

# Ionic Liquids in Electrochemical Devices and Processes: Managing Interfacial Electrochemistry

DOUGLAS R. MACFARLANE,<sup>\*,†</sup>  
 MARIA FORSYTH,<sup>‡</sup> PATRICK C. HOWLETT,<sup>‡</sup>  
 JENNIFER M. PRINGLE,<sup>†</sup> JIAZENG SUN,<sup>†</sup>  
 GARY ANNAT,<sup>†</sup> WAYNE NEIL,<sup>‡</sup> AND  
 EKATERINA I. IZGORODINA<sup>†</sup>

*School of Chemistry and Department of Materials Engineering, Australian Centre of Excellence for Electromaterials Science, Monash University, Wellington Road, Clayton, VIC 3800, Australia*

Received April 18, 2007

## ABSTRACT

Many ionic liquids offer a range of properties that make them attractive to the field of electrochemistry; indeed it was electrochemical research and applications that ushered in the modern era of interest in ionic liquids. In parallel with this, a variety of electrochemical devices including solar cells, high energy density batteries, fuel cells, and supercapacitors have become of intense interest as part of various proposed solutions to improve sustainability of energy supply in our societies. Much of our work over the last ten years has been motivated by such applications. Here we summarize the role of ionic liquids in these devices and the insights that the research provides for the broader field of interest of these fascinating liquids.

## 1. Introduction

Ionic liquids (ILs) potentially offer many things to many fields, not the least of which is the field of Electrochemistry. As we have discussed recently,<sup>1</sup> while there are many properties that individual members of the family exhibit, the single *ubiquitous* property that we can expect to find in *all* ILs is ionic conductivity. This intrinsically makes them of interest to the electrochemist, and it was for this reason that we first became interested in the properties

Professor Doug MacFarlane, School of Chemistry at Monash University, is an Australian Research Council Federation Fellow and program leader in the Australian Centre of Excellence for Electromaterials Science (ACES). He was a Ph.D. graduate of the Angell group at Purdue University in 1982 and after postdoctoral work at Victoria University Wellington took up a faculty position at Monash University. His interests include the chemistry, properties, and applications of ionic liquids and solids.

Professor Maria Forsyth is Associate Director of ACES at Monash University. A Ph.D. graduate from Monash in 1990, she took up a Fulbright Fellowship at Northwestern University before returning to Melbourne to join the Defence Science and Technology Organisation. She took up a faculty position in the Department of Materials Engineering at Monash University in 1994 and became an Australian Professorial Fellow in 2003. Her interests are electrochemical processes at interfaces and electroactive materials.

Dr. Jenny Pringle is a graduate of Edinburgh University, Scotland, and is currently a senior postdoctoral research fellow in ACES and the School of Chemistry at Monash University. Her research into ionic liquids currently focuses on the use of these materials as media for the synthesis and use of conducting polymers.

of ILs at Monash around 1995. At that time there was much interest in ion conducting materials for lithium battery applications.<sup>2,3</sup> Such materials needed to have “apparent” stability to below lithium plating potentials (−3.0 V vs NHE). Not many salts or solvents are stable under such strongly reducing conditions, and the field was actively researching polymer electrolytes and ceramic materials to solve the problem. About that time, we were collaborating with Prof. Michael Grätzel and his group at École Polytechnique Fédérale de Lausanne (EPFL) who were developing liquid salts for the photoelectrochemical solar cell.<sup>4</sup> In this device, it is the low volatility of the liquid salts that is the appealing property, but some of the ILs described by Grätzel also had amazing electrochemical properties; cyclic voltammetry experiments showed that they produced no appreciable electrochemical processes down to at least −2.5 V (vs Fc/Fc<sup>+</sup>)<sup>5</sup> in the reducing direction. Similarly they showed high stability against oxidation, typically to >2.0 V vs Fc/Fc<sup>+</sup>. This type of potential window made these materials of immediate interest to both the lithium battery world and the emergent field of high energy density double-layer (or “super”) capacitors. It was with motivations in both these areas, and also recalling the work that had been done by Angell’s group on organic iodide melts many years earlier,<sup>6</sup> that we began our first ionic liquids work in 1996. The challenge then, as it still is today in many respects, was to develop stable ILs that were also sufficiently conductive to be of interest in real device applications. Unfortunately, while ILs are intrinsic ion conductors, their ion conductivity often falls short of that of solvent-based electrolytes because of the high viscosity. Of course, the viscosity of ILs is a consequence of the electrostatic interactions that are intrinsic to their ionic nature. Understanding and untangling this conundrum has been one of the underlying themes of our research interests since then. In this Account, we survey the electrochemistry applications in which ionic liquids have become important and discuss the challenges that they present.

\* Corresponding author. Tel: +613 9905 4540. Fax: +613 9905 4597. E-mail: Douglas.MacFarlane@sci.monash.edu.au.

<sup>†</sup> School of Chemistry.

<sup>‡</sup> Department of Materials Engineering.

Dr. Patrick Howlett is a graduate of Monash University and is currently a senior postdoctoral fellow in ACES. His interests involve interfacial electrochemistry of reactive metals in ionic liquids.

Dr. Jiazeng Sun is a graduate of Monash University and is currently a senior postdoctoral fellow in ACES at Monash. His interests include the design and synthesis of electrolyte materials.

Gary Annat is a Ph.D. student in ACES. His work involves the physical properties of ionic liquids.

Wayne Neil is a Ph.D. student in ACES. His work involves the use of ionic liquids in corrosion protection of Mg alloys.

Dr. Ekaterina Izgorodina is a graduate of the University of Münster, Germany, and is currently a postdoctoral fellow in the Monash Ionic Liquids Group. Her goal is to provide theoretical/computational understanding of the way ionic liquids behave.



**FIGURE 1.** Electron density as a function of position on the  $[\text{NTf}_2]^-$  anion displayed using electrostatic potential values. The red color indicates the positive values of potential, while blue indicates negative values. The four sulfonyl oxygens carry a significant fraction of the overall negative charge in this molecule. The electron density and electrostatic potential were calculated at the HF/aug-cc-pVTZ level of theory.<sup>14</sup>

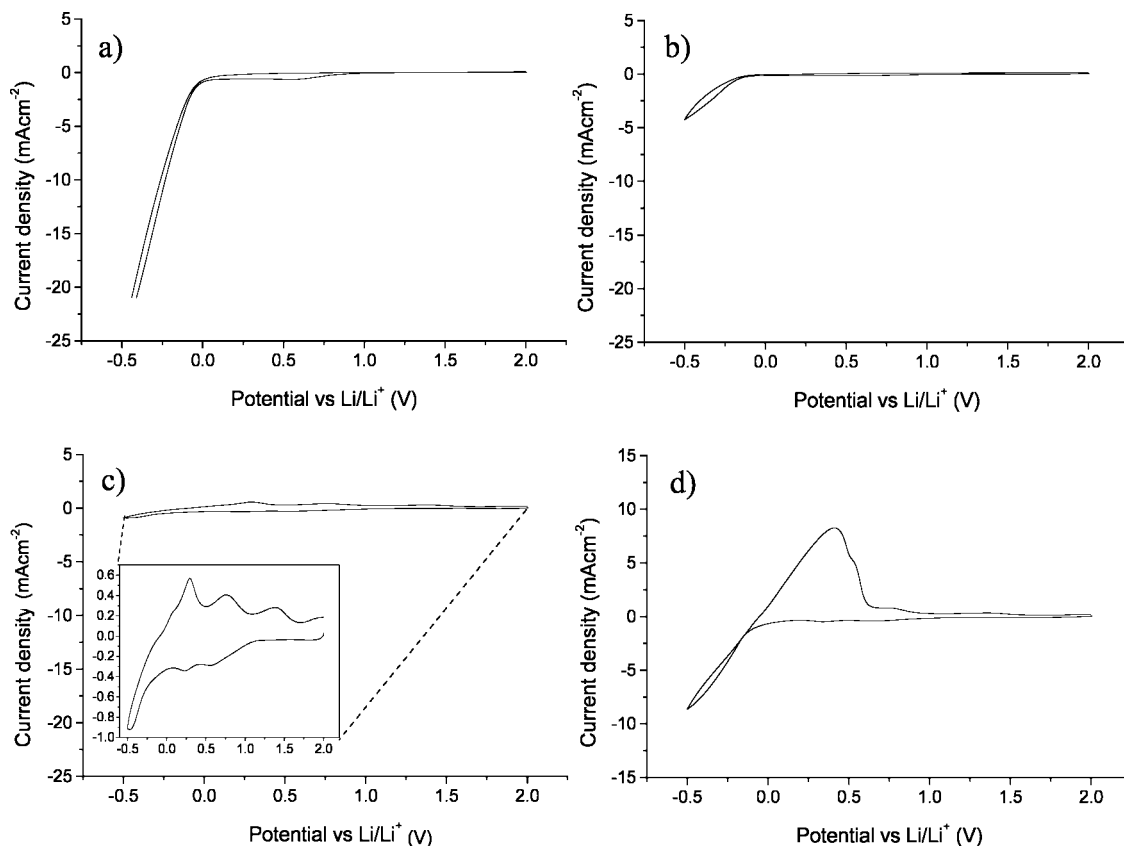
## 2. Lithium Electrochemistry

For lithium cell applications, the 1-alkyl-3-methylimidazolium cation  $[\text{C}_n\text{mim}]^+$  is not quite stable enough to be unreactive toward lithium. This is probably the result of the acidity of the C-2 proton in this ring.<sup>7</sup> The C-2 substituted imidazolium based ionic liquids are all significantly more viscous than their unsubstituted analogues, in itself a very interesting effect but not helpful in finding a fluid IL of sufficient stability against Li metal. To overcome this, we investigated a large family of ammonium<sup>8</sup> and pyrrolidinium<sup>9</sup> bis(trifluoromethanesulfonyl)amide<sup>10</sup> ( $[\text{NTf}_2]^-$ ) salts, this anion (Figure 1) typically providing the highest ion conductivity among the ILs known at the time. Work since has probed crystal structures involving this anion<sup>11–13</sup> and also ab initio calculations of its structure as shown in Figure 1,<sup>14</sup> to understand why such a large and massive ion could provide champion ion mobility. The answer, in a nutshell, is charge delocalization; the single negative charge, which formally resides on the amide nitrogen, is highly delocalized, as shown in Figure 1. Recently,<sup>14</sup> we have proposed an energetic criterion as a basis on which to gauge the degree of charge delocalization. In this approach, we use a proton as a probe charge to examine the net charge at various locations on the anion. The calculated relative proton affinities correlate well with experimental data such as melting point. For example, for the methylethylimidazolium (often abbreviated as  $[\text{C}_2\text{mim}]^+$ ) based ionic liquids, the melting points vary from 87 °C ( $\text{Cl}^-$ ) and 38 °C ( $[\text{NO}_3]^-$ ) for anions having a high degree of charge localization to –10 °C (tricyanomethanide) and –12 °C ( $[\text{NTf}_2]^-$ ) for the more diffuse anions. The diffuse ions are more able to move independently of other ions in an electric field and thus produce higher conductivity. Further extension of the concept by extending the perfluoroalkyl chain produces little further delocalization, thus suggesting that the negative charge can be delocalized only to a certain effective extent. The properties of the corresponding ILs unfortunately reflect this fact,<sup>15</sup> showing little additional improvement in transport properties.

The pyrrolidinium  $[\text{NTf}_2]^-$  salts, in particular, show a noticeable increase in reductive stability compared with the imidazolium salts, sufficiently so that we were subsequently able to demonstrate highly reversible electrodeposition and dissolution of lithium metal from these ILs.<sup>16</sup> In situ monitoring of the electrode over hundreds of cycles showed that the IL seemed to suppress the troublesome formation of dendrites, which had plagued earlier lithium/electrolyte combinations. Of the large family of alkylmethylpyrrolidinium<sup>17</sup>  $[\text{NTf}_2]^-$  salts available, the propyl and butyl derivatives proved to be the most fluid and conductive of the family, and these have been the focus of much research since.

Although ionic conductivity is the most frequently discussed property with respect to applications such as batteries, it is not, under most circumstances, the key transport property. In a device where lithium is produced at one electrode and consumed at the other, it is lithium ion diffusivity that is of importance. Unfortunately, addition of a lithium salt to the IL to provide a reservoir of lithium ions, typically causes a decrease in conductivity as a result of relatively strong binding of the anion by the lithium ion to form ion pairs or even  $\text{LiA}_2^-$  triple ions. Thus direct probes of the lithium diffusivity become important in understanding these electrolytes, including pulsed field gradient (pfg) NMR and ultra-microelectrode electrochemical methods. The pfg-NMR method of determining diffusion coefficients, at one level, appears to be a simple and ideal approach to obtaining this vital information. However, there are subtleties in the way that this experiment is carried out that are still being clarified.<sup>18</sup> Certainly it appears that the “spin-echo” method of the pfg-NMR technique (known as the pulse gradient spin-echo, or PGSE, method) is capable of producing spurious diffusion coefficient results, by as much as 25%.<sup>18</sup> In the relatively viscous medium that the ILs represent, this occurs because of a failure of some of the underlying assumptions of the method. On the other hand, the “stimulated echo” variant of the pulsed field gradient method appears to provide a superior approach. However, one learns from this that it is important to confirm satisfactory consistency with the underlying physical assumptions when applying these methods.

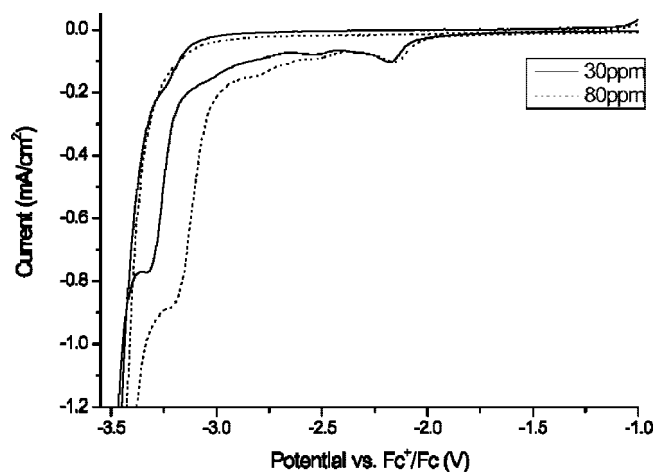
While the electrochemical window of the alkylmethylpyrrolidinium  $[\text{NTf}_2]^-$  ILs appears to extend well below the deposition potential for lithium, especially in the presence of an added lithium salt (Figure 2), a closer analysis of electrodeposited lithium quickly reveals the presence of a layer of breakdown products covering the surface of the lithium deposit. Such layers are well known in the lithium electrochemistry field. Detailed analysis of the data indicates a multilayer film with heavily reduced inorganic species dominating close to the metal surface, whereas at the outer surface the film is dominated by less reduced fragments of the  $[\text{NTf}_2]^-$  anion ( $\text{Li}_2\text{S}_2\text{O}_4$ ,  $\text{LiSO}_2\text{CF}_3$ ,  $\text{LiNSO}_2\text{CF}_3$ , ...) and organic species that appear to be precipitated salts of the cation.<sup>16,19</sup> The origins of these layers certainly include trace impurities remaining in the IL and the other cell components (the counter



**FIGURE 2.** Cyclic voltammograms showing the influence of LiNTf<sub>2</sub> concentration in [C<sub>4</sub>mpyr][NTf<sub>2</sub>]: (a) neat; (b) 0.005 mol kg<sup>-1</sup>; (c) 0.05 mol kg<sup>-1</sup>; (d) 0.5 mol kg<sup>-1</sup>. Only (d) shows the characteristic deposition and stripping peaks associated with Li cycling.

electrode, cell body, etc) including water, O<sub>2</sub>, and N<sub>2</sub> but also clearly involve some breakdown of the IL ions. Appearance of such breakdown products at potentials quite close to the apparent IL reductive limit is perhaps not surprising; however more detailed electrochemical experiments have now revealed that there are electrochemical processes taking place well before this low potential limit is reached in [NTf<sub>2</sub>]<sup>-</sup> ILs.<sup>20–22</sup> The current understanding is that the anion is susceptible to a series of electrochemically initiated breakdown reactions starting at around -2.0 V vs Fc/Fc<sup>+</sup>.<sup>20</sup> The products of these eventually precipitate onto the electrode as a film, which inhibits further reaction but which is able to transport the lithium ion such that lithium electrochemistry remains possible. The demonstration of several hundred Li oxidation and reduction cycles at high Coulombic efficiency indicates that further growth of the film is slowed, although it may ultimately limit the life of the electrode.

The role of impurities in these processes has been demonstrated by experiments in which additional trace levels of water are spiked into the sample.<sup>20,22,23</sup> At these potentials where common atmospheric impurity species (O<sub>2</sub>, N<sub>2</sub>, H<sub>2</sub>O) are electrochemically active, this approach is preferable to ultimately futile attempts to lower these species below the level of chemical significance (<1 ppb?). The water spiking experiments clearly demonstrated the role of water in the IL breakdown processes (Figure 3) but at a level greater than could be directly accounted for in terms of the water content present in the sample. Hence

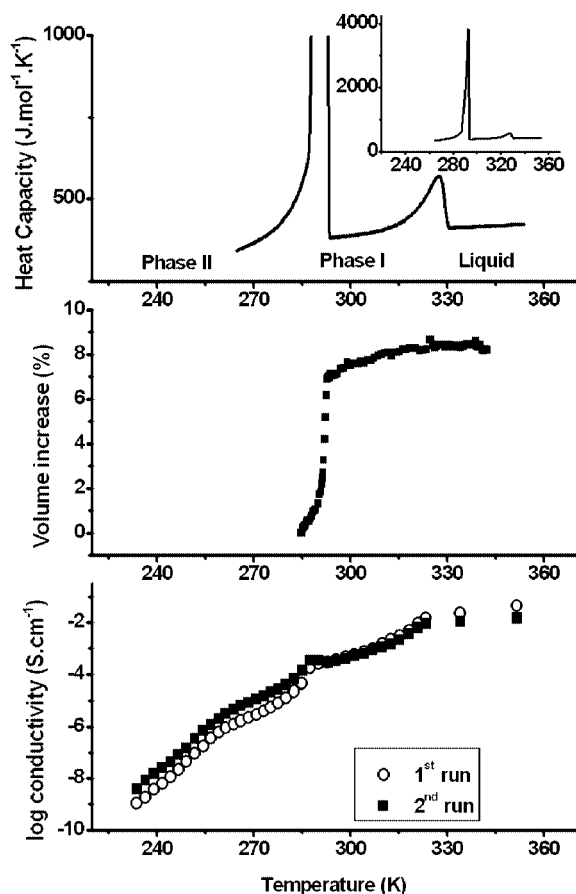


**FIGURE 3.** The [C<sub>3</sub>mpyr][NTf<sub>2</sub>] cyclic voltammogram at negative potentials with varying water concentrations on a Pt electrode.

a catalytic role for the reduction products of water (\*OH, etc.) is indicated. Further evidence for such processes has been provided by ab initio modeling of some of the proposed breakdown reactions.<sup>20</sup>

### 3. Organic Ionic Plastic Crystals

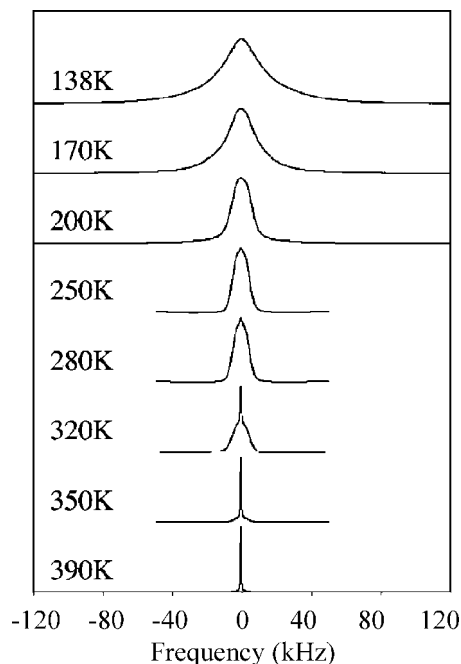
Of course, a solid or elastomeric form of electrolyte is preferred in most, if not all, of the device applications discussed here, and it is important to note in this context that many of the organic salt families that form ILs also



**FIGURE 4.** Phase behavior and conductivity of  $[\text{Et}_4\text{N}][\text{dca}]$  showing plastic behavior around room temperature. The inset to the heat capacity plot shows the same data on a larger scale such that the whole of the 290 K peak can be displayed.

contain members that form plastic crystalline phases. These organic ionic plastic crystals (OIPCs) are characterized by high diffusivities of both the ions themselves and solute ions that can be added to the material.<sup>24</sup> In many cases, the plastic phases correspond to a polymorph of the crystalline compound in which one or both of the ions is able to execute rotational motions (in some cases, fully isotropic rotational motion) on their lattice sites. This introduces some of the liquid-like motional degrees of freedom into the solid state and raises the thermodynamic state closer to the liquid state.

One of the classic examples of this behavior is tetraethylammonium dicyanamide ( $[\text{Et}_4\text{N}][\text{dca}]$ ),<sup>25</sup> which melts at 54 °C to form a fluid and highly conductive IL (Figure 4). However, it melts with very little change in volume and entropy, suggesting that the solid phase (termed phase 1) just below the melting point has much of the disorder and motional properties of the liquid. The material is also quite plastic. On cooling, it enters a more ordered crystalline phase (phase II) around 17 °C via a transition involving much more substantial changes in entropy and volume. At room temperature, the plastic crystal is as conductive as many ILs and hence is of interest in many of the device applications where a solid-state electrolyte is of value.



**FIGURE 5.** Temperature dependence of the  $^1\text{H}$  NMR spectra for crystalline  $[\text{Me}_4\text{N}][\text{dca}]$  showing line narrowing at the transition to the plastic phase ( $\sim 390$  K) reflecting the onset of isotropic tumbling and diffusion in the solid state. The melting point of this material is 450 K.

In a series of reports, we have described a number of these families of plastic crystalline compounds and their properties, with particular emphasis on their transport properties.<sup>9,26,27</sup> In cases where the electrochemically active ion of interest is not intrinsic to the material, for example,  $\text{Li}^+$  ions for Li battery applications or  $\text{H}^+$  for fuel cell applications, it is possible to dope/mix the plastic solid with a salt of the active ion. Cooper and Angell have also described interesting ion conductive binary inorganic/organic plastic phases.<sup>28</sup> In some cases, the conductivity is enhanced by as much as 2 orders of magnitude.<sup>29–31</sup> In a tangential development from this work, we and others have shown that molecular plastic crystalline materials such as succinonitrile containing dissolved salts could also be highly conductive and thereby useful as solid-state electrolyte materials.<sup>32–36</sup>

The detail of the link between the rotational degrees of freedom and the transport properties in these materials remains to be fully explained, but it appears clear that there is a direct cause and effect relationship in operation. NMR spectroscopy has been particularly useful in probing the rotational motions that are active in these solids, the NMR linewidths of a nucleus being a strong function of the state of motion of other nuclei in its environment (Figure 5). In cases where a crystal structure was available, calculation techniques were developed that allowed the prediction of linewidths, *ab initio*, from the crystal structure and assumed modes of rotational motion.<sup>37</sup>

#### 4. Actuators and Conducting Polymers

Ionic liquids also have much to offer the field of conducting polymers (CPs). CPs such as poly(pyrrole) and poly-

(thiophene) are, under most circumstances, conductive only in their partially oxidized state. The required counterion is typically an anion such as iodide,  $\text{ClO}_4^-$ , or tosylate. In fact, the overlap between the anions that are of utility in this respect and those that are often found in ILs is remarkable. The origins of this similarity lie in a common set of properties required in such ions. Like the IL, the conducting polymer is optimized by an anion that has a relatively delocalized charge, such that it interacts rather weakly with the positive charge on the backbone of the polymer. Thus the appropriate IL can provide an excellent source of counterions in an otherwise inert medium and hence represents a potentially ideal medium for both the synthesis and electrochemical action of CPs.

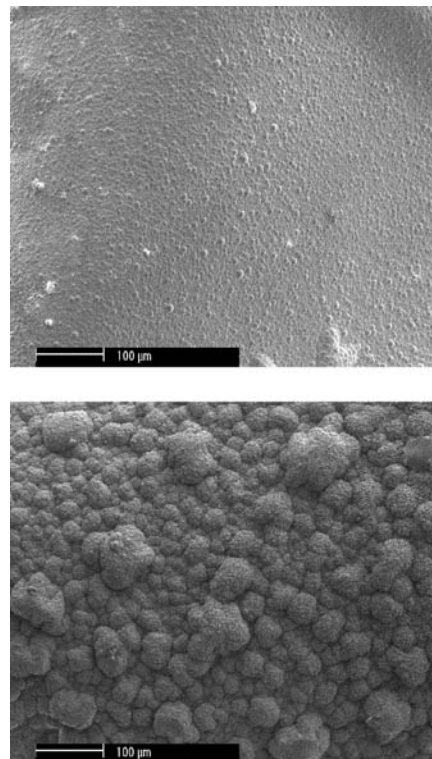
In the context of electrochemical action, the results can be dramatic. One example involves the CP-based electro-mechanical actuator device, which functions on the basis of the volume change that takes place in poly(pyrrole) when it is oxidized and incorporates the anion. Such “actuators” have the potential to provide electromechanical action in microdevices comparable to human muscle. Unfortunately, when constructed with a solvent-based electrolyte, their lifetime is limited to a few thousands of cycles, utterly insufficient for any practical device. However, when an IL of an appropriate anion is used, the cycle life exceeds  $10^6$  cycles.<sup>38</sup> The low volatility of such IL-based electrolytes is also ideal for practical applications; the IL can also be gelled such that it exhibits no flow characteristics.<sup>39</sup>

The availability of the counterion in the IL medium is also an ideal situation with respect to the synthetic routes from which conducting polymers are obtained. For example, the electrochemical polymerization of monomers such as pyrrole,<sup>40</sup> thiophene<sup>41</sup> and benzene<sup>42</sup> is simply achieved in an IL. The resultant polymer can have a range of morphological characteristics quite different from the solvent based polymerization process (Figure 6). The high oxidative stability of the IL also allows polymerizations of monomers such as terthiophene that otherwise require too high an oxidation potential to be tolerable by most solvents.

In a similar vein, ILs have proven to be very useful solvents for the *chemical* polymerization of monomers such as thiophene, allowing the use of high potential oxidants such as  $\text{AuCl}_3$  (Figure 7a).<sup>43</sup> The use of  $\text{AuCl}_3$  or  $\text{AgNO}_3$  as the oxidant in these systems is also advantageous because it can result in the incorporation of metal nanoparticles into the polymer (Figure 7b). Using a biphasic IL/water system, with the  $\text{AuCl}_3$  in the water layer and the monomer in the IL, produces polymers with very unusual nanodimensional fibrillar morphologies (Figure 7c).<sup>44</sup>

## 5. Photoelectrochemical Solar Cells

As originally proposed by Grätzel,<sup>4,45,46</sup> ILs are potentially the ideal basis of a liquid or gel electrolyte for the photoelectrochemical solar cell, by virtue of their low volatility. However, their relatively high viscosity is a

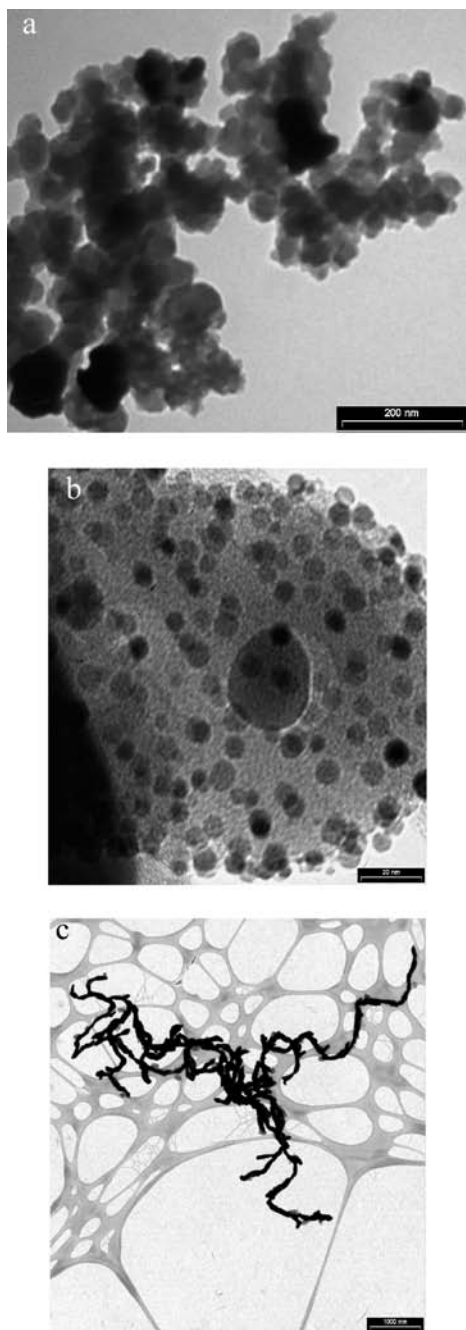


**FIGURE 6.** Poly(pyrrole) films grown in  $[\text{C}_4\text{mpyr}][\text{NTf}_2]$  (top) and propylene carbonate/ $\text{Bu}_4\text{N PF}_6$  (bottom), at constant potential onto Pt. Scanning electron micrographs show very different morphologies achieved from the different electrolytes.

significant detraction; in the context of the solar cell, mass transport limitation produces poor efficiency. As part of an ongoing effort to design and synthesize novel ILs we described the use of the dicyanamide,<sup>47</sup> thiocyanate,<sup>48</sup> and tricyanomethanide<sup>49</sup> ions in producing champion low-viscosity ILs. All of these proved to be of interest for solar cell applications,<sup>50–52</sup> as well as in a variety of other contexts where low viscosity is important, including room temperature synthesis. One of the interesting features of these anions, and the ILs that they produce, is a distinct degree of basicity not present in the more typical IL families.<sup>53</sup> This basicity provides a range of interesting and useful solvent effects including a specific base catalysis effect in which the ionic liquid solvent can serve as a nucleophilic catalyst in organic reactions in a fashion typically only observed in aqueous systems.<sup>54</sup> In the solar cell, a degree of basicity is usually ideal; however, it would appear that the basicity of dca is too great for long-term stability.<sup>51</sup> The interesting ILs formed by the  $\text{SeCN}^-$  and the  $[\text{B}(\text{CN})_4]^-$  ions may provide the ideal situation.<sup>55,56</sup> Ultimately, solid materials are the electrolytes of choice in this device, and among a variety of approaches, the use of plastic crystal based electrolytes has shown some promise.<sup>33,36</sup>

## 6. Fuel Cells

For many of the same reasons that ILs have ideal properties in the device applications described above, they are also potentially ideal for use as proton conducting media



**FIGURE 7.** Transmission electron micrographs of conducting polymers chemically synthesized in  $[C_2mim][NTf_2]$ : (a) poly(thiophene) nanoparticles synthesized in a one-phase system using  $AuCl_3$  (200 nm scale bar); (b) poly(pyrrole) from one phase using  $AgNO_3$ , which results in the incorporation of silver nanoparticles (20 nm scale bar); (c) poly(3,4-ethylenedioxythiophene) (PEDOT) synthesized in an IL/water biphasic system (1000 nm scale bar).

in fuel cells.<sup>57–60</sup> Xu and Angell<sup>59</sup> have investigated these in detail, and the Arizona State group has now shown how binary (inorganic) liquid salt mixtures can produce impressive fuel cell performance at temperatures above 100 °C.<sup>61</sup> One of the curious aspects of these proton transfer liquids is that the *degree* of proton transfer, and therefore the ionicity of the resultant material, turns out to be substantially less than is predicted by simple aqueous  $pK_a$  estimations.<sup>60</sup> The origins of this shift in acidity are

becoming clearer as a result of ab initio calculations of the gas-phase acid–base pairs, which suggest that it is mainly associated with the absence of the aqueous hydrogen bonding and solvation environment.<sup>53</sup>

## 7. Passivation of Reactive Metals

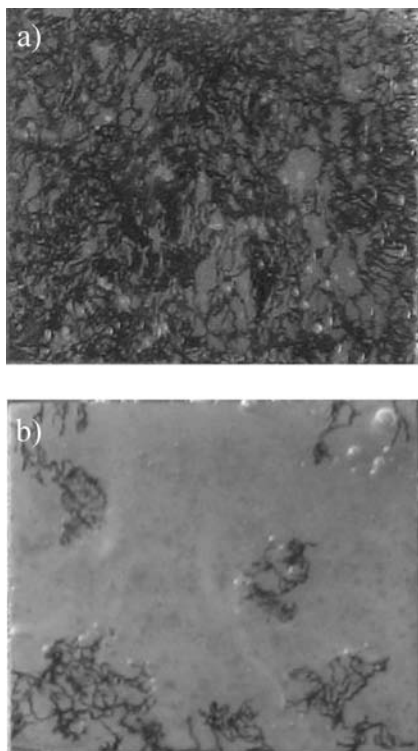
In considering the property that allowed lithium metal batteries to become viable in ILs, that is the surface layer, it became apparent that the charge transfer at the lithium electrode was dominated by the ability of  $Li^+$  ions to transport across the  $LiF$  and  $Li_2O$  inorganic nanolayers that form when Li metal comes into contact with the  $NTf_2^-$  anion in the ILs. At the same time, it is well understood that the key to controlling the charge transfer on reactive metals such as aluminum, steel, and magnesium in engineering applications, and hence their corrosion, is that these metals can be passivated by formation of thin inorganic oxide and hydroxide layers that can restrict ionic and electronic conductivity. While defective  $LiF$  and  $Li_2O$  are good lithium ion conductors, fluoride and oxides of Mg and Al are relatively insulating and hence a hypothesis developed that it may be possible to passivate Mg and its alloys by treatment in an IL.

Given the electrochemical breakdown of  $NTf_2^-$  at around  $-2.0$  V vs  $Fc^+/Fc$  and the position of Mg in the electrochemical series, we hypothesized that when this anion came into contact with a Mg or Mg alloy surface, it would react to form inorganic fluorides, which would passivate the metal surface. Indeed, exposure of pure Mg and AZ31 (a magnesium alloy containing aluminum and zinc) to  $NTf_2^-$  ILs produced an order of magnitude reduction in corrosion rates.<sup>62,63</sup> The trihexyl(tetradecyl)phosphonium ( $[P_{6,6,6,14}]$ )  $NTf_2^-$  IL, in particular, produced homogeneous films that were protective against  $Cl^-$  aqueous solutions (Figure 8). The time that the alloy was exposed to the IL and its temperature during this treatment had a significant influence on the composition, thickness, and protectiveness of the passivating layer.

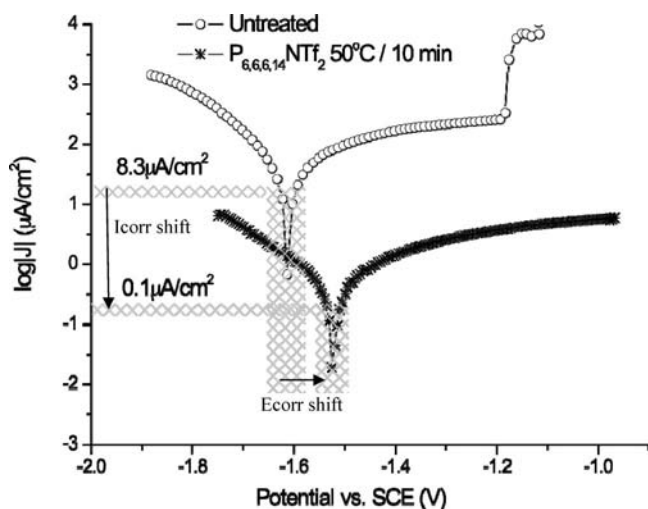
Electrochemical polarization (Figure 9) and ac impedance measurements confirmed the increased resistance to corrosion of these “IL treated” surfaces. The results obtained thus far indicate that IL treatments are promising replacements for the highly toxic hexavalent chromium passivation treatments currently used.

Surface analysis of the treated Mg surfaces confirm that, similar to the Li metal surface, a metal fluoride is present together with the oxide and hydroxide (Figure 10). In addition, the outermost layers appear to have entrapped organic components, possibly the IL constituent ions themselves. This latter observation is significant because it suggests that IL components are retained in the film and are thus available for repassivation, should the film be breached in some way. Our electrochemical tests suggested that “self-healing” of these surfaces is indeed possible.

Given the reactivity of phosphates with magnesium, we then proceeded to investigate the passivation behavior of an IL based on an organophosphinate.<sup>65</sup> In the presence

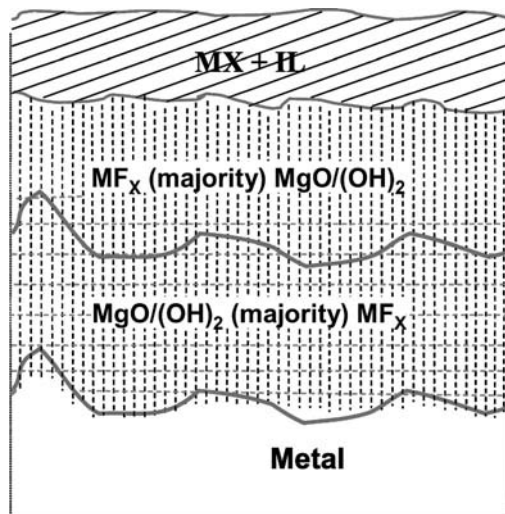


**FIGURE 8.** (a) Untreated and (b) 1 h  $[P_{6,6,6,14}][NTf_2]$  immersed, magnesium coupons after exposure to 0.1 M NaCl showing the effect of an ionic liquid generated protective coating on the coupon.



**FIGURE 9.** Microcell cyclic polarization scans for a control and a 50 °C/10 min  $[P_{6,6,6,14}][NTf_2]$ -treated Mg coupon showing a shift to more noble corrosion potentials,  $E_{corr}$ , and a decrease in corrosion current density,  $I_{corr}$ . Multiple scans were acquired for each sample; hatched areas indicate the range of  $I_{corr}$  and  $E_{corr}$  values obtained. The scans were acquired at  $10 \text{ mV s}^{-1}$  in 0.1 M NaCl, pH = 7. Data were taken from ref 64.

of an equilibrium amount of water (approximately 6 wt % in the IL), a very thin film formed on the AZ31 magnesium alloy surface, which apparently offered even more protection than the  $NTf_2$ -based IL. However, the mechanism of passive film formation in this case is more likely to be due to direct reaction with the phosphinate group forming a thin insoluble compound by reaction with functional groups on the alloy surface (as opposed



**FIGURE 10.** General schematic of the IL film structure derived from spectroscopic evidence. M can be Mg, Al, or Zn (pure or intermetallic) and X might be  $S_2O_4$ , F,  $SO_3CF_3$ ,  $NSO_2CF_3$ ,  $SO_3$ , S, O, or OH.

to electrochemical reactivity). The mechanism, however, is still not clear, although it does seem to involve water.

## 8. Concluding Remarks and Future Prospects

Undoubtedly, the attractive features of some ionic liquids will generate increasingly widespread interest in the electrochemistry field and in electrochemical device applications. However, the very features that make these liquids attractive, also create challenges in understanding the electrochemical process that take place at extremes of potential and the role of the inevitable impurities. The occurrence of passivating films on lithium, magnesium, and magnesium alloy surfaces in the presence of some ILs is likely to have significant implications in attempts to electrodeposit metals such as Ti and Ta at cathodic potentials in the vicinity of  $-2.0 \text{ V}$  vs  $Fc^+/Fc$ . Thus, it can be expected that, in many cases, unusual morphologies or deposit compositions will result. Nonetheless, understanding and controlling these processes will certainly be of technological significance in the production and application of a number of important materials. Equally, there is a huge data gap emerging with respect to the thermodynamic and transport properties over a wide range of temperatures, as well as the effect of solutes and impurities on these properties. Answers to these challenges will hopefully be forthcoming in the near future given the increasing interest of a broader spectrum of researchers.

*Funding from the Australian Research Council for several Discovery Projects in the ILs field and the Australian Centre of Excellence for Electromaterials Science is gratefully acknowledged.*

## References

- (1) MacFarlane, D. R.; Seddon, K. R. Ionic liquids - Progress on the fundamental issues. *Aust. J. Chem.* **2007**, *60*, 3–5.
- (2) Forsyth, M.; Meakin, P. M.; Macfarlane, D. R. A C-13 Nmr-Study of the Role of Plasticizers in the Conduction Mechanism of Solid Polymer Electrolytes. *Electrochim. Acta* **1995**, *40*, 2339–2342.

- (3) Forsyth, M.; Meakin, P.; MacFarlane, D. R.; Hill, A. J. Free-Volume and Conductivity of Plasticized Polyether-Urethane Solid Polymer Electrolytes. *J. Phys.: Condens. Matter* **1995**, *7*, 7601–7617.
- (4) Bonhote, P.; Dias, A. P.; Papageorgiou, N.; Kalyanasundaram, K.; Gratzel, M. Hydrophobic, highly conductive ambient-temperature molten salts. *Inorg. Chem.* **1996**, *35*, 1168–1178.
- (5) Reference potential systems were not available in that early work, and it was common to use a Pt pseudo-reference electrode. More recent work (ref 19 below) has established the ferrocene/ferrocinium redox couple as a useful reference electrode in ionic liquids and discussed reference electrodes based on this.
- (6) Cooper, E. I.; Angell, C. A. Versatile Organic Iodide Melts and Glasses with High Mole Fractions of Li - Glass-Transition Temperatures and Electrical Conductivities. *Solid State Ionics* **1983**, *9–10*, 617–622.
- (7) Fuller, J.; Carlin, R. T.; Osteryoung, R. A. The Room-Temperature Ionic Liquid 1-Ethyl-3-methylimidazolium Tetrafluoroborate: Electrochemical Couples and Physical Properties. *J. Electrochem. Soc.* **1997**, *144*, 3881–3886.
- (8) Sun, J.; Forsyth, M.; MacFarlane, D. R. Room-temperature molten salts based on the quaternary ammonium ion. *J. Phys. Chem. B* **1998**, *102*, 8858–8864.
- (9) MacFarlane, D. R.; Meakin, P.; Sun, J.; Amini, N.; Forsyth, M. Pyrrolidinium Imides: A New Family of Molten Salts and Conductive Plastic Crystal Phases. *J. Phys. Chem. B* **1999**, *103*, 4164–4170.
- (10) There are a number of abbreviations and names for this anion currently in use. It is also routinely called bis(trifluoromethanesulfonyl) imide and is also given acronyms such as TFSA and TFSI. In the authors' understanding of IUPAC naming guidelines, and consistent with usage in the inorganic literature, this structure is most appropriately described as an "amide" (analogous to dicyanamide). To provide some degree of uniformity, a number of the ionic liquids research groups have agreed in recent years to use  $\text{NTf}_2^-$  as the preferred abbreviation to avoid the confusion created by TFSA vs TFSI.
- (11) Golding, J. J.; MacFarlane, D. R.; Spiccia, L.; Forsyth, M.; Skelton, B. W.; White, A. H. Weak Intermolecular Interactions in Sulfonamide Salts: Structure of 1-Ethyl-2-methyl-3 benzyl imidazolium Bis(trifluoromethyl)sulfonylamide. *Chem. Commun.* **1998**, 1593–1594.
- (12) Forsyth, C. M.; MacFarlane, D. R.; Golding, J. J.; Huang, J.; Sun, J.; Forsyth, M. Structural Characterization of Novel Ionic Materials Incorporating the Bis(trifluoromethanesulfonyl)amide Anion. *Chem. Mater.* **2002**, *14*, 2103–2108.
- (13) Pringle, J. M.; Golding, J.; Baranyai, K.; Forsyth, C. M.; Deacon, G. B.; Scott, J. L.; MacFarlane, D. R. The Effect of Anion Fluorination in Ionic Liquids - Physical Properties of a Range of Bis(methanesulfonyl)amide Salts. *New J. Chem.* **2003**, *27*, 1504–1510.
- (14) Izgorodina, E. I.; Forsyth, M.; MacFarlane, D. R. Towards a Better Understanding of 'Delocalized Charge' in Ionic Liquid Anions. *Aust. J. Chem.* **2007**, *60*, 15–20.
- (15) Johansson, K. M.; Adebahr, J.; Howlett, P. C.; Forsyth, M.; MacFarlane, D. R. *N*-Methyl-*N*-alkylpyrrolidinium Bis(perfluoroethylsulfonyl) Amide ([NPf(2)]<sup>-</sup>) and Tris(trifluoromethanesulfonyl) Methide ([CTf3]<sup>-</sup>) Salts: Synthesis and Characterization. *Aust. J. Chem.* **2007**, *60*, 57–63.
- (16) Howlett, P. C.; MacFarlane, D. R.; Hollenkamp, A. F. High Lithium Metal Cycling Efficiency in a Room-Temperature Ionic Liquid. *Electrochem. Solid State Lett.* **2004**, *7*, A97–A101.
- (17) The literature has also spawned a variety of abbreviations for this cation. Our original work created the abbreviation  $\text{P}_{1x}$  for the methylalkylpyrrolidinium cations, but the more recent increase in interest in the phosphonium cation based ionic liquids has made that abbreviation confusing. For this reason, it was recently agreed that [C<sub>x</sub>mpyr] be used as a preferable abbreviation for the alkylpyrrolidinium cations, the "pyr" being used to distinguish the cation from the pyridinium family of cations.
- (18) Annat, G.; MacFarlane, D. R.; Forsyth, M. Transport Properties in Ionic Liquids and Ionic Liquid Mixtures: The Challenges of NMR Pulsed Field Gradient Diffusion Measurements. *J. Phys. Chem. B* **2007**, *111*, 9018–9024.
- (19) Howlett, P. C.; Brack, N.; Hollenkamp, A. F.; Forsyth, M.; MacFarlane, D. R. Characterization of the Lithium Surface in *N*-Methyl-*N*-alkylpyrrolidinium Bis(trifluoromethanesulfonyl)amide Room-Temperature Ionic Liquid Electrolytes. *J. Electrochem. Soc.* **2006**, *153*, A595–A606.
- (20) Howlett, P. C.; Izgorodina, E. I.; Forsyth, M.; MacFarlane, D. R. Electrochemistry at Negative Potentials in Bis(trifluoromethanesulfonyl)amide Ionic Liquids. *Z. Phys. Chem.-Int. J. Res. Phys. Chem. Chem. Phys.* **2006**, *220*, 1483–1498.
- (21) El Abedin, S. Z.; Borissenko, N.; Endres, F. Electrodeposition of nanoscale silicon in a room temperature ionic liquid. *Electrochem. Commun.* **2004**, *6*, 510–514.
- (22) Endres, F.; El Abedin, S. Z.; Borissenko, N. Probing Lithium and Alumina Impurities in Air and Water Stable Ionic Liquids by Cyclic Voltammetry and in Situ Scanning Tunneling Microscopy. *Z. Phys. Chem.-Int. J. Res. Phys. Chem. Chem. Phys.* **2006**, *220*, 1377–1394.
- (23) Endres, F.; El Abedin, S. Z. Air and Water Stable Ionic Liquids in Physical Chemistry. *Phys. Chem. Chem. Phys.* **2006**, *8*, 2101–2116.
- (24) MacFarlane, D. R.; Forsyth, M. Plastic Crystal Electrolyte Materials: New Perspectives on Solid State Ionics. *Adv. Mater.* **2001**, *13*, 957–966.
- (25) Annat, G.; Adebahr, J.; McKinnon, I. R.; MacFarlane, D. R.; Forsyth, M. Plastic Crystal Behavior in Tetraethylammonium Dicyanamide. *Solid State Ionics* **2007**, *178*, 1065–1071.
- (26) Golding, J.; Hamid, N.; MacFarlane, D. R.; Forsyth, M.; Forsyth, C.; Collins, C.; Huang, J. *N*-Methyl-*N*-alkylpyrrolidinium Hexafluorophosphate Salts: Novel Molten Salts and Plastic Crystal Phases. *Chem. Mater.* **2001**, *13*, 558–564.
- (27) Forsyth, S. A.; Fraser, K. J.; Howlett, P. C.; MacFarlane, D. R.; Forsyth, M. *N*-Methyl-*N*-alkylpyrrolidinium Nonafluoro-1-butanesulfonate Salts: Ionic Liquid Properties and Plastic Crystal Behaviour. *Green Chem.* **2006**, *8*, 256–261.
- (28) Cooper, E. I.; Angell, C. A. Ambient-Temperature Plastic Crystal Fast Ion Conductors (Plicfics). *Solid State Ionics* **1986**, *18–9*, 570–576.
- (29) MacFarlane, D. R.; Huang, J.; Forsyth, M. Lithium-Doped Plastic Crystal Electrolytes Exhibiting Fast Ion Conduction for Secondary Batteries. *Nature* **1999**, *402*, 792–794.
- (30) Forsyth, M.; Huang, J.; MacFarlane, D. R. Lithium Doped *N*-Methyl-*N*-ethylpyrrolidinium Bis(trifluoromethanesulfonyl)amide Fast-Ion Conducting Plastic Crystals. *J. Mater. Chem.* **2000**, *10*, 2259–2265.
- (31) Henderson, W. A.; Passerini, S. Phase Behavior of Ionic Liquid-LiX Mixtures: Pyrrolidinium Cations and TFSI<sup>-</sup> Anions. *Chem. Mater.* **2004**, *16*, 2881–2885.
- (32) Abouimrane, A.; Abu-Lebdeh, Y.; Alarco, P. J.; Armand, M. Plastic Crystal-Lithium Batteries: An Effective Ambient Temperature All-Solid-State Power Source. *J. Electrochem. Soc.* **2004**, *151*, A1028–A1031.
- (33) Dai, Q.; MacFarlane, D. R.; Howlett, P. C.; Forsyth, M. Rapid I-/3(-) Diffusion in a Molecular-Plastic-Crystal Electrolyte for Potential Application in Solid-State Photoelectrochemical Cells. *Angew. Chem., Int. Ed.* **2005**, *44*, 313–316.
- (34) Long, S.; Howlett, P. C.; MacFarlane, D. R.; Forsyth, M. Fast Ion Conduction in an Acid Doped Pentaglycerine Plastic Crystal. *Solid State Ionics* **2006**, *177*, 647–652.
- (35) Long, S.; MacFarlane, D. R.; Forsyth, M. Fast Ion Conduction in Molecular Plastic Crystals. *Solid State Ionics* **2003**, *161*, 105–112.
- (36) Wang, P.; Dai, Q.; Zakeeruddin, S. M.; Forsyth, M.; MacFarlane, D. R.; Gratzel, M. Ambient Temperature Plastic Crystal Electrolyte for Efficient, All-Solid-State Dye-Sensitized Solar CeN. *J. Am. Chem. Soc.* **2004**, *126*, 13590–13591.
- (37) Seeber, A. J.; Forsyth, M.; Forsyth, C. M.; Forsyth, S. A.; Annat, G.; MacFarlane, D. R. Conductivity, NMR and Crystallographic Study of *N,N,N,N*-Tetramethylammonium Dicyanamide Plastic Crystal Phases: An Archetypal Ambient Temperature Plastic Electrolyte Material. *Phys. Chem. Chem. Phys.* **2003**, *5*, 2692–2698.
- (38) Lu, W.; Fadeev, A. G.; Qi, B. H.; Smela, E.; Mattes, B. R.; Ding, J.; Spinks, G. M.; Mazurkiewicz, J.; Zhou, D. Z.; Wallace, G. G.; MacFarlane, D. R.; Forsyth, S. A.; Forsyth, M. Use of Ionic Liquids for Pi-Conjugated Polymer Electrochemical Devices. *Science* **2002**, *297*, 983–987.
- (39) Zhou, D. Z.; Spinks, G. M.; Wallace, G. G.; Tiyaiboonchaiya, C.; MacFarlane, D. R.; Forsyth, M.; Sun, J. Z. Solid State Actuators Based on Polypyrrole and Polymer-in-Ionic Liquid Electrolytes. *Electrochim. Acta* **2003**, *48*, 2355–2359.
- (40) Pringle, J. M.; Efthimiadis, J.; Howlett, P. C.; Efthimiadis, J.; MacFarlane, D. R.; Chaplin, A. B.; Hall, S. B.; Officer, D. L.; Wallace, G. G.; Forsyth, M. Electrochemical Synthesis of Polypyrrole in Ionic Liquids. *Polymer* **2004**, *45*, 1447–1453.
- (41) Pringle, J. M.; Forsyth, M.; MacFarlane, D. R.; Wagner, K.; Hall, S. B.; Officer, D. L. The Influence of the Monomer and the Ionic Liquid on the Electrochemical Preparation of Polythiophene. *Polymer* **2005**, *46*, 2047–2058.
- (42) Schneider, O.; Bund, A.; Ispas, A.; Borissenko, N.; Zein El Abedin, S.; Endres, F. An EQCM Study of the Electropolymerization of Benzene in an Ionic Liquid and Ion Exchange Characteristics of the Resulting Polymer Film. *J. Phys. Chem. B* **2005**, *109*, 7159–7168.
- (43) Pringle, J. M.; Ngamna, O.; Chen, J.; Wallace, G. G.; Forsyth, M.; MacFarlane, D. R. Conducting Polymer Nanoparticles Synthesized in an Ionic Liquid by Chemical Polymerization. *Synth. Met.* **2006**, *156*, 979–983.
- (44) Pringle, J. M.; Ngamna, O.; Lynam, C.; Wallace, G. G.; Forsyth, M.; MacFarlane, D. R. Conducting Polymers with Fibrillar Morphology Synthesized in a Biphasic Ionic Liquid/Water System. *Macromolecules* **2007**, *40*, 2702–2711.



- (45) Wang, P.; Zakeeruddin, S. M.; Exnar, I.; Gratzel, M. High Efficiency Dye-Sensitized Nanocrystalline Solar Cells Based on Ionic Liquid Polymer Gel Electrolyte. *Chem. Commun.* **2002**, 2972–2973.
- (46) Papageorgiou, N.; Athanassov, Y.; Armand, M.; Bonhote, P.; Pettersson, H.; Azam, A.; Gratzel, M. The Performance and Stability of Ambient Temperature Molten Salts for Solar Cell Applications. *J. Electrochem. Soc.* **1996**, *143*, 3099–3108.
- (47) MacFarlane, D. R.; Forsyth, S. A.; Golding, J.; Deacon, G. B. Ionic Liquids Based on Imidazolium, Ammonium and Pyrrolidinium Salts of the Dicyanamide Anion. *Green Chem.* **2002**, *4*, 444–448.
- (48) Pringle, J. M.; Golding, J.; Forsyth, C. M.; Deacon, G. B.; Forsyth, M.; MacFarlane, D. R. Physical Trends and Structural Features in Organic Salts of the Thiocyanate Anion. *J. Mater. Chem.* **2002**, *12*, 3475–3480.
- (49) Forsyth, S. A.; Batten, S. R.; Dai, Q.; MacFarlane, D. R. Ionic Liquids Based on Imidazolium and Pyrrolidinium Salts of the Tricyanomethanide Anion. *Aust. J. Chem.* **2004**, *57*, 121–124.
- (50) Wang, P.; Zakeeruddin, S. M.; Humphry-Baker, R.; Gratzel, M. A Binary Ionic Liquid Electrolyte To Achieve  $\geq 7\%$  Power Conversion Efficiencies in Dye-Sensitized Solar Cells. *Chem. Mater.* **2004**, *16*, 2694–2696.
- (51) Wang, P.; Zakeeruddin, S. M.; Moser, J. E.; Gratzel, M. A New Ionic Liquid Electrolyte Enhances the Conversion Efficiency of Dye-Sensitized Solar Cells. *J. Phys. Chem. B* **2003**, *107*, 13280–13285.
- (52) Dai, Q.; Menzies, D. B.; MacFarlane, D. R.; Batten, S. R.; Forsyth, S.; Spiccia, L.; Cheng, Y. B.; Forsyth, M. Dye-Sensitized Nanocrystalline Solar Cells Incorporating Ethylmethylimidazolium-Based Ionic Liquid Electrolytes. *C. R. Chim.* **2006**, *9*, 617–621.
- (53) MacFarlane, D. R.; Pringle, J. M.; Johansson, K. M.; Forsyth, S. A.; Forsyth, M. Lewis Base Ionic Liquids. *Chem. Commun.* **2006**, 1905–1917.
- (54) Forsyth, S. A.; MacFarlane, D. R.; Thomson, R. J.; von Itzstein, M. Rapid, Clean, and Mild O-Acetylation of Alcohols and Carbohydrates in an Ionic Liquid. *Chem. Commun.* **2002**, 714–715.
- (55) Wang, P.; Zakeeruddin, S. M.; Moser, J. E.; Humphry-Baker, R.; Gratzel, M. A Solvent-Free,  $\text{SeCN}^+/\text{(SeCN)}_3^-$  Based Ionic Liquid Electrolyte for High-Efficiency Dye-Sensitized Nanocrystalline Solar Cells. *J. Am. Chem. Soc.* **2004**, *126*, 7164–7165.
- (56) Kuang, D. B.; Wang, P.; Ito, S.; Zakeeruddin, S. M.; Gratzel, M. Stable Mesoscopic Dye-Sensitized Solar Cells Based on Tetracyanoborate Ionic Liquid Electrolyte. *J. Am. Chem. Soc.* **2006**, *128*, 7732–7733.
- (57) Matsuoka, H.; Nakamoto, H.; Susan, M.; Watanabe, M. Bronsted Acid-Base and -Polybase Complexes As Electrolytes for Fuel Cells under Non-Humidifying Conditions. *Electrochim. Acta* **2005**, *50*, 4015–4021.
- (58) Susan, A. B. H.; Yoo, M. Y.; Nakamoto, H.; Watanabe, M. A Novel Bronsted Acid-Base System As Anhydrous Proton Conductors for Fuel Cell Electrolytes. *Chem. Lett.* **2003**, *32*, 836–837.
- (59) Xu, W.; Angell, C. A. Solvent-Free Electrolytes with Aqueous Solution-Like Conductivities. *Science* **2003**, *302*, 422–425.
- (60) Yoshizawa, M.; Xu, W.; Angell, C. A. Ionic Liquids by Proton Transfer: Vapor Pressure, Conductivity, and the Relevance of  $\Delta pK_a$  from Aqueous Solutions. *J. Am. Chem. Soc.* **2003**, *125*, 15411–15419.
- (61) Belieres, J. P.; Gervasio, D.; Angell, C. A. Binary Inorganic Salt Mixtures As High Conductivity Liquid Electrolytes for  $> 100^\circ\text{C}$  Fuel Cells. *Chem. Commun.* **2006**, 4799–4801.
- (62) Birbilis, N.; Howlett, P. C.; MacFarlane, D. R.; Forsyth, M. Exploring Corrosion Protection of Mg via Ionic Liquid Pretreatment. *Surf. Coat. Technol.* **2007**, *201*, 4496–4504.
- (63) Shkurankov, A.; El Abedin, S. Z.; Endres, F. AFM-Assisted Investigation of the Corrosion Behaviour of Magnesium and AZ91 Alloys in an Ionic Liquid with Varying Water Content. *Aust. J. Chem.* **2007**, *60*, 35–42.
- (64) Howlett, P. C.; Tan, S. K.; Zhang, S.; MacFarlane, D. R.; Forsyth, M. Novel Conversion Coatings for Magnesium Alloys AZ31 Using Ionic Liquids. *Corros. Prev.* **2006**, 079.
- (65) Howlett, P. C.; Zhang, S.; MacFarlane, D. R.; Forsyth, M. An Investigation of a Phosphinate-Based Ionic Liquid for Corrosion Protection of Magnesium Alloy AZ31. *Aust. J. Chem.* **2007**, *60*, 43–46.

AR7000952