

Ionic Liquids for the Future Electrochemical Applications

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1. Introduction

Room temperature ionic liquids (RTILs) are the salts with weak interactions between the ions, which allows them to be liquid at room temperature (typically below 100°C). The scientific and technological importance of RTILs nowadays have spanned a wide range of applications, owing to their unique physicochemical properties, such as thermal and chemical stability, low melting point, negligible volatility, flame retardancy, high ionic conductivity, moderate viscosity, high polarity, and solubility (affinity) with many compounds (Fischer et al.; 1999; Welton, 1999; Earle & Seddon, 2000; Wasserscheid & Keim, 2000; Wasserscheid & Welton, 2003). For instance, RTILs are good solvents for a wide range of organic and inorganic compounds, which makes them an attractive solvent alternative for environmentally friendly processes. To date, there have been many reviews dealing with these topics. In particular, the easy modification of the cation and anion in RTILs is an advantage for the development of task-specific RTILs for organic synthesis, extraction, dissolution, etc. (Blanchard et al., 1999; Earle et al., 1999; Kubo et al., 2002). Electrochemical processes have been another important application area for RTILs since their early development. Key advantages of RTILs over common aqueous or organic media in this field are their wide electrochemical window (up to 6 V in some cases), high conductivity, and vanishingly low vapor pressure. These features not only facilitate investigations into metal electrodeposition (Hamelin et al., 1987; Schmickler, 1996; Freyland et al., 2003; Mann et al., 2009), electrocapacitor, and electrocatalysis in a less demanding manner, but also open up new possibilities for increased reactivity of processes and/or stability of reactants/products in ionic liquids (Hamelin et al., 1987; Dom & Mar, 2008).

The subject of this chapter covers the newest aspects of ionic liquids in applications where their ion conductivity is exploited. Our goal in this chapter is to survey the recent key developments and issues within ionic liquid research in these areas. First, the current state of the knowledge of the ionic liquid/electrode interfaces, which is vital for applications and whose studies are still in its infancy, has been reviewed. As the range of available surface techniques and systematic, investigations increase, our understanding will improve which lead to advances on this field. Then, updated researches on the electrochemical applications of ionic liquids are exploited. In particular, their potentials as electrochemical solvents for metal/semiconductor electrodeposition, batteries and fuel cells are reviewed where conventional medias fail. Finally, the applications of ionic liquids in electrosynthesis, electrocatalysis, and electrochemical biosensing are briefly discussed. We conclude this

chapter with personal perspectives on the directions to which future research on this field might be directed.

2. Ionic liquid / electrode interfaces

During the last years, the electrochemical applications of RTILs have been highly explored (Buzzeo et al., 2004; Zhang & Bond, 2005; Endres & Abedin, 2006) from both experimentally and theoretically. It has been recognized that the ionic liquid/electrode interfaces greatly influence the electrochemical processes. Thus, it is necessary to study these interfacial systems, especially to obtain a molecular level perspective. Moreover, RTILs provide an interesting system in physical chemistry because they are composed purely of ions yet are liquid at room temperature. While the surface chemistry of aqueous electrolytic systems has been under extensive study for nearly a century, the study of neat ions in the liquid state is very new and highly investigated. In addition, there are various experimental techniques, e.g. electrochemical, spectroscopic and microscopic instruments available to study surfaces.

2.1 Electrochemical studies

To obtain a better picture of the structure of the ionic liquid/electrode interface, different models including Helmholtz, Gouy Chapman-Stern, and multilayer (Fig. 1) have been developed to describe and predict the experimental behavior of electrochemical systems observed in electrochemical studies, such as interfacial capacitance and electrocapillary measurements (Aliaga et al., 2007). Among the three models, the Helmholtz and the multilayer conceptions seemed to best describe the structure at the interfaces, although they both failed at some point (Inman & Lovering, 1983). In addition, as far as the studies of ionic liquid/electrode interface are concerned, techniques such as EIS, differential capacitance measurements, and voltammetry at DME (dropping mercury electrode) were found to be useful.

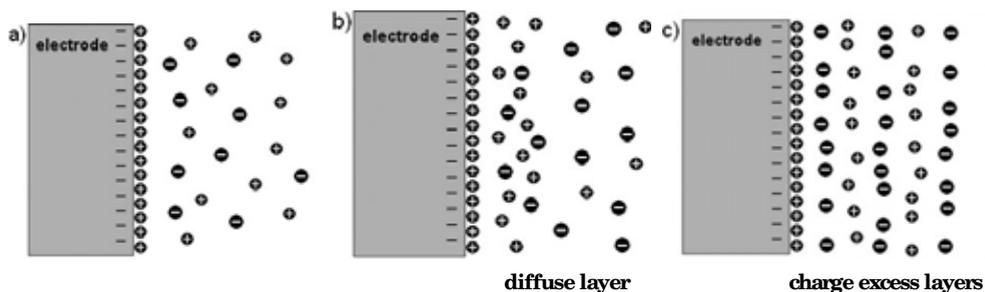


Fig. 1. Models of the electrical double layer. (a) Helmholtz, (b) Gouy Chapman-Stern, (c) multilayer.

Note that the number of papers concerning research of the ionic liquid/electrode interface is limited. Most of the efforts have been aimed at the study of the ionic liquid/platinum interface as a method of proving the structure of the adjacent ionic environment and the study of the ionic liquid/carbon interface with an emphasis on the design of electrochemical double layer capacitors. The results have revealed that different structures may form at the surface of the electrode depending on the nature of the ions that constitute an ionic liquid. Subsequently, anions such as dicyanamide, tend to form multilayers of adsorbed ions due to

their coordinating properties and others will simply assemble as monolayers. For instance, Baldelli (2005) studied the structure of the [BMIM][BF₄]/platinum interface by EIS. The works showed that the ionic liquid corresponds to a Helmholtz layer with a double layer thickness of ~0.5 nm.

2.2 Spectroscopic studies.

Surface sensitive vibrational spectroscopic techniques such as surface enhanced Raman scattering (SERS), sum-frequency generation (SFG), surface-enhanced infrared absorption spectroscopy (SEIRAS), and in situ Fourier transform infrared reflection absorption spectroscopy (FT-IRAS) have been used to investigate the structure of the ionic liquid-electrode interface (Baldelli, 2005). The advantages of these techniques are their capabilities to perform experiments at controlled electrochemical conditions. On the other hand, by relating spectroscopic information with previous electrochemical measurements, a more complete description of the electrified interface, such as double layer thickness, orientation of the ions at the surface, and identification of the ionic species adsorbed, can be obtained. Note that this is very important since the structure of the interfacial layer dramatically influences the electron transfer reactions.

Recently, Vianney et al. (2006) carried out the SERS at the BMIMPF₆/silver electrode interface. It has been shown that the BMIM⁺ cations adsorb on the silver electrode at potentials more negative than -0.4 V vs a Pt quasi-reference electrode (Fig.2). The potential dependence of the SERS intensities of Py adsorbed on a silver electrode in BMIMPF₆ has also been investigated by Rivera-Rubero and Baldelli (2004). Their results have shown that at potentials less negative than -0.8 V Py adsorbs at an end-on configuration forming an Ag-N bond. The simulation results further confirmed this assumption. It was concluded that Py molecules lie flat on the electrode surface from the -0.9V to 1.4V potential range and Py is replaced by the BMIM⁺ at potentials < -1.4 V. In the previous studies (Reed et al., 2007), ionic molecular dynamics simulation model for an electroactive interface in which a metallic electrode is maintained at a preset electrical potential was described.

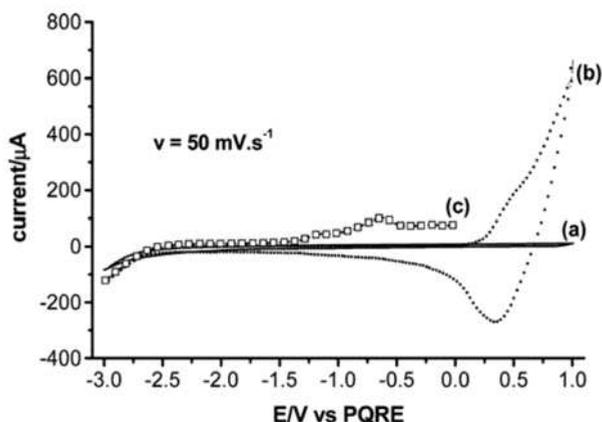


Fig. 2. Cycle voltammograms of a Au (a) and Ag (b) electrodes in BMIPF₆; (c) the voltammogram of the Ag electrode after staying at -3.0 V for 60 s and then scanning the potentials in the positive.

In brief, the spectroscopic surface studies of the ionic liquid/electrode interface of compounds based on the imidazolium cation using techniques such as SFG, SERS, FT-IRAS and SEIRAS agree with the fact that the structure of electrified interface can be specifically probed and is strongly influenced by the applied potentials. In all the cases, the ring planes of the cation tends to align themselves parallel to the surface as the excess charge becomes negative, and is repelled when it turns positive, to allow for the adsorption of the anion. The anionic species may adsorb on the surface of the electrode in single or multilayers depending on the nature of the anion, as probed by the relative increase of their surface concentration as a function of the applied potential.

2.3 Microscopy studies.

Scanning tunneling microscopy (STM) and atomic force microscopy (AFM), which can provide atomic and sub-molecular resolution images of adsorbed targets, were used in the investigation of the electrified ionic liquid-metal interface as in situ techniques. Recently, we have studied the structuring of adsorbed ions at the electrified [BMIM][PF₆]/Au(111) interface by means of STM under potential control at 0 V (Pan & Freyland, 2006). The formation of ordered PF₆⁻ adlayers was observed in a potential range from -0.5 to 0.5 V *vs* a Pt reference electrode. The results indicate that the anion molecules formed Moiré-like patterns at potentials above -0.2 V and adopted a ($\sqrt{3} \times \sqrt{3}$) structure at approximately -0.45 V although the Moiré patterns often co-existed with uncompressed structures (Fig.3). Mao et al. (2003) have observed the drastic long-range surface restructuring with the appearance of small pits. The enlargement of the pits has resulted in forming wormlike structures.

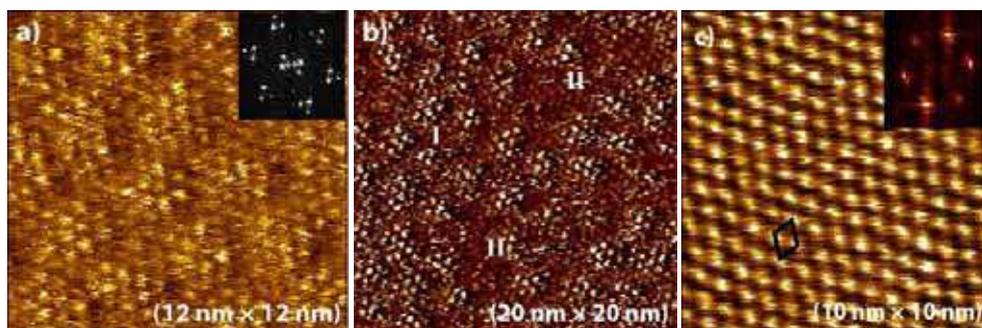


Fig. 3. Typical STM images of a Au(111) electrode recorded under different potential controls in pure ionic liquid of [BMIM][PF₆]. (a) E = 0.5 V; (b) E = 0.0 V; (c) E = -0.25 V.

The use of high-resolution techniques such as STM and AFM for the study of the ionic liquid/electrode interface is then evident. The spatial arrangement of the adsorbed ions in ordered layers on the surface of metallic electrodes was probed and ordered arrays of ions were observed, which is also supported by the SFG results. In addition, the surface reconstruction effect that the ionic liquids have on metals when the electric field is applied at the surface of the electrode, which seems due to the charge transfer from the metal to the adsorbed ions.

3. Electrochemical applications

RTILs can provide exciting opportunities for overcoming the limitations encountered in traditional chemical processes, in particular in electrochemistry. The nonvolatile, noncombustible, and heat resistance nature of RTILs is observed for applications in electrodeposition, batteries, fuel cells, electrosynthesis, electrocatalysis, and electrochemical biosensing.

3.1 Electrodeposition

Electrodeposition is essential for a variety of industries including electronics, optics, sensors, automotive and aerospace. Most of conventional solutions, e.g., water, suffer from the drawback that it has a relatively narrow potential window, and hence the deposition of metals with large negative reduction potentials is hindered by poor current efficiencies. RTILs are superior media for the electrodeposition of metals and semiconductors, and have an unprecedented potential to revolutionize electroplating. The use of ionic liquids heralds not only the ability to electrodeposit metals that have hitherto been impossible to reduce in aqueous solutions but also the capability to engineer the redox chemistry and control metal nucleation characteristics.

Quite a large number of ionic liquids, especially those based on NTf_2 , BF_4 and PF_6 anions, are stable in some cases to below Li/Li^+ reductive region. Therefore, semiconductors that previously could not be deposited from conventional water baths by turning to ionic liquids or be directly electroplated. Recently, the photoluminescent $\text{Si}_x\text{Ge}_{1-x}$ with a band gap of at least 1.5–3.2 eV has been successfully electrodeposited from pure ionic liquid containing silicon and germanium halides (Fig.4) (Al-Salman et al., 2008). During the deposition, different colors from orange to green are observed in the visible spectrum. These are due to a quantum size effect of the semiconductor particles with sizes between 2 and 20 nm. The results show that the ionic liquid allows deposits very pure and photoluminescence effects can be seen. In addition, the material absorbs visible light and may open the way to a simple electrochemical fabrication of inexpensive solar cells.

The electrodeposition of metals and alloys using a variety of ionic liquids has also been demonstrated by previous studies (Abbott et al., 2008). Electroplating electronegative metals, e.g. Al, Ta, Nb, Mo, W; direct electroplating of metals on water sensitive substrate materials such as Al and Mg can be achieved, removal of hydrogen embrittlement from the substrate; alloy deposition is easier to achieve; the possibility exists to develop novel immersion plating baths; potential energy savings compared with aqueous solutions, replacement of many hazardous and toxic materials currently using and access to novel deposit morphologies. The electrolytic deposition of nickel is also demonstrated using a solution of the metal chloride salt separately in either a urea or ethylene glycol/choline chloride based ionic liquid (Haerens, 2009).

Moreover, it has been shown that the deposition kinetics and thermodynamics of ionic liquids differ from them in the aqueous processes, which results in different deposit morphologies. Dobbs et al. (2006) have produced silver and gold nanoparticles by electrodeposition from ionic liquid-crystal precursors, illustrated by the electrolysis of imidazolium liquid crystals containing dicyanoargentate and dicyanoaurate anions. We have recently studied the Pb and Sb deposition on Au (111) from a Lewis acidic ionic liquid of MBIC- AlCl_3 . A quasi-equilibrium process has been observed and the results indicate that Pb UPD is kinetically

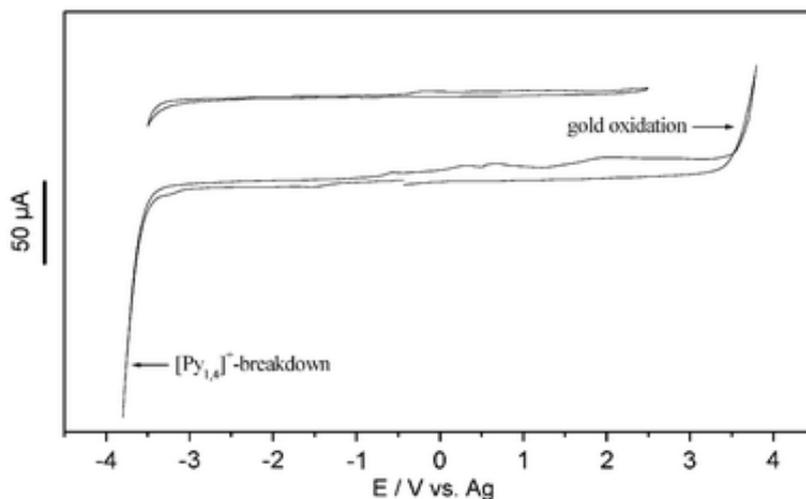


Fig. 4. CVs of pure $[\text{Py}_{1,4}]\text{Tf}_2\text{N}$ on Au(111) showing the electrochemical window of this ionic liquid. Scan rate: 10 mV s^{-1} , 25°C .

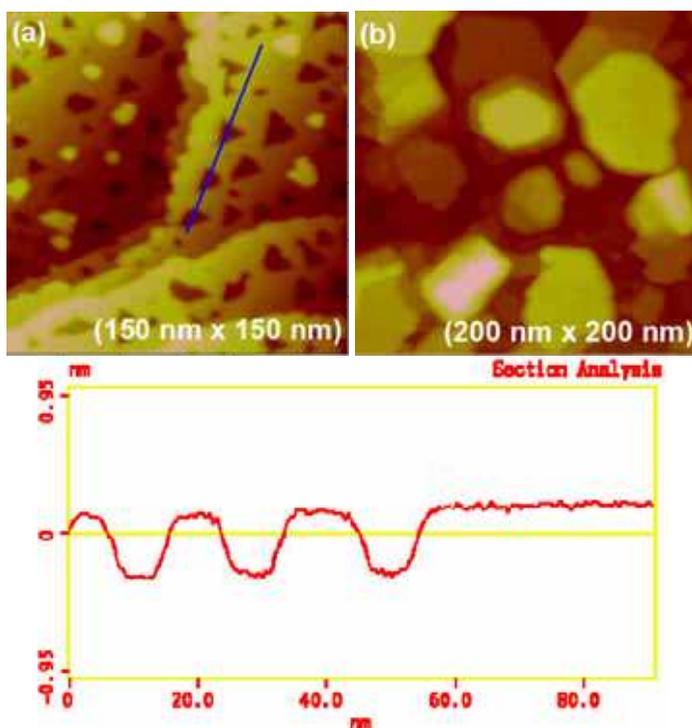


Fig. 5. Typical large-scale STM images of Pb electrodeposition on Au(111) in MBIC- AlCl_3 + 5 mM PbCl_2 solution. (a) $E = 0.5 \text{ V}$; (b) $E = 0.27 \text{ V}$.

controlled (Fig. 5). In the OPD range, the nucleation of 3D Pb crystal occurs (Pan et al., 2010, a, b). As for the Sb deposition, 2D-nanostripe architectures have been observed. In addition, the ionic liquids have the ability to obtain high concentrations of aluminium in a highly conducting aprotic medium for aluminium deposition (Buzzeo et al., 2004).

For ionic liquids, anions such as BF_4^- and PF_6^- were initially used quite extensively because of their wide potential window, however, slow hydrolysis by water, yielding HF, has led to an increase in the use of water stable anions such as $(\text{CF}_3\text{SO}_2)_2\text{N}^-$ (Ramesh & Ang, 2010). As a result, other anions such as $(\text{CN})_2\text{N}^-$ p-toluenesulfonate and methylsulfonate have recently been extensively used for metal deposition (Borra et al., 2007). Besides anions, ionic liquids with alternative cations such as those derived from biodegradable imidazoles, lactams, amino acids and choline have been prepared and used for metal deposition (Haerens et al., 1987). This area is still needed to be further investigated although Endres et al. (2006) have shown that the cation appears to control the morphology of aluminium deposited from various triflamide based ionic liquids.

3.3 Batteries and fuel cells

RTILs are important in the field of energy, especially, lithium batteries and fuel cells, which greatly benefit from the switch of non-volatile, non-flammable, ionic liquid-based electrolytes. They have the excellent energy efficiency of all known electrochemical storage systems. It has been found that ionic liquids based on the NTf_2^- , BF_4^- and PF_6^- anions, exhibiting wide and stable electrochemical windows, in some cases, can reach in some cases to below Li/Li^+ reductive potential region.

Lithium ion (Li-ion) batteries have been utilized as power supplies of electronic devices such as cell phones and laptop computers. However, Li-ion batteries consist of conventional electrolytes, such as ethylene carbonate, dimethyl carbonate, and diethyl carbonate, may suffer thermal runaway and cell rupture if over heated or overcharged. A significant research effort into RTILs-based electrolytes have been thus made to pursue a safe battery in the last years (Matsumoto et al., 2005; Sakaebe et al., 2007; Noto et al., 2010). An electrolyte of lithium batteries based on the ionic liquid PMIMTFSI complexed with lithium bis LiTFSI at a molar ratio of 1:1 has been reported by Kim et al. (2010). The electrolyte shows a high ionic conductivity at room temperature (Fig.6). Ionic liquids like BMIMBF₄ or BMIMPF₆ and PyBF₄ were also mixed with organic solvents for the use of batteries such as butyrolactone and acetonitrile (Diaw et al., 2005). In recently studies (Lee et al., 2010), Lithium salt (LiBF_4 or LiPF_6) was added to the ionic liquids mixtures for possible application in the field of energy storage (batteries or supercapacitors), electrolytes are stable toward oxidation and exhibit a vitreous phase transition.

RTILs have also been widely used in fuel cells. Although polymer-electrolyte-membrane fuel cells have been used very long time, they have not reached large-scale development as some issues are still unresolved. These issues may lead to an extent by switching to ionic-liquid-based polymer membranes. The diethylmethylammonium trifluoromethanesulfonate ([dema][TfO]) ionic liquid, functions as a proton conductor and is suitable for use as an electrolyte in H_2/O_2 fuel cells, which can be operated at temperatures higher than 100 °C under non-humidified conditions. In earlier reports (Su et al., 2009), in order to fabricate a polymer electrolyte fuel cell, matrix polymers for [dema][TfO] are explored and sulfonated polyimides, in which the sulfonic acid groups are found to be highly compatible with [dema][TfO]. Polymer electrolyte membranes for non-humidified fuel cells are prepared by the solvent casting method using [dema][TfO]. The composite membranes have good

thermal stability ($>300\text{ }^{\circ}\text{C}$) and ionic conductivity ($>10^{-2}\text{ Scm}^{-1}$ at $120\text{ }^{\circ}\text{C}$ when the [dema][TfO] content is higher than 67 wt%) under anhydrous conditions (Fig. 7).

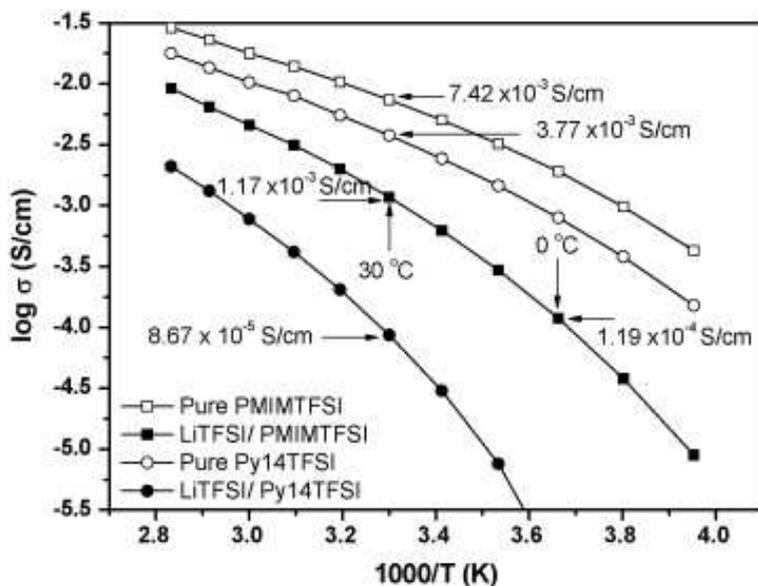


Fig. 6. Ionic conductivity as a function of temperature for pure PMIMTFSI, Py₁₄TFSI and the two corresponding liquid electrolytes obtained after complexation with LiTFSI at molar ratio of 1:1

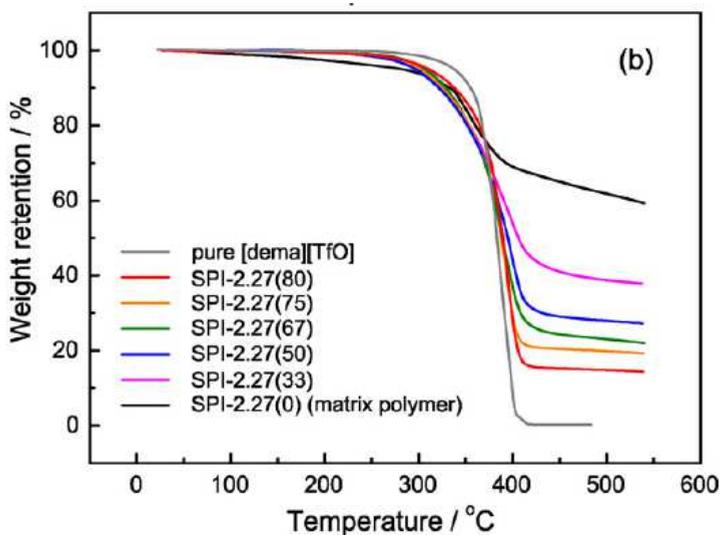


Fig. 7. Thermogravimetric curves for [dema][TfO] and composite membranes

3.4 Electrosynthesis and electrocatalysis

RTILs have also been utilized in the fields of electrosynthesis and electrocatalysis. These features open up new possibilities for increased reactivity of processes and stability of reactants/products in ionic liquids (Zhang et al., 2008). A potential advantage in the use of ionic liquids during electrosynthesis is their unique solvent capabilities. Many advances made in the field to implement electrochemical methodology at preparative-scales. The electrosynthetic processes would inevitably have the limitations associated with organic electrosynthesis. Since several years, RTILs are increasingly being applied for electrochemical and electrosynthetic purposes.

A vast array of chemical processes using ionic liquids at electrodes, the obvious advantages of adopting ILs as 'clean' reagents for synthetic processes compared with the organic electrochemical reactions. Due to its low cost, ease of fabrication, high sensitivity, RTILs can be used as the supporting electrolyte, or the binder in the carbon paste electrode, or the modifier on the chemically modified electrodes (Sun et al., 2007). Indeed, it has already been demonstrated that a wide range of organic syntheses, including catalysed reactions, can be carried out in these alternative non-volatile, non-flammable solvents. Ionic liquids are attractive according to their easy access, thermal stability, low vapor pressure and simple product recovery (Liu et al., 2010). Makeli et al. (2006) applied *n*-octylpyridinium hexafluorophosphate (OPFP) as binder to fabricate a carbon composite electrode, which provided a remarkable increase in the electron transfer rate and decreased the overpotentials of some organic substances (Fig.8). Besides, the electrochemical reduction of benzaldehyde at a Pt microelectrodes in 1-butyl-1-methyl pyrrolidinium triflimide ([Bmpyr][NTF₂]) ionic liquid is reported by Doherty and Brooks.(2003), the reaction process is shown in scheme 1.

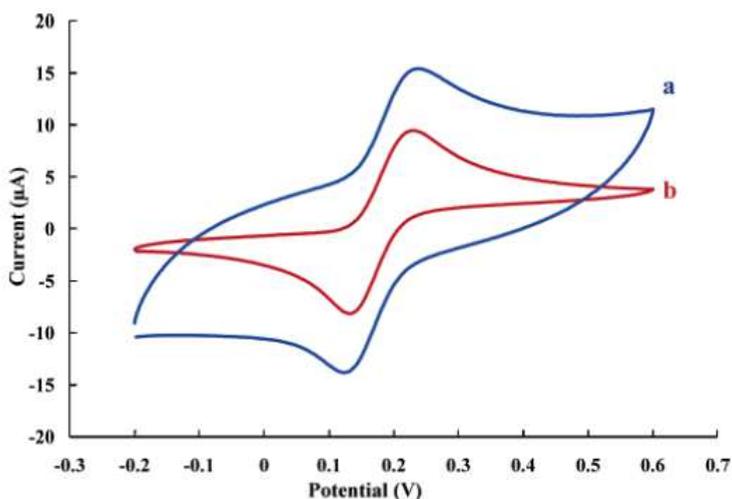
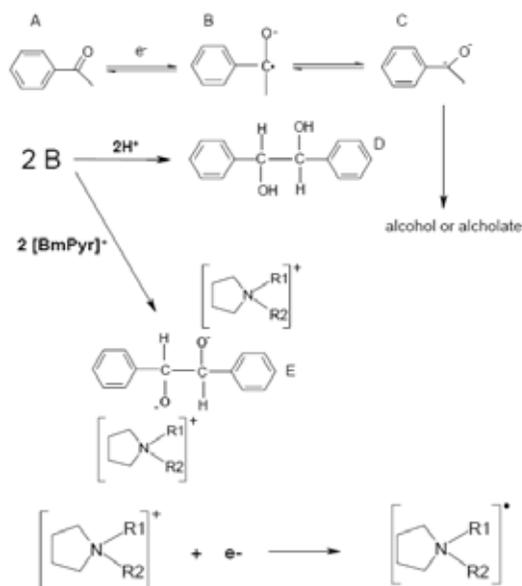


Fig. 8. Cyclic voltammograms of 1 mM catechol in phosphate buffer pH 7, on CILE (a) before heating and (b) after heating. The scan rate was 100 mV.s⁻¹.



Scheme 1. Proposed reaction sequence to account for the three reduction process.

Due to the specific characteristics such as good electronic and mechanical properties, RTILs can also be used in the process of electrocatalysis. IL/CNTs modified electrodes had been applied in the field of electroanalysis. By incorporating IL/CNTs on the surface of modified electrode, the electron transfer rate of electroactive substances are greatly improved. Sun et al. (2007) reported an electrocatalysis of hemoglobin on multi-walled carbon nanotubes (MWCNTs) modified carbon ionic liquid electrode (Fig.9) with hydrophilic EMIMBF₄ as modifier. The as-obtained carbon ionic liquid electrode showed excellent electrocatalytic activity to the reduction of trichloroacetic acid (TCA) and hydrogen peroxide.

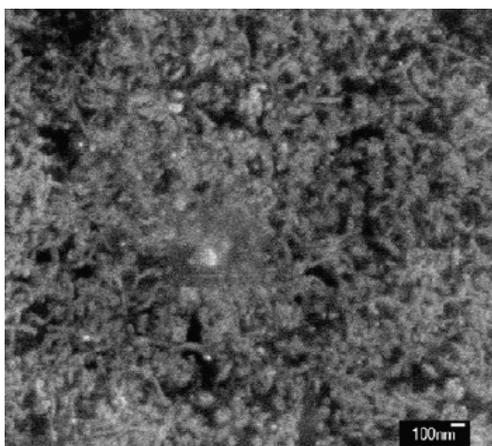


Fig. 9. SEM image of MWCNTs/IL carbon electrode.

3.5 Electrochemical biosensing

Bioscience is an interesting and emerging area where ionic liquids are beginning to play an important role. In general, water has been believed to be the unique solvent for biomolecules and biosystems. However, for long-life biodevices, there are a number of drawbacks to this situation, such as the volatility of water, the limited temperature range and the very narrow pH range for protein stability. On the other hand, immobilization of electron transfer mediators to electrode surfaces is a key step for design, fabrication and performance of the sensors and biosensors. In conventional methods, however, most of these electrodes presented quasi-reversible electrochemical behavior with poorly defined cyclic voltammograms with large background currents and low electrocatalytic activity. The use of RTILs might overcome these drawbacks and proved to be efficient pasting binder in place of non conductive organic binders of the preparation of electrodes.

Recently, a colloidal gold-modified carbon ionic liquid electrode was constructed by mixing colloidal gold-modified graphite powder with a solid RTIL n-octyl-pyridinium hexafluorophosphate (OPPF₆) (Ren et al., 2010). The electrode has shown the good bioactivity and excellent stability. This sensor was capable of distinguishing the complementary target DNA at low concentration from the three-base mismatched DNA at higher concentration (Fig.10). The response time of the biosensor is fast (within 10 s), and the life time is over two months. By using a hydrophilic ionic liquid EMIMBF₄ as the modifier, a new carbon ionic liquid electrode (CILE) was fabricated and further modified with MWCNTs to get the MWCNTs/CILE. The proposed electrode showed the potential application in the third generation reagentless biosensor (Choi et al., 2009; Ding, et al., 2009).

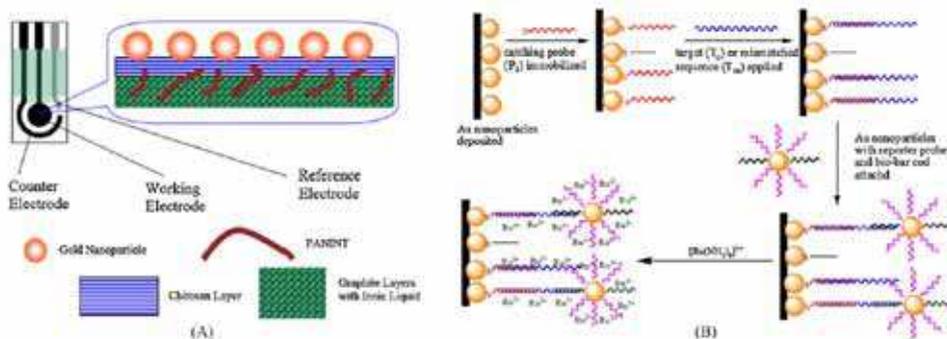


Fig. 10. The pattern of the PANINT-IL/chitosan/AuNP SPE and the structure of the working electrode. (B) Procedure for the detection of DNA with RuHex as electrochemical probe.

On the other hand, nanomaterials have been widely used in the electrochemical biosensors. Among the nanomaterials used for protein film electrochemistry, ionic liquids had been extensively studied. Due to the specific characteristics such as good electronic and mechanical properties, electric conductivity and biocompatibility, RTILs electrodes had been applied in the field of electroanalysis. For example, a DNA-modified carbon paste electrode (DNACPIE) was designed by using a mixture of the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate and paraffin oil as the binder (Xi et al., 2010). The electrode exhibits higher sensitivity compared to DNA modified carbon paste electrode without ionic liquid and better selectivity compared with electrodes without DNA. Adenine

showed an irreversible adsorption-controlled oxidation reaction with enhanced electrochemical response, which was due to the presence of high conductive MWCNTs on the CILE surface. The electrode showed good stability and selectivity, and was further applied to milk powder samples with satisfactory results. Salimi et al. (2010) recently have reported a new carbon nanotubes-ionic liquid and chlorpromazine modified electrode (Fig.11) biosensor for determination of NADH and fabrication of Ethanol. The nanocomposite modified electrode displays excellent electrocatalytic activity toward oxidation of NADH. The proposed electrode showed the potential application in the third generation reagentless biosensor.

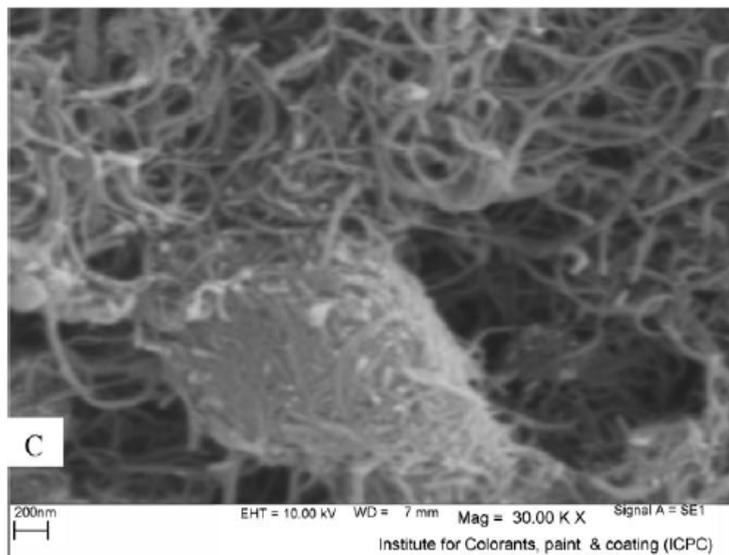


Fig. 11. SEM images of MWCNTs-IL modified electrode

4. Conclusions

RTILs have wide electrochemical windows and high conductivities, they are of current interest the research field of electrochemically. RTILs hold a great promise for various electrochemical applications, even for broad electrochemical applications. Previous attempts have revealed that the RTILs have advantageous for electrochemical applications, in particular, in electrosynthesis, electrocatalysis, electrodeposition and batteries and fuel cells. Nonetheless, there remain many aspects of the behavior of ionic liquids that need urgent investigation if the applications discussed here are to be better understood and developed. Examples are fundamental electrochemical issues such as the structure of the double layer at an electrode in an ionic liquids; the speciation of solute ions such as metal ions; transference numbers and how these are influenced by speciation; ion association and its effect on thermodynamic and transport properties; and interactions of ionic liquids with solutes and interfaces. For ionic liquids, there are essentially advanced properties to the use of electrochemistry and energy devices. It is taken into account in the trends in this novel materials developed for practical applications. In the future, more developments in ionic

liquids are expected to be seen. The simple dissolution of a lithium salt always results in electrolytes in which only a fraction of the current is actually carried by Li^+ ions. It would be interesting to see whether the incorporation of poly(Li salts), that is, lithium salts with a polyanionic chain, through specific interaction with the fixed negative charge of polarizing Li^+ ions, could change the flux balance. All of these fundamental aspects of the physical chemistry and electrochemistry of ionic liquids remain to be thoroughly explained, and they promise to further improve the potential of their various electrochemical applications. We can easily expect wider applications in electrochemical fields of using these remarkable materials.

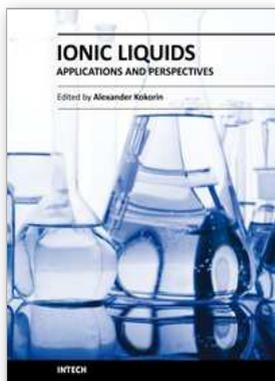
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This book is the second in the series of publications in this field by this publisher, and contains a number of latest research developments on ionic liquids (ILs). This promising new area has received a lot of attention during the last 20 years. Readers will find 30 chapters collected in 6 sections on recent applications of ILs in polymer sciences, material chemistry, catalysis, nanotechnology, biotechnology and electrochemical applications. The authors of each chapter are scientists and technologists from different countries with strong expertise in their respective fields. You will be able to perceive a trend analysis and examine recent developments in different areas of ILs chemistry and technologies. The book should help in systematization of knowledges in ILs science, creation of new approaches in this field and further promotion of ILs technologies for the future.

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