Design and Materialization of Ionic Liquids Based on an Understanding of Their Fundamental Properties

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ABSTRACT
Ionic liquids (ILs) are defined as salts that have melting points lower than 100°C. Most are organic salts, and these may be designed and tailored to have suitable properties. ILs are recognized as a third group of solvents (and electrolytes), after water and organic solvents. They are characterized by their unique properties such as non-volatilities, high thermal stabilities, and high ionic conductivities. In this article, our work on the design and preparation of ILs is briefly reviewed. The concept of ionicity is proposed as a metric to characterize the basic nature (dissociativity) of ILs, which is affected by the Lewis acidity/basicity of cations/anions (i.e., coulombic interactions), the directionality of interactions between cations and anions, and van der Waals interactions between ions. The ionicity of ILs is dominated by a subtle balance between coulombic and van der Waals interactions, which clearly discriminates ILs from conventional high-temperature inorganic molten salts. Here, the design of protic ILs for fuel cell electrolytes, electron-transporting ILs for dye-sensitized solar cell electrolytes, and Li⁺-conducting solvate ILs for lithium battery electrolytes are discussed based on an understanding of the fundamental properties of ILs. Furthermore, the combination of ILs with polymers and colloidal particles affords intriguing quasi-solid materials (ion gels), and the ion transport in these gels is decoupled from the mechanical relaxation time of these materials, yielding new solid electrolytes. The possibility of temperature and photo-sensitive solubility dependence of polymers in ILs allows the creation of stimuli-responsive materials. Finally, protic ILs/protic salts are demonstrated to be good precursors for N-doped carbon materials.

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1. Introduction

Ionic liquids (ILs) are now being recognized as a third group of solvents, following water and organic solvents. They are readily available and possess unique properties such as non-volatility, high thermal stability, and designability, making ILs designed for specific tasks or for use under unusual conditions possible. Our studies on ILs have focused on understanding their unique properties. Furthermore, we have investigated their uses as new electrolytes and solvents for the new materials and devices necessary for a sustainable society. More specifically, ILs can serve as new electrolytes in electrochemical energy conversion systems. H⁺- and Li⁺-conducting ILs are being designed to develop innovative fuel cells, batteries, and dye-sensitized solar cells. ILs also have unique polymer solubilities, opening up a new field of advanced, intelligent materials chemistry. These challenges encourage the development of new materials and devices necessary for a sustainable society based on a thorough understanding of ILs.

Before reviewing our previous studies on ILs, I will discuss why these studies were initiated. I started my academic career in the 1980s, and my research interests at that time concerned polymer electrolytes, in particular, ion dynamics in polymeric phases in relation to polymer dynamics and the electrochemical applications of these materials. During 1988–1990, I was a visiting scientist with R. W. Murray at the University of North Carolina. We developed electrochemical measurement methods using microelectrodes and polymer electrolytes as solvents, so-called solid-state voltammetry. We accumulated fundamental knowledge on the diffusion dynamics of redox solutes as well as their homogeneous and heterogeneous electron transfer dynamics in polymeric phases. After returning to Japan and having been stimulated by a discussion with J. Kawamura at Tohoku University, I conceived the idea of using ionic liquids (room-temperature molten salts; the term “ionic liquid” was not used at that time) as doping salts for polymer electrolytes. In conventional polymer electrolytes, typically consisting of a polymer solvent and a lithium salt, increases in the number of carrier ions and their mobility (diffusivity) are incompatible due to slowed polymer dynamics with salt doping and coupling transport of ions with the polymer dynamics, which limits their conductivity and utility at ambient temperatures. In 1993, one of the most important papers of my career was published. This communication reported highly conductive polymer electrolytes using ionic liquids that serve as plasticizing salts for polymers.

Since then, we have conducted comprehensive and detailed studies to gain an understanding of the nature of ILs, to design new task-specific ILs, and to assess their electrochemical applications. Our studies on ILs cover a broad range of chemistry areas and can be categorized into different topics as follows:

- Fundamental Characterization of ILs.
- Polymer Electrolytes of ILs (Ion Gels).
- H⁺-Conducting Protic ILs and Fuel Cells.
- Electron-Transporting ILs and Dye-Sensitized Solar Cells.
- Li⁺-Conducting ILs and Solvate ILs.
- Phase Behavior of Polymers in ILs and Materialization.
- Colloidal Stability in ILs and Materialization.
- IL and Nanocarbon Materials.

Now, these selected topical studies are briefly reviewed.
2. Fundamental Characterization of ILs

To fundamentally characterize ILs, especially concerning their transport properties, we used (in collaboration with K. Hayamizu at AIST) pulsed-gradient spin-echo NMR (PGSE-NMR) from the early stages of our studies.\textsuperscript{15,16} We have compared molar conductivity ($\Lambda_{\text{MMK}}$) values calculated from the Nernst-Einstein equation using NMR diffusion coefficients of the cations and anions with the molar conductivity ($\Lambda_{\text{imp}}$) obtained from impedance measurements. The molar conductivity ratio ($\Lambda_{\text{imp}}/\Lambda_{\text{MMK}}$) is defined as the “ionicity” and is considered to reflect the ion-ion interactions and the dissociativity of ILs.\textsuperscript{15,16} The physicochemical meaning of $\Lambda_{\text{imp}}/\Lambda_{\text{MMK}}$ is much clearer compared to that of the conventionally determined ionicity derived from Walden plots, although the Walden plot method is much easier to use.\textsuperscript{17} Angell et al. proposed that a negative deviation of the Walden plot from that of the ideal line for KCl indicates the ionicity, where a small deviation means high ionicity and a large deviation means low ionicity.\textsuperscript{17} ILs having high ionicity are categorized as “good ILs,” whereas those having low ionicity are classed as “poor ILs.”\textsuperscript{17} By using PGSE-NMR, we systematically examined the ionicity of a variety of ILs\textsuperscript{18–25} having different anions with the same cation,\textsuperscript{19} different cations with the same anion,\textsuperscript{22} and different alkyl chain lengths on imidazolium cation with the same anion.\textsuperscript{20} As shown schematically in Fig. 1, it is clear that ionicity is affected by the Lewis basicity of anions, Lewis acidity of cations, and the alkyl chain length attached to cations.\textsuperscript{23,24} The former Lewis basicity/acidity of cation greatly affects the coulombic interactions between the component cations and anions of ILs; the stronger is the Lewis basicity/acidity of anion/cation, the smaller the ionicity becomes due to increasing coulombic interactions. A typical example is NaCl, where the Lewis basicity/acidity of Cl$^-$/Na$^+$ is strong, resulting in a high-melting-point ionic crystal. A wide variety of Lewis basicities of anions results in large differences in the interaction energies of the most stable ion pairs, which is calculated by ab initio calculation in collaboration with T. S. Suzuki at AIST.\textsuperscript{21} The Lewis acidity of the cations of typical ILs does not change as significantly as the Lewis basicity of anions; consequently, the interaction energy of the most stable ion pairs does not greatly change.\textsuperscript{21} Nevertheless, the ionicity of ILs having different cations with the same anion does change to some extent.\textsuperscript{22,23} This behavior can be interpreted as arising from differences in the directionality of ion interactions.\textsuperscript{22} When the interaction energies of an ion pair of an IL change significantly depending on relative position of the cation and anion, the directionality of interactions is considered to be large. ILs composed of aromatic cations, such as imidazolium and pyridinium, have larger interaction directionalsities due to the presence of acidic protons in their structures than those based on aliphatic cations, such as quaternary ammonium and pyrrolidinium.\textsuperscript{21} Surprisingly, ILs based on aromatic cations have lower ionicities than those based on aliphatic cations.\textsuperscript{22} In addition, interestingly, ILs having different alkyl chain lengths on imidazolium cations exhibit lower ionicities with increasing alkyl chain length, as shown in Fig. 2.\textsuperscript{20} Because the density the ILs decreases while their formula weight increases with increasing alkyl chain length, the average distance between the cations and anions increases, reducing the coulombic interactions. Nevertheless, the ionicity decreases with the alkyl chain length. This finding shows that the ionicity of ILs is dominated by the subtle balance between coulombic and molecular interactions (dispersive and induced forces), and the latter interactions dominate over coulombic interactions in determining the ionicity.\textsuperscript{20,23} Such behavior is not observed in inorganic high-temperature molten salts and is characteristic of the nature of organic ionic liquids. Figure 2 also indicates that the ionicity significantly decreases when the number of C atoms in the alkyl chain changes from 2 to 4.\textsuperscript{20} Lopes et al. conducted molecular dynamics simulations of ILs having different alkyl chain lengths on imidazolium cations paired with the same anion. Their results indicated that nanophase separation between the ionic and nonpolar domains occurs.\textsuperscript{20} A sudden decrease in the ionicity concomitantly occurs with phase separation and the formation of a continuous phase of the nonpolar domains.\textsuperscript{20} Heterogeneous dynamics in ILs with alkyl chains is also demonstrated.\textsuperscript{20}

3. Polymer Electrolytes of ILs (Ion Gels)

In parallel with fundamental transport studies of ILs, systematic studies on polymer electrolytes of ILs have also been carried out since we first proposed these in 1993.\textsuperscript{14} Polymer electrolytes of ILs (ion gels) are polymer networks in which ILs are incorporated. In the initial stages of the study, chloroaluminate-based ILs were used,\textsuperscript{14,28} but later, non-chloroaluminate-based ILs\textsuperscript{29–31} were included. Compatibility between ILs and polymers is crucial for the preparation of polymer electrolytes. In this context, we have also conducted fundamental studies on the compatibility and phase behavior of polymers in ILs.\textsuperscript{32} Later, we extended out studies of
polymer electrolytes further to include the combination of task-specific ILs such as protic liquid ions (vide infra) and Li⁺-solvate liquid ions.33

The most striking differences of polymer electrolytes of ILs ("ion gels") from polyether electrolytes are the plasticizing effect of the ILs on the polymers and the decoupling of ion transport from the segmental motion of the polymer, enabling fast ion transport that is close to that of ILs themselves.34 In addition, the useful properties of ILs, non-volatility and thermal stability, are preserved. Figure 3 shows the ionic conductivity at the glass transition temperatures (σ(Tg)) for two polymer electrolytes, poly(methyl methacrylate) (PMMA) network polymers incorporating EMITFSI ([C2mim][N(SO2CF3)2]) and polyether network polymers incorporating LiTFSI ([Li][N(SO2CF3)2]) as a function of salt concentration.35 The decoupling of ion transport from the segmental motion of the polymer matrix can be expressed by using the decoupling index (R), which is defined as:35,36

\[ R = \frac{\tau_s}{\tau_R} \]

where \( \tau_s \) is the structural relaxation time that determines the mechanical properties of the materials and \( \tau_R \) is conduction relaxation time. When \( \tau_s \) is much longer than \( \tau_R \), the material is a decoupled system. The decoupling index, \( R \), can roughly be estimated by the following equation based on universal values of relaxation time or viscosity at \( T_g \):35,36

\[ \log R = 14.3 + \log(\sigma(T_g)) \]

where \( \sigma \) is expressed in S cm⁻¹. This eq. indicates that a positive deviation of (Tg) from 10⁻¹⁴.₅ S cm⁻¹ indicates the decoupling of ion transport from the segmental motion of the polymer. As can be seen from Fig. 3, the value of (Tg) of polyether/LiTFSI is on the order of 10⁻¹⁴ to 10⁻¹¹ S cm⁻¹ and gradually increases with increasing electrolyte concentration, reflecting an increase in the number of carrier ions. In contrast, (Tg) of PMMA/EMITFSI is far higher than 10⁻¹⁴.₅ S cm⁻¹, especially when the IL concentration is relatively low, i.e., the IL itself behaves as a coupled system (the highest concentration in Fig. 3 signifies neat IL). The decoupled nature of the PMMA/EMITFSI ion gel is supported by relatively weak interactions of the cation and anion with PMMA.34,37 This behavior clearly contrasts with that of polyether/LiTFSI, where Li⁺ is strongly coordinated by the polyether chains.

Polymers electrolytes of task-specific ILs have been successfully applied to non-humidified polymer electrolyte fuels cells (vide infra) and lithium polymer batteries.35 Herein, I discuss the application of an ion gel to ion polymer actuators.38-42 As a material for manufacturing polymer actuators with bio-mimetic soft motion, electronic and ion polymer actuators have been proposed and applied to manipulators and robotic devices. Ionic polymer actuators driven by migration or diffusion of ions can achieve relatively large deformations in response to the application of low voltages. However, these actuators suffer from some serious issues; for example, their lack of durability on exposure to the atmosphere due to the evaporation of the solvent that provides an environment for ion transport. To overcome these issues, ILs have been applied as the electrolytes of ionic polymer actuators. In order to prepare the electrolytes, hydrophobic [C2mim][N(SO2CF3)2] is incorporated into the ABA-triblock copolymer polystyrene-b-poly(methyl methacrylate)-b-poly(styrene). These triblock co-polymers are synthesized by successive atom-transfer radical polymerizations (Fig. 4).39 Although polyisoprene is incompatible with [C2mim][N(SO2CF3)2], PMMA is compatible. This difference in compatibility leads [C2mim][N(SO2CF3)2] and PS-b-PMMA-b-PSt to form self-assembled structures, where PSi is phase-separated to form spherical domains that serve as physical crosslinking points, while a continuous PMMA phase containing dissolved [C2mim][N(SO2CF3)2] is formed and serves as an ion conduction pathway. These structures have been observed in atomic force microscope phase images of the ion gels (Fig. 4). Ion gels with high ionic conductivities (>10⁻¹ S cm⁻¹) at room temperature are used as the electrolytes of an ionic polymer actuator, where the ion-gel electrolyte is sandwiched between two composite carbon electrodes containing high-surface-area activated carbon powders. By applying low voltages (<3.0 V) to the electrodes, the actuator exhibited a soft bending motion toward the anodic side. The deformation mechanism is interpreted regarding the differences in cationic and anionic mobilities (transference number) and sizes.40,41 Such differences induce a volume imbalance between the cathode and anode, resulting in a bending motion of the actuators.

4. H⁺-Conducting Protic ILs and Fuel Cells

"Protic ILs" are ILs that have chemically/electrochemically active (reactive) protons. They form a sub-class of ILs and are frequently prepared by proton transfer reactions between Bronsted acids and bases. Early in our IL studies, we applied protic ILs for use as H⁺-conducting electrolytes for non-humidified H2/O2 fuel cells operating at temperatures greater than 100°C based on the expectations that cations having active protons (typically ammonium cations) are highly mobile and electrochemically active for use in fuel cell reactions, i.e., the hydrogen oxidation reaction (HOR) and oxygen reduction reaction (ORR).43,44 In the case of acidic aqueous systems (including polymer electrolyte membrane fuel cells), water molecules act as a base, accepting protons to form hydronium cations (H₃O⁺). H⁺ can be conducted through such media by the migration of H₂O⁺ cations themselves or by proton exchange between H₂O⁺ and H₂O, the so-called vehicle and Grotthuss mechanisms, respectively. Therefore, our idea is based on the simple replacement of H₂O⁺ in acidic aqueous systems by the ammonium cations in protic IL systems.35

Our initial interest in H⁺-conducting electrolytes concerned the transport properties of H⁺ in protic ILs.32-47 At that time, K.-D. Kreuer at the Max Planck Institute for Solid State Research was carrying out pioneering research with non-aqueous proton carriers.48-51 His research focused on the autoprotolysis reactions of neutral species such as imidazole and pyrazole, which form proton defects in the systems and accelerate Grotthuss transport. The remarkable changes in conductivity that occur on changing the composition of systems of imidazole or pyrazole and H₂SO₄ opened a new route to the design of non-aqueous proton conductors.39 This

Figure 3. (Color online) Ionic conductivity at glass transition temperature (σ(Tg)) as a function of salt (EMITFSI or LiTFSI) concentration: EMITFSI = [C2mim][N(SO2CF3)2], LiTFSI = [Li][N(SO2CF3)2]. Redrawn from Ref. 34.
research stimulated us, and we focused on protic ILs. In the binary system of imidazole and \( \text{H}[\text{N(SO}_2\text{CF}_3)\text{]} \), Grothuss transport is remarkable when there is excess imidazole over \( \text{H}[\text{N(SO}_2\text{CF}_3)\text{]} \), which accelerates proton transport in addition to the vehicle transport of imidazolium cations.\(^5^3\) Liquid fuel cells can operate under non-humidified conditions by using electrolytes containing excess imidazole over \( \text{H}[\text{N(SO}_2\text{CF}_3)\text{]} \) and equimolar protic ILs.\(^4^3,4^4\) However, in the base-rich conditions, the thermal stability is disappointingly low due to evaporation of the neutral species.\(^5^3,4^7\)

The thermal stability and electrochemical activity of protic ILs for fuel cell reactions are greatly affected by the chemical structure of protic ILs. The most important factor affecting the thermal stability of protic ILs is the difference in \( p_K_a \) values (\( \Delta p_K_a \)) between the constituent acids and the conjugate acids of the constituent bases.\(^5^2\) Because proton transfer reactions are in equilibrium between the salt and neutral forms and because neutral species are less thermally stable, complete proton transfer is a prerequisite for thermal stability. By using a super-strong organic base and a variety of acids, different protic ILs are formed, where the thermal stability is greatly affected by \( \Delta p_K_a \).\(^5^3,5^4\) Protic ILs with \( \Delta p_K_a > 15 \) are thermally stable, suggesting that proton transfer is complete.\(^5^4\) Interestingly, the ionity of protic ILs is also a function of \( \Delta p_K_a \), increasing with increasing \( \Delta p_K_a \) and leveling off at \( \Delta p_K_a > 15 \).\(^5^4\) The attained ionivities for protic ILs are ca. 0.5, being lower than that of typical aprotic ILs (for examples, see Fig. 2). The lower ionity is due to the hydrogen-bonding interactions between the NH protons and the anions and the directionality of these interactions.\(^5^5\)

The electrochemical activity of protic ILs for fuel cell reactions is complex and is not yet fully understood. Through extensive research, it has been found that diethylmethylammonium trifluoromethanesulfonate ([dem][TIO]) exhibits not only excellent bulk properties as a \( \text{H}^+ \)-conducting IL, i.e., high conductivity, low melting point (\( T_m \)), and high decomposition temperature (\( T_d \)), but also fascinating electrochemical properties (Fig. 5).\(^5^6\) It should be noted that HOR and ORR (especially ORR) at a Pt electrode in [dem][TIO] is facile, and the open circuit potential (OCP) of a liquid fuel cell using [dem][TIO] is greater than 1 V. The OCPs of liquid fuel cells formed using a variety of protic IL show a parabolic dependence, exhibiting a maximum at \( \Delta p_K_a = 17-18 \).\(^5^7\) and a similar parabolic OCP dependence has also been observed by other researchers.\(^5^8\) Determining the relationship between the chemical structure of protic ILs and their bulk and electrochemical properties, especially ORR activity, is of great interest\(^5^9-6^2\) and remains a challenge for the future.

To demonstrate the practical utility of [dem][TIO] as a proton conductor under non-humidified conditions, polymer electrolyte membranes containing [dem][TIO] have been prepared using a sulfonated polyimide (Fig. 6).\(^6^3,6^4,6^5\) The obtained polymer electrolyte membranes are mechanically reliable even at a high doping of [dem][TIO], making it possible to construct polymer electrolyte fuel cells that can operate under non-humidified conditions and at temperatures greater than 100°C.\(^6^4\) The maximum current density and maximum power density of these fuel cells reach 400 mA cm\(^{-2}\) and 150 mW cm\(^{-2}\), respectively, at 120°C under non-humidified conditions.\(^6^5,6^6\) The following reactions may occur in the fuel cell:

Cathode: \( 2\text{BH}^+ + (1/2) \text{O}_2 + 2e^- \rightarrow \text{H}_2\text{O} + 2\text{B} \) (HOR),
Anode: \( 2\text{B} + \text{H}_2 \rightarrow 2\text{BH}^+ + 2e^- \) (ORR).
where B denotes a base (amine). In neat [dema][TfO], proton is transported by the migration/diffusion of the [dema]+ cation (vehicle mechanism)\(^6\) because there are no proton vacant sites due to the complete proton transfer; however, the situation is different when the fuel cell reactions proceed at the electrode/electrolyte interfaces. At the cathode, the free base is continuously generated and is shuttled to the anode to be protonated, regenerating the cation. If this transport occurs by physical diffusion back to the anode, the diffusion time would be so long and the temperature is so high (120°C) that the neutral [dema] would evaporate, resulting in the failure of fuel cell polarization experiments. However, proton exchange reactions between BH\(^+\) and B by Grotthuss transport appear to proceed, and we have succeeded in obtaining evidence for this.\(^6\)

5. Electron-Transporting ILs and Dye-Sensitized Solar Cells

One of the characteristics of ILs is their high ionic concentration (strength) in fluids, which may screen interionic interactions. Consequently, our attention focused on the charge transport of the \(\Gamma^-/I_3^-\) redox couple in ILs because consistent, rapid charge transport with low–volatility electrolytes is necessary for their use in dye-sensitized solar cells (DSSCs).\(^6\) The diffusion coefficients of the \(\Gamma^-/I_3^-\) redox couple in ILs can be estimated using microelectrode technique.\(^8\) As shown in Fig. 7, the diffusivity linearly increases with increasing redox couple concentration; in contrast, in a molecular solvent having a similar viscosity to that of the IL (polyethyleneglycol dimethyl ether, PEGDE), diffusivity does not increase under the same conditions.\(^9\) Such fast charge transport at high redox concentrations is attributed to the exchange reactions of the \(\Gamma^-/I_3^-\) redox couple, as rationalized by the Dahms-Ruff equation. This fast charge transport at high redox concentrations is attributed to the exchange reactions of the \(\Gamma^-/I_3^-\) redox couple, as rationalized by the Dahms-Ruff equation. This fast charge transport is observed in ILs due to the reduction of the interionic repulsion between \(\Gamma^+\) and \(I_3^-\) caused by their high ionic strengths, an effect that cannot occur in molecular liquids.\(^10\) The specific charge transport contributes to the high performance of DSSCs using ILs despite their high viscosities.\(^11,12\) Furthermore, exchange reaction-based high redox diffusivity becomes more pronounced in ionic liquid crystals having a smectic A phase,\(^13,14\) nanoparticle-dispersed IL gels,\(^15\) and polymerized ILs\(^16\) because of a local concentrating effect of \(\Gamma^-/I_3^-\) redox couples. This concentrating effect is due to the nanophase separation between

**Figure 6.** (Color online) Polymer electrolyte membranes consisting of a sulfonated polyimide (SPI) and a protic IL (PIL), [dema][TfO], and their application to polymer electrolyte fuel cells under non-humidified conditions. Polarization measurements were conducted by using dry \(H_2\) and \(O_2\) gases at 120°C.

**Figure 7.** (Color online) Electrochemically measured diffusion coefficients of \(\Gamma^-/I_3^-\) redox couple in EMImTFSI ([C\(_2\)mim][N(SO\(_2\)CF\(_3\))\(_2\)]) increase with an increase in the redox couple concentration and are rationalized by Dahms-Ruff equation, whereas those in PEGE (polyethyleneglycol dimethyl ether) do not change.

\[D_{app} = \frac{D_{max}}{1/6 \ k_\text{ex}\delta^2} + D_{phys}\]

\(\delta^2\) is the concentration of redox couple.
6. Li⁺-Conducting ILs and Solvate ILs

In common with many researchers, we are also interested in ILs for use as electrolytes in lithium batteries. In the initial stages of our studies in this area, two approaches were chosen. One is the synthesis of lithium ILs,87-89 and the second is the addition of suitable lithium salts to aprotic ILs.88-91 For the first approach, room-temperature lithium ILs were successfully synthesized by designing borate anions having both electron-withdrawing groups and oligo(ethylene oxide) groups. The electron-withdrawing groups contribute to the lowering of the Lewis basicity of the anion and the oligo(ethylene oxide) structure contributes to the dissociation of Li⁺ from the anionic center.88-90 This type of molecular design was inspired by that for aluminates carried out by T. Fujinami at Shizuoka University.84 One exciting property of the lithium ILs is that no concentration polarization occurs because they are solvent-free, molten Li⁺-salts, i.e., the electrochemical transference number of Li⁺ during lithium-ion battery operation is unity. However, the lithium ILs have very high viscosities, limiting their transport properties.87-89 For the second approach, by selection of suitable chemical structures for aprotic ILs, the electrochemical window can be increased allowing their use as lithium battery electrolytes. Unfortunately, the addition of lithium salts into ILs significantly increases the viscosity of the mixtures because the strongly Lewis acidic Li⁺ cations require strong coordination by the anions to form bulky ion-multiplets.85-86

Furthermore, the Li⁺-transference number is low due to the presence of at least two different cations (Li⁺ and IL cation) and one anion (the common anion of Li-salt and IL).85-86 The Li⁺-conducting IL electrolytes may improve the safety issue of lithium batteries, but their performance is not good due to poor transport properties.

During our research into ILs for use in lithium batteries, our attention was drawn to the work by Henderson et al. They reported their performance is not good due to poor transport properties.106

Figure 8 shows how the anionic structures of solvate cations and anions, and their electrode reactions interact with lithium ions in solvate ILs.121,122 Figure 8 shows how the anionic structures of solvate ILs are suitable for use as electrolytes in lithium-ion batteries111-112 and lithium-sulfur batteries.115-120

The most striking and significant findings of our research on solvate ILs are the formation criteria of solvate ILs,101 the enhanced oxidation stability of coordinating solvents,102 the low coordinating properties of solvate cations and anions, and their electrode reactions with graphite.121,122 Figure 8 shows how the anionic structures of lithium salts affect the formation of solvate ILs.120 The amount of free glyme, determined by Raman spectroscopy, strongly depends on the anionic structures (Fig. 8(a)). Although these one-to-one mixtures of lithium salts and both G3 (triethylene glycol dimethyl ether) or G4 (tetraethyleneglycol dimethyl ether) are clear colorless liquids, their physicochemical properties greatly depend on the lithium salt species.97 Mixtures containing much free glyme have high vapor pressures, low thermal stabilities, and low ionicities, whereas those containing a trace amount of free glyme have low vapor pressures, high thermal stability, and high ionicities. The amount of free glyme present in the mixture can be rationalized by the magnitude of the Lewis basicity of the anions; the higher the basicity, the greater the amount of free glyme. There are competitive interactions between Li⁺ and the anion or the glyme, and roughly speaking, if the interactions between Li⁺ cations and the anions dominate those between Li⁺ and the glyme, the mixtures cannot form a solvate IL, resulting in a concentrated electrolyte solution containing a substantial amount of free glyme.107,108 On the other hand, if Li⁺ is stabilized by glyme solvation and the anion is interacted with such solvates, the mixtures form solvate ILs containing trace amounts of free glyme.107,108 In particular, this type of behavior occurs in lithium salts with imide-type anions such as [TFSA]- and [BETI]- [Fig. 8(a)].99 This stabilization has also been validated by PGSE-NMR measurements of these mixtures, as shown in Fig. 8(b).79,80 This figure correlates the amount of free glyme in the mixtures and the diffusivity ratios between glyme and Li⁺ (Dglyme/DLi⁺), which is an indicator of the stabilities and lifetimes of the solvate cations ([Li(glyme)]). When the stabilities and lifetimes...
increase, the \(D_{Li}/D_{Li}^+\) ratio approaches unity. Furthermore, as the ratio approaches unity, the amount of free glyme diminishes rapidly.

The oxidative stability of glymes is also enhanced by complexation with alkali metal cations. The electrochemical oxidation of \([Li(glyme)_2][TFSA]\) \([TFSA] = [N(SO_2CF_3)_2]\) takes place at an electrode potential of \(\sim 4.6\) V vs. \(Li/Li^+\), while the oxidation of mixtures containing excess free glymes \([Li(glyme)_x][TFSA], x > 1\) occurs at around 4 V. This increase in oxidative stability is caused by the donation of lone pairs of the ether oxygen atoms to the \(Li^+\) cation, resulting in the lowering in energy of the highest occupied molecular orbital (HOMO) of the coordinating glyme molecule; this energy change has been confirmed by ab initio molecular orbital calculations (Fig. 9). The mechanism of ion conduction mechanism in \([Li(glyme)_x][TFSA]\) solutions has been explored by NMR and electrochemical methods, and the experimental results strongly suggest that \(Li^+\) cation conduction in the equimolar complex occurs by migration of \([Li(glyme)_1]^+\) cations, whereas the ligand exchange mechanism also occurs when interfacial electrochemical reactions of \([Li(glyme)_x]^+\) cations occurs (Fig. 9). The ligand-exchange conduction mode is typically seen in lithium batteries with the configuration \([Li^+ \text{anode} | Li(glyme)_x][TFSA] | LiCoO_2\) cathode] when the discharge reaction of the \(LiCoO_2\) cathode (i.e., de-solvation of \([Li(glyme)_x]^+\) and insertion of the resultant \(Li^+\) into the cathode) occurs at the electrode-electrolyte interface. Due to the increase in the oxidative stability of the glymes and the presence of the ligand-exchange conduction mode, the solvate ILs can be used as battery electrolytes and are compatible with \(4\) V-class cathodes such as \(LiCoO_2\) in the cell voltage range of 3.0–4.2 V. This is true regardless of the use of ether-based electrolytes because the ligand exchange rate is much faster than the electrode reaction rate. The discovery that oxidative stability is increased by the coordination of solvent molecules to \(Li^+\) has inspired many researchers to use concentrated organic and aqueous electrolyte solutions to widen the potential windows and to apply these electrolytes in innovative batteries.

The solvate ILs (glyme–\(Li^+\) salt molten complexes) are excellent electrolyte candidates for \(Li-S\) batteries because they greatly suppress the dissolution of lithium polysulfides. The theoretical capacity of the \(S\) cathode is ten times greater than that of conventional cathode materials used in current \(Li-\)ion batteries. However, \(Li-S\) batteries suffer from the dissolution of lithium polysulfides, which are formed by the redox reactions at the \(S\) cathode. The solvate ILs do not readily dissolve other ionic solutes due to the extremely low coordinating nature of the constituent cations and anions, i.e., because \([Li(glyme)_x]\) and \([TFSA]\) have low Lewis acidity and basicity, respectively. Figure 10 shows the saturation concentrations (atomic concentration of \(S\)) of molecular sulfur \((S_8)\) and \(Li_2S, (x = 1–8)\) in different one-to-one mixtures of lithium salts and glymes. A concentration based on the formula weight of \(Li_2S_x\), for example, is one-eighth of the atomic concentration. It should be noted that the one-to-one mixtures (high concentration of lithium salt) do not always yield low saturated concentrations, which are typically seen in ca. 10 M saturated concentration of \(Li_2S, \text{ in } [Li(G3)][OTf]\). When solvate ILs are formed, as seen in \([Li(G3) or G4)][TFSA]\) and \([Li(G4)][BETI]\), the saturated concentrations of \(Li_2S_x\), especially of \(Li_2S_8\), are reduced by a factor of \(10^2\) to \(10^3\). Such low solubilities lead to the stable operation of \(Li-S\) batteries for more than 400 cycles with discharge capacities higher than 700 mAh g\(^{-1}\) S\(^{-1}\) and coulombic efficiencies higher than 98\% throughout the cycles. Furthermore, the addition of low polar solvents, which do not disrupt the structure of the \([Li(glyme)]\) solvates, greatly enhances the power densities of \(Li-S\) batteries.

Electrochemical \(Li^+\) intercalation into graphite electrodes is solvent-selective, and the formation of a favorable solid electrolyte interphase (SEI) that enables desolvation of \(Li^+\) at the interface and conduction \(Li^+\) in the layer is considered to be essential. A typical example of such an SEI is the product of reductive decomposition of ethylene carbonate, which is one component of typical electrolyte solutions. Interestingly, \(Li^+\) intercalation/deintercalation is electrochemically reversible in the \([Li(G3)][TFSA]\) solvate IL. The

\[G3 = \text{triglyme}\] 
\[\text{HOMO Level}\] 
\[\text{G3} = -11.45\text{ eV}\] 
\[\text{[Li(G3)][TFSA]} = -12.10\text{ eV}\] 

![Figure 9](image_url) (Color online) The most probable structure of \([Li(G3)][TFSA]\) \([TFSA] = [N(SO_2CF_3)_2]\) and the highest occupied molecular orbital (HOMO) energy level lowering of G3 in the probable structure, estimated by ab initio molecular orbital calculations, and schematic representation of ligand exchange conduction mode typically seen when electrochemical reactions occur at the electrode-electrolyte interfaces. Reproduced from Ref. 95 with permission of the American Chemical Society.

![Figure 10](image_url) (Color online) Saturation concentrations (atomic concentration of \(S\)) of molecular sulfur \((S_8)\) and \(Li_2S, (x = 8 - 1)\) in different one-to-one mixtures of lithium salts and glymes. The abbreviations of the anions are the same as those in Fig. 8. Reproduced and redrawn from Ref. 116 with permission of the American Chemical Society.
desolvation of Li$^+$ ions takes place at the graphite/[Li(G3)]$_x$[TFSA] interface in the electrode potential range 0.3–0 V vs. Li.$^{121}$ In contrast, the co-intercalation of G3 and Li$^+$ (intercalation of solvate [Li(G3)]$^+$ cation) into graphite occurs in [Li(G3)]$_x$[TFSA] electrolytes containing excess G3 ($x > 1$) in the potential range 1.5–0.2 V of the [Li/ [Li(G3)]][TFSA] | graphite] cell. Moreover, exfoliation of the graphite occurs on further intercalation.$^{121}$ The success of the electrochemical intercalation/deintercalation can be correlated with the activity the Li$^+$-solvating free solvent, and very low activity of such solvent makes electrochemical intercalation/deintercalation possible.$^{122}$

7. Phase Behavior of Polymers in ILs and Materialization

Our studies on polymer electrolytes of ILs led us to uncover the unique phase behavior of certain polymers in ILs.$^{33,126}$ We reported for the first time the upper critical solution temperature (UCST) phase behavior (low-temperature-insoluble and high-temperature-soluble behavior)$^{127}$ and lower critical solution temperature (LCST) phase behavior (low-temperature-soluble and high-temperature-insoluble behavior)$^{128-134}$ for certain polymers in ILs (Fig. 11). These findings open up the possibility of stimuli-responsive molecular assemblies,$^{135-137}$ volume-phase transitions of ion gels,$^{128}$ and temperature-induced sol/gel transitions$^{138-140}$ in ILs. Recently, stimuli-responsiveness has expanded to include photo-stimuli using photochromic compounds,$^{141-146}$ and photo-healing materials$^{147,148}$ have been proposed.

A soft functional material that can spontaneously repair damage on light illumination is schematically represented in Fig. 12.$^{146,147}$ The ion gel material is composed of an IL, 1-butyl-3-methylimidazolium hexafluorophosphate ([C$_4$mim][PF$_6$], and an ABA triblock copolymer consisting of an IL-compatible poly(ethylene oxide) (PEO) middle block, and UCST and photosensitive random copolymers combining N-isopropylacrylamide (NIPAm) and 4-
phenylazophenyl methacrylate (AzoMA) including the azobenzene chromophore in the terminal A blocks. The material undergoes a gel-to-solid transition with increasing temperature due to the UCST transition of the terminal A blocks. Interestingly, the gel-to-solid transition temperature differs depending on the photochromic states of the azobenzene moieties; the material shows a sol-gel transition under UV light (366 nm) irradiation at 47°C (a cis-rich state), whereas that observed under visible light (437 nm) is 55°C (a trans-rich state). The ABA triblock copolymer undergoes a reversible gel-sol-gel transition cycle at the bistable temperature (53°C), with a reversible association/disassociation of the A blocks resulting from the photoinduced self-assembly change of the ABA triblock copolymer in [C₄mim]PF₆. A damaged ABA ion gel can be healed by irradiation with UV light (366 nm, 64 h), followed by visible light (437 nm, 30 min). The damaged part is fluidized by exposure to UV light, resulting in the filling of the crack. Subsequent exposure to visible light causes gelation, fixing the crack. Stress-strain tests confirm the favorable recovery efficiency of the resultant photohealed ABA ion gel, which reaches values as high as 80% fracture energy relative to that of the original sample. The photo-induced sol-gel transition and the photo-healing property allow not only greater processability and longer lifetimes but also specific functionality imparted by the IL, such as high ionic conductivity, selective gas permeation, and thermal stability.

8. Colloidal Stability in ILs and Materialization

The systematic investigation of colloidal dispersions in ILs is a fascinating research topic. At first glance, ILs do not seem to be suitable solvents for nanoparticles because of their high ionic strengths; however, many studies on nanomaterials in ILs have been reported. We have clarified that colloidal materials (nanoparticles) in ILs are normally unstable and easily aggregate, forming gels due to the network formation of the nanoparticles. However, stable dispersions in ILs can be produced if there are IL-phile structures at the interfaces or strong interactions between the surface of the nanoparticles and either the cation or anion of the IL (Fig. 13). Colloidal gels based on unstable dispersions can be used as quasi-solid electrolytes because even with the addition of a small amount of nanoparticles (see Fig. 13, left photo with 5 wt% addition), the mixture becomes a gel and further addition of nanoparticles (for example, 15 wt% addition) yields dry powders. Up to the addition of 15 wt% nanoparticles, although there is a marked change in appearance, ranging from a liquid to a gel and further to dry powders, the ionic conductivities of the mixtures do not change appreciably and remain close to that of a neat IL. Therefore, the colloidal gels can be used as quasi-solid electrolytes for DSSCs and lithium batteries. On the other hand, stable colloidal dispersions, enabled by grafting a compatible polymer (for example PMMA) to the surfaces of the nanoparticles, become colloidal glasses (gels) at critical concentrations. Interestingly, by choosing a suitable particle size, the colloidal glasses exhibit angular independent structural colors due to the selective reflection of visible light (Fig. 13, right photo). The wavelengths of light of the selective reflection can be controlled and become shorter with increasing particle content in an IL due to the decrease in inter-particle distances. These structural-colored colloidal glasses also exhibit comparable ionic conductivity to that of the corresponding neat IL and are expected to find applications as photo-ionic materials.

9. IL and Nanocarbon Materials

Very recently, we have found that protic ILs/protic salts are good precursors for N-doped carbon materials. Instead of using traditional polymer precursors and complex procedures to prepare N-doped carbons, easily prepared and widely obtainable nitrogen-containing protic ILs/protic salts are used as novel small molecule precursors for the preparation of carbon materials via direct carbonization, without any other treatment. Resulting from a detailed investigation of the relationship between the precursor structures and the resulting carbon materials, it has become possible to prepare N-doped carbons with controllable N content and high surface areas with controllable pore structures with or without the use of hard templates. The resulting N-doped carbons exhibit very interesting properties, such as high O₂ reduction activity, high CO₂ adsorption capability, and high electric double layer capacitance. These low-cost and versatile precursors are promising building blocks for new carbon materials.

10. Conclusion and Outlook

In this review, we have shown that our work on the design and materialization of ILs are based on a deep understanding of their nature, underpinned by electrochemistry, polymer science, and colloid and interfacial science. We proposed that “ionicity” is an excellent metric to describe the nature of ILs. The ionicity is affected by the Lewis acidity/basicity of cations/anions of ILs (i.e.,...
coulombic interactions between cations and anions), the directionality of interactions between ions, and the van der Waals interaction between ions. The most striking difference of ILs from conventional high-temperature inorganic molten salts is that the ionicity of ILs is dominated by the subtle balance between coulombic and van der Waals interactions. We have developed new protic ILs for use as fuel cell electrolytes, new electron transporting ILs for DSSC electrolytes, and Li⁺-conducting solvate ILs for lithium battery electrolytes. ILs can also serve as interesting solvents for polymers and colloidal particles, resulting in the formation of ion gels. The transport of ions in such ion gels is decoupled from the mechanical relaxation time of the materials due to the weak interactions between the ions and the surrounding matrix (polymers and colloidal particles); this results in high ionic conductivity of the gels despite the solid state reliability of the materials. In addition, certain combinations of ILs and polymers undergo interesting phase transitions on temperature change or photo-irradiation. These findings add the possibility of developing stimuli-responsive materials based on ILs and polymers. We have also demonstrated that protic ILs/protic salts are good precursors for N-doped carbons and have the potential to become important building blocks for new carbon materials.

A fundamental understanding of ILs is expected to accelerate the development of new ionic liquids, the establishment of polymer science and colloid and interfacial science in ILs, and the design of new materials and devices, as discussed in this review. We will continue to devote our efforts to the development and understanding of ILs.

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