the sequence of OMIC > HMIC > BMIC is obtained.
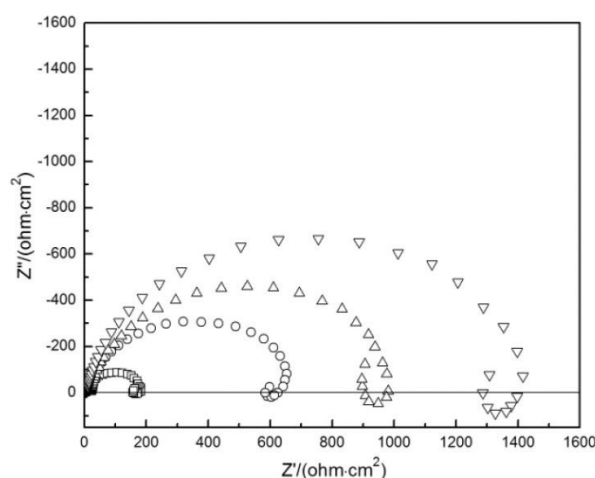

Figure 8. Effect of inhibitors on the impedance response of aluminum in 1.0 M HCl solution in the absence (□) and presence of 5×10^{-4} M (○) BMIC, (△) HMIC, (▽) OMIC at 303 K [26].

4.3. Copper

Copper and its alloys have been found widespread applications in many industrial processes such as industrial equipment, building construction, electricity, electronics, coinages and ornamental parts due to their electrical, thermal, mechanical and corrosion resistance properties [112]. However, the presence of aggressive ions such as chlorides, sulphates or nitrates creates extensive localized attack [113]. One effective approach to protect metals against the general aggression of acid solutions is the use of organic inhibitors, which can effectively control the metal dissolution and eliminate the undesirable acid consumption. Many organic compounds including triazole, imidazole, thiazole, tetrazole, indole and its derivatives [114, 115] have been developed as corrosion inhibitors to inhibit copper corrosion in aggressive environments. As an example of ILs, alkylimidazolium-based ILs ([BMIM]HSO$_4$, [HMIM]HSO$_4$ and [OMIM]HSO$_4$) have proved to be excellent inhibitors for the corrosion inhibition of copper

in 0.5 mol·L^{-1} H$_2$SO$_4$ solution [27], which behave as mixed type inhibitors with a pre-dominantly cathodic action. The corresponding electrochemical impedance results suggested that these imidazolium-based molecules act by adsorbing at the copper/solution interface. The adsorption of these imidazolium-based compounds on the copper surface in an acidic solution is found to fit the Langmuir adsorption isotherm and occurs by a physisorption-based mechanism involving a spontaneous process.

The anodic dissolution of copper proceeds via a two-step reaction mechanism and can be described as follows: [116]

a. $Cu + SO_4^{2-} - e^- \leftrightarrow (CuSO_4^-)_{ads}$

b. $(CuSO_4^-)_{ads} - e^- \leftrightarrow Cu^{2+} + SO_4^{2-}$
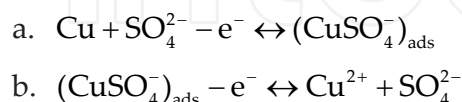
where $(CuSO_4^-)_{ads}$ is an adsorbed species at the copper surface and does not diffuse into the bulk solution [52]. Consequently, the mass transport has little influence on dissolution of copper.

It is assumed that the negative sulphated ions are first adsorbed onto the positively charged metal surface by columbic attraction. Since the imidazolium group as well as nitrogen atom in the heteroaromatic ring of imidazolium compounds can be protonated in acidic solutions [117]. The protonated inhibitor molecules can be adsorbed through electrostatic interactions between the positively charged molecules and the negatively charged metal surface [2]. These adsorbed imidazolium compound molecules will interact with $(CuSO_4^-)_{ads}$ ions generated from (a) to form a protective layer (by forming a complex) at active sites, which hiders both mass and charge transfers and blocks the further oxidation reaction of $(CuSO_4^-)_{ads}$ to Cu^{2+} as shown in step (b).

5. Conclusions

In this chapter, two perspective application studies of ILs in using as additives for metal electrodeposition and inhibitors for metal anti-corrosion were summarized. It was shown that ILs had some intrinsic advantages over traditional organic agents. Due to their stability, high conductivity, low vapour pressure and environmental friendly nature, ILs were excellent levelling agents for both zinc and copper electrodeposition, which were superior to traditional additives, and showed favourable corrosion resistant performance on mild steel, aluminium and copper in acidic solutions.

It is apparent that the future for ILs-based technology in these two aspects is extremely bright; however, more fundamental aspects issues have to be solved so that their applications will become a practical reality instead of laboratorial studies. What is the adsorption mechanism of ILs on the metal surface? What is the effect of ILs on the nucleation and growth of metal? And how is the influence of ILs on the structures of electric double layer, etc.? All these issues are the critical problems for further study.

Author details

Zhang Qibo* and Hua Yixin

*Address all correspondence to: qibozhang@kmust.edu.cn

Key Lab of Ionic Liquids Metallurgy, Faculty of Metallurgical and Energy Engineering, Kunming University of Science and Technology, Kunming, Yunnan, China

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