

Physical Properties of Substituted Imidazolium Based Ionic Liquids Gel Electrolytes

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The physical properties of solid gel electrolytes of either polyvinylidene difluorohexafluoropropylene or a combination of polyvinylidene hexafluoropropylene and polyacrylic acid, and the molten salts 1-ethyl-3-methylimidazolium tetrafluoroborate, 1,2-dimethyl-3-*n*-propylimidazolium tetrafluoroborate, and the new molten salts 1,2-dimethyl-3-*n*-butylimidazolium tetrafluoroborate, and 1,2-dimethyl-3-*n*-butylimidazolium hexafluorophosphate were characterized by temperature dependent ionic conductivity measurements for both the pure molten salt and of the molten salt with 0.5 M Li⁺ present. Ionic conductivity data indicate that for each of the molten salts, the highest concentration of molten salt allowable in a single component polymer gel was 85%, while gels composed of 90% molten salt were possible when using both polyvinylidene hexafluorophosphate and polyacrylic acid. For polymer gel composites prepared using lithium containing ionic liquids, the optimum polymer gel composite consisted of 85% of the 0.5 M Li⁺/ionic liquid, 12.75% polyvinylidene hexafluoropropylene, and 2.25% poly (1-carboxyethylene). The highest ionic conductivity observed was for the gel containing 90% 1-ethyl-3-methyl-imidazolium tetrafluoroborate, 9.08 mS/cm. For the lithium containing ionic liquid gels, their ionic conductivity ranged from 1.45 to 0.05 mS/cm, which is comparable to the value of 0.91 mS/cm, observed for polymer composite gels containing 0.5 M LiBF₄ in propylene carbonate.

Key words: Ionic Liquid; Polymer; Electrolyte; Lithium; Composites.

Introduction

The physical and electrochemical properties of air stable 1,3-dialkyl imidazolium based room-temperature molten salts have been extensively studied for their application as electrolytes for batteries and capacitors [1 - 4]. These ionic liquids possess several properties which make them attractive alternatives to traditional nonaqueous electrolytes. Chief among these are their non-volatility, non-flammability, and high thermal and electrochemical stability [5].

The alkyl imidazolium based ionic liquids have been investigated as possible electrolytes for lithium and lithium ion cells [6, 7]. Recently, work in our laboratory has shown that several of these alkyl imidazolium ionic liquids are capable of dissolving up to molar concentrations of lithium salts and functioning as the electrolytic material in a lithium ion cell [8]. Although an increase in viscosity is associated with

increasing amounts of lithium ions in these systems, it was shown that this was not prohibitive in terms of their overall ionic conductivity, which remained comparable to lithium salts in propylene carbonate. Additionally, the 1,3 dialkyl imidazolium ionic liquids have been investigated as a component in a unique battery concept that utilizes the cations and anions of these ionic liquids as the electrochemical intercalates into layered graphitic electrodes. This Dual Intercalating Molten Electrolyte (DIME) battery, while not as energetic as lithium based systems, is an extremely simple and robust design, and it is the subject of continued study [9, 10].

Recently, Fuller and Carlin have demonstrated that stable solid gel electrolytes and membranes can be formed by the addition of a polymer, polyvinylidene hexafluoropropylene (PVdF-HFP), to 1,3-dialkylimidazolium ionic liquids [11 - 13]. These solid gel electrolytes have the potential to provide the

structural and stability advantages of a polymer with the ionic conductivity approaching that of the pure molten salt. However, current preparation methods limit the conductivity of these gels due to the relatively high content of non-conducting polymer. In addition, the two cationic species previously studied in these ionic liquid gels, 1-ethyl-3-methylimidazolium, EMI^+ , and 1-butyl-3-methylimidazolium, BMI^+ , have limited electrochemical stability in the presence of active metal anodes such as sodium and lithium metal [14 - 16]. It has been proposed that this instability is largely due to the presence of an acidic proton at the C-2 position on the imidazolium ring [7, 9], and it has been shown that the substitution of a methyl group for the proton at the C-2 position can increase the electrochemical stability of the imidazolium cation by over 0.25 V [7].

In this work we present an alternate method for preparing polymer ionic liquid gel electrolytes that significantly reduces the total polymer content of the gel. In addition we investigate the behavior of more electrochemically stable ionic liquids utilizing four different ionic liquids: 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIBF_4), 1,2-dimethyl-3-*n*-propylimidazolium tetrafluoroborate (DMPIBF_4), 1,2-dimethyl-3-*n*-butylimidazolium tetrafluoroborate (DMBIBF_4) and 1,2-dimethyl-3-*n*-butylimidazolium hexafluorophosphate (DMBIPF_6). These molten salts are inherently much more stable in air relative to the metal halide anion based salts (i. e., DMPIAlCl_4), since exposure to air does not lead to hydrolysis of the tetrafluoroborate or hexafluorophosphate anion [17]. These two anions are also known to readily intercalate graphite [18], thus making them an ideal choice as the cathodic intercalative species. EMIBF_4 , DMPIBF_4 and DMBIBF_4 have been shown to possess high thermal and electrochemical stability, while the last exhibits high hydrophobicity in a manner similar to BMIPF_6 . Additionally, since any real life use of these electrolytes will need to be done in the presence of Li^+ , solid polymer gel electrolytes were prepared from a solution of lithium salts dissolved in the aforementioned ionic liquids.

Experimental

Preparation of the Initial Salts: EMICl, DMPICl, and DMBICl

1-ethyl-3-methylimidazolium chloride (EMICl) was prepared as previously reported [18]. The prepa-

ration of 1,2-dimethyl-3-*n*-butylimidazolium chloride (DMBICl) and the 1,2-dimethyl-3-*n*-propylimidazolium chloride (DMPICl) involved the direct reaction of 1,2-dimethylimidazole (Aldrich, 98%) and the appropriate 1-chloroalkane in a 1:1.15 molar ratio.

The 1,2-dimethylimidazole (m. p. 38 °C) was vacuum distilled (10^{-3} torr) at ca. 135 °C prior to use. The purified 1,2-dimethylimidazole was re-melted at 50 °C in an inert atmosphere dry-box (O_2 and H_2O < 1 ppm). 500 g were then poured into a 2 l thick-walled, single neck round bottom flask. To this was added a 15% molar excess of the appropriate 1-chloroalkane (1-chlorobutane, 99% Aldrich, for DMBICl , and 1-chloropropane, 99% Aldrich, for DMPICl) and 50 ml of dry acetonitrile. The addition of the acetonitrile served to keep the product in solution as the reaction proceeded. The round bottom flask was then removed from the dry-box and fitted with a reflux condenser. The solution was degassed several times with dry nitrogen, gradually heated to 60 °C for the DMPICl reaction or 95 °C for the DMBICl reaction, and allowed to reflux for 7 days under nitrogen pressure. Cooling the solution produced a white precipitate (product) and a very faint, yellow supernatant. 300 ml of ethyl acetate was added to the round bottom flask to precipitate the remaining substituted imidazolium chloride salt. The material was filtered and washed with five 100 ml washings of ethyl acetate in order to remove all of the unreacted 1,2-dimethyl imidazole. The precipitate was dissolved in a minimum amount of hot acetonitrile and quickly crashed out of solution by the addition of a large excess of ethyl acetate. It was found that slow recrystallization resulted in the formation of slightly yellowed crystals. For both DMPICl and DMBICl , the product was a white crystalline material. Finally, the substituted imidazolium chlorides were heated to 100 °C under an active vacuum (10^{-3} torr) for 2 days to remove volatile contaminants. The final product yield was normally in the range of 80%.

Preparation of the BF_4 and PF_6 Salts

The preparation of EMIBF_4 , DMPIBF_4 , and DMBIBF_4 was done by a direct anion exchange reaction of the respective chloride salt with NH_4BF_4 (Aldrich, 99.98%) in acetonitrile [12]. The preparation of DMBIPF_6 used NH_4PF_6 (Aldrich 99.98%) at identical reaction conditions. For each molten salt, this reaction step was performed in a dry-box in order

to limit the possible inclusion of water into the final product. For a typical reaction, one mole of the substituted imidazolium chloride salt was placed in a 1-liter reaction flask fitted with a threaded Teflon plug and dissolved in a minimum amount of acetonitrile. To this solution, a 5% molar excess of the appropriate ammonium salt was added. The flask was sealed and allowed to stir at room temperature for 7 days, after which the flasks were removed from the dry-box for the last purification steps.

Upon completion of the anion exchange, the resulting solid material (NH_4Cl and the unreacted initial ammonium salt) was removed by vacuum filtration using a glass frit of medium pore size. Subsequently, 30 g of decolorizing carbon (Aldrich) and 30 g of neutral alumina (Aldrich) were added to the remaining molten salt / acetonitrile solution and allowed to stir at room temperature in the sealed reaction flask for two days. The carbon black and Alumina were then removed by successive filtration. Prior to the final filtration, the solution volume was reduced by half using a rotovap. The solution was then diluted back to its original volume by addition of dry acetone. This was found to help precipitate the last remaining ammonium salts still in solution. These ionic liquid / acetonitrile / acetone solutions were then filtered through a medium pore size glass frit, a 1 μ filter disc (Whatman, PTFE Membrane), and a 0.45 μ filter disc (Whatman, PTFE Membrane). The molten salt solutions were heated to 85 °C under an active vacuum (10^{-3} torr) for 1 day to remove volatile contaminants. The resulting ionic liquids were clear and colorless.

Preparation of the 0.5 M LiX Solutions

Lithium ion was added to the ionic liquids as LiBF_4 (Aldrich, 99.999%) for the tetrafluoroborate based ionic liquids, and as LiPF_6 (Aldrich, 99.999%) for the DMBIPF₆ molten salt. For comparison, the LiBF_4 salt was directly dissolved into propylene carbonate (PC) (Aldrich 99.5%). For propylene carbonate, EMIBF₄, DMPiBF₄, and DMBiBF₄, the lithium salt readily dissolved into solution (50 ml of liquid and 2.344 g LiBF_4) with only minor heating to accelerate the dissolution. For DMBIPF₆, the addition of 0.5 M LiPF_6 resulted initially in the formation of an extremely viscous mixture. After two days of stirring and heating at 60 °C, the LiPF_6 completely dissolved producing a clear viscous liquid. It is important to note that in both the pure and lithium containing form, the DMBIPF₆

molten salt exhibited a tendency to solidify at temperatures near 20 °C.

Preparation of the Polymer Gel Electrolytes

The methods employed to prepare polymer gel electrolytes were modifications of the originally published procedures [11, 12]. The most significant change from the past work was the application of sonication, via a sonication horn (Sonics and Materials Vibracell), in our procedure to accelerate and enhance mixing. This simple change allowed us to prepare stable single polymer gel electrolytes with as little as 15% versus 33% polymer for the previously published work. (Note that all percentages reported in this manuscript are percent by mass.)

Polymer Gel Electrolytes containing a single polymer component were prepared using poly-vinylidene difluoride hexafluoropropylene (PVdF-HFP, Kynar -2801-00, Elf Atochem), 4-methyl-2-pentanone (MP, 98%, Aldrich) as the solvent, and the appropriate ionic liquid. For each gel prepared, a ratio of 20 ml of MP per 1 g of PVdF-HFP was used. Each specific % composition was prepared by placing the correct amount of polymer and ionic liquid in a 30 ml sample vial, and then adding the appropriate amount of MP. This mixture was sonicated for 1 minute at high power, allowed to cool, and then resonicated for one minute. Sonication was continued, with intermittent pauses to allow for sample cooling, until there was a marked drop off in the sound of cavitation produced. This drop off in sound was taken as the point where the polymer was fully flocculated into solution. The sample was removed from the sonicator and allowed to stir at 60 °C under flowing N_2 until the composite mixture became extremely viscous. The sample was removed from the heat, poured into a 6.35 cm diameter aluminum weighing boat and cured at room temperature for 24 h under flowing dry N_2 . The samples were then dried in a vacuum oven for an additional 24 h under an active vacuum (approximately 10^{-3} torr) at 60 °C.

Polymer ionic liquid gel electrolytes containing two polymer components were prepared by the addition of poly-acrylic acid (PAA, GC Thorsen) to the PVdF-HFP. The procedure used to prepare the dual polymer ionic liquid gels was identical to that described above with the exception of the addition of the PAA. In order for the PAA to be readily miscible with the other gel components it was first diluted 3 to 1 with MP.

For polymer gels using the lithium ion containing ionic liquids, it was also found that a dual polymer gel composition allowed for the maximum amount of ionic liquid to be present in a stable gel. However, due to the highly ionic nature of the lithium containing ionic liquid, the best gel contained only 85% 0.5 M Li⁺ molten salt, 12.75% PVdF-HFP, and 2.25% PAA. The most significant difficulty in preparing these gels was the tendency of the polymer gel solution to separate into two layers, one of which contained the MP and the polymers, and the other containing the 0.5 M Li⁺/ionic liquid. Several techniques were used to overcome this problem, the simplest being to remove nearly all of the MP before pouring the gels into the Al pans. Other techniques involved the addition of 5 ml of either acetonitrile or acetone, both of which aided in the prevention of layer formation. Thus, these gels were able to be prepared in the same manner as the gels containing pure ionic liquid, although care had to be taken in order to prevent this separation from taking place.

Finally, preparation of the 0.5 M LiBF₄ in a PC gel followed the above procedure. However, due to the volatility of the propylene carbonate, the samples were removed from the heat, poured into a 6.35 cm diameter aluminum weighing boat and cured at room temperature for 24 h in a dry box under flowing N₂. The samples were dried in a vacuum oven for an additional 2 h (as opposed to 24 h for gels of the ionic liquids) under an active vacuum (approximately 10⁻³ torr) at 50 °C. After this drying, the PC gels remained somewhat flexible, although a faint odor of MP was detectable. Typical gels prepared by the above procedures were clear to slightly opaque in appearance. The thickness of all ionic liquid gels ranged between 1 - 2 mm.

Impedance Measurements

Temperature dependent impedance measurements were made with a Solitron SI 1260 Gain Phase Analyzer at frequencies from 100 kHz to 1 Hz, using an AC amplitude of 5 mV. The impedance of the ionic liquids and the ionic liquid gels were measured in the same impedance cell (Figure 1). The cell was made from a 2" diameter Teflon bar with a 1/2" hole drilled through the center for the sample. A 1/8" diameter hole for the thermocouple was drilled 2 mm from and parallel to the 1/2" hole. The sample was situated between two 1/2" diameter Al rods, each capped with

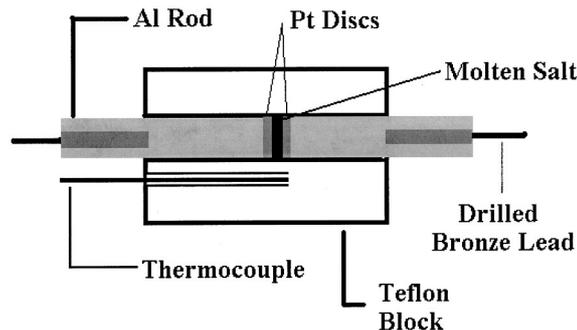


Fig. 1. Schematic drawing of Impedance Cell.

a platinum disc, inside this Teflon cell. Note that for the lithiated samples, the Teflon cell was loaded in the dry box, but removed for the impedance measurements since the sealed Teflon cell would allow only minimal exposure to air. Compressing the two Al rods in a microbar clamp completed the cell. It should be noted that when subjected to significant pressure some ionic liquid has been observed to seep out of the gels. This is most commonly observed in the low polymer content gels. However, this property helps improve the connectivity between the gel and the electrodes pressed against it by wetting the surface with a thin film of molten salt. The thickness of the sample could be calculated by caliper-measurements of the end-to-end length of the Al rods. This Teflon sample holder was wrapped in Pyrex wool, Al foil, and placed into a well shaped, 500 ml capped heating mantle. The mantle was attached to a calibrated temperature controller. The temperature equilibration time for each data point was ten minutes prior to measurements. The ionic conductivity (κ) was calculated from the measured resistance when the imaginary component at high frequency fell to zero [19].

Result and Discussion

Ionic Conductivity of Pure Ionic Liquids

The temperature dependent ionic conductivity data as derived from the electrochemical impedance measurements for the pure molten salts are shown in Figure 2. The data agree well with those previously reported [4, 12]. Glass forming liquids like the ionic liquids are not expected to follow strict Arrhenius behavior [20]. However, over the relatively narrow temperature range studied, the plots of $\ln(\kappa)$ vs. $T^{-1}(\text{K}^{-1})$ for all the ionic liquids studied are essentially linear.

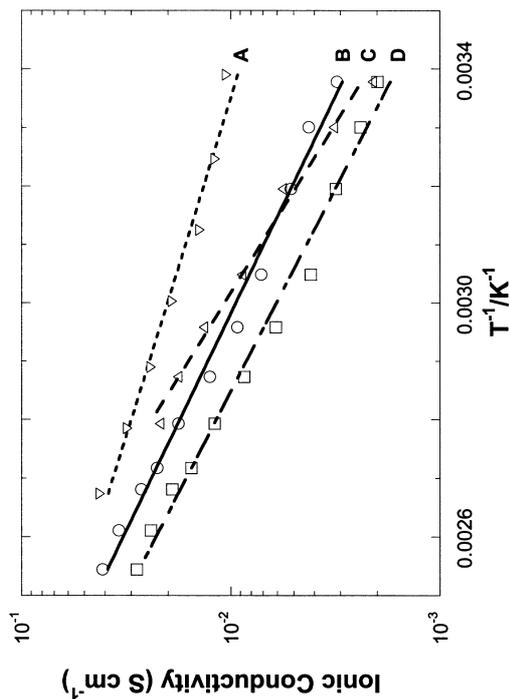


Fig. 4. Effect of lithium ion on the temperature dependent conductivity: (A) 100% EMIBF₄; (B) 0.5 M LiBF₄ in EMIBF₄; (C) 0.5 M LiBF₄ in propylene carbonate; (D) 0.5 M LiBF₄ in DMPPIBF₄.

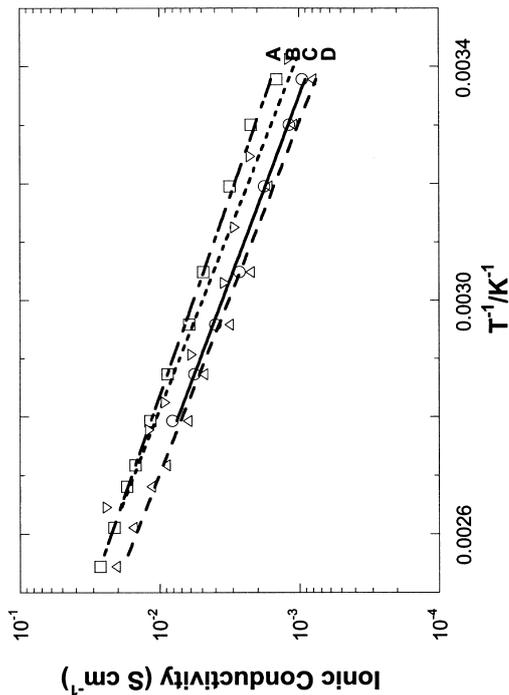


Fig. 6. Effect of 0.5 M LiBF₄ on the temperature dependent conductivity of dual polymer gel electrolytes; 2.25% PAA/12.75% PVdF-HFP/85% Molten Salt or Propylene Carbonate: (A) 85% DMPPIBF₄, no LiBF₄; (B) 85% LiBF₄/EMIBF₄; (C) 85% LiBF₄/propylene carbonate; (D) 85% LiBF₄/DMPPIBF₄.

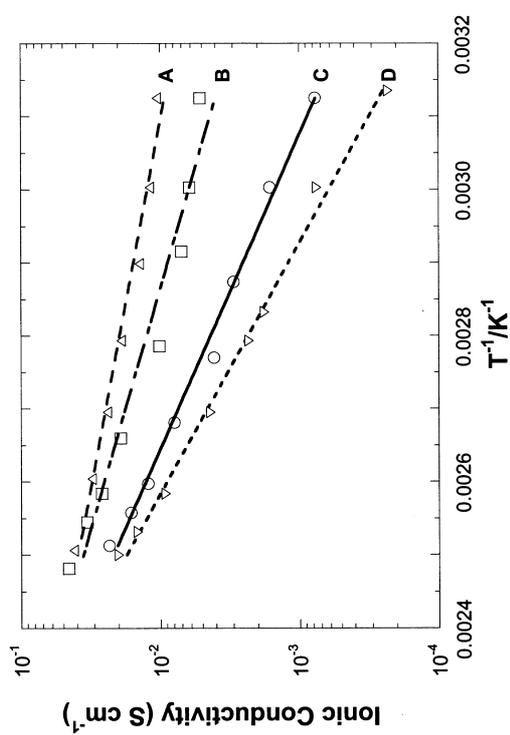


Fig. 2. Effect of ionic liquid composition on the temperature dependent conductivity: (A) EMIBF₄; (B) DMBIPF₄; (C) DMBIPF₄; (D) DMBIPF₄.

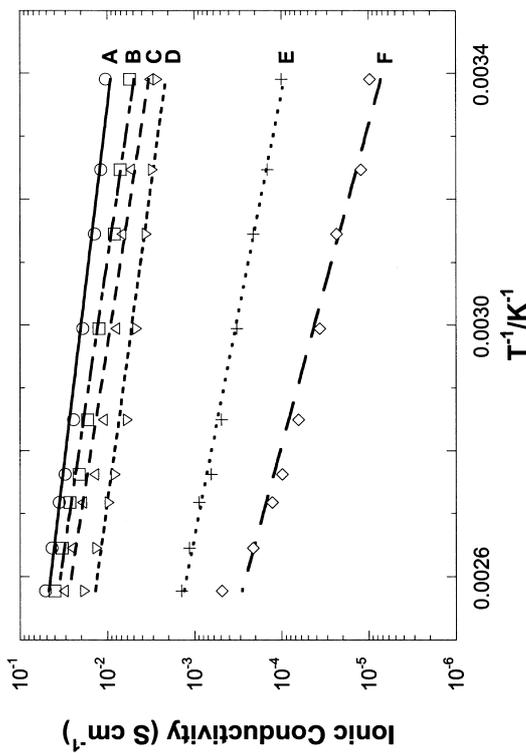


Fig. 3. Effect of molten salt content on the temperature dependent conductivity of PVdF(HFP)-EMIBF₄ gel electrolytes: (A) pure EMIBF₄; (B) 85% EMIBF₄; (C) 80% EMIBF₄; (D) 75% EMIBF₄; (E) 65% EMIBF₄; (F) 50% EMIBF₄.

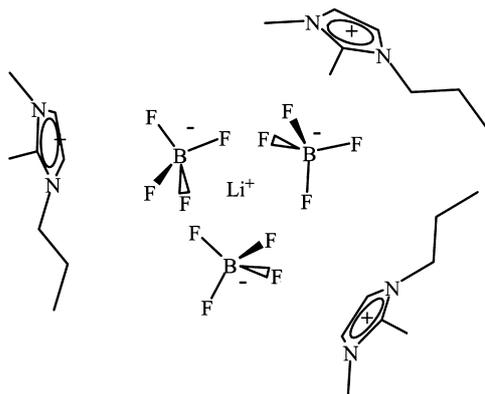


Fig. 5. Schematic Molecular Drawing indicating the increasing order of the ionic liquids when Li^+ is present.

The Arrhenius fit of the data in Fig. 2 gives activation energies of 19.2 kJ/mol, 29.2 kJ/mol, 44.5 kJ/mol, and 55.7 kJ/mol for the conductivities of EMIBF₄, DMPiBF₄, DMBiPF₆, and DMBiBF₄, respectively. The trend in activation energies is consistent with the apparent viscosities of the ionic liquids, EMIBF₄ being the least viscous and DMBiBF₄ the most one. Interestingly, DMBiPF₆ has a lower activation energy and higher conductivity than DMBiBF₄, although it has the larger anion.

Single Polymer Gel Electrolytes

The effect of the ionic liquid to polymer ratio was investigated for the single polymer gels. For each of the four ionic liquids studied (EMIBF₄, DMPiBF₄, DMBiBF₄, and DMBiPF₆), a series of gels was prepared using the formula (x)% Ionic Liquid to $(100 - x)$ % PVdF-HFP, where $x = 50, 35, 25, 20, 15, 10,$ and 5 . In all cases, gels with less than 15 weight percent PVdF-HFP failed to form stable solids. Figure 3 shows representative $\ln(\kappa)$ vs. T^{-1} (K^{-1}) curves for the series of single polymer gels prepared with EMIBF₄. (Similar results were obtained for the other single polymer ionic liquid gels.) For comparison Fig. 3 also shows the data for pure EMIBF₄. These data clearly show the dramatic effect of polymer content on the gel conductivity. For example, the gel containing 50% polymer content has a room temperature conductivity more than three orders of magnitude less than that of the pure EMIBF₄, $9.8 \cdot 10^{-6}$ S/cm versus $1.1 \cdot 10^{-2}$ S/cm. When the polymer content is reduced to 15%, the room temperature conductivity of the gel increases to $5.5 \cdot 10^{-3}$ S/cm; 50% of the value for the

the pure EMIBF₄. More importantly this difference in conductivity between the 85% ionic liquid gel and the pure EMIBF₄ decreases with increasing temperature. At 378 K the 85% ionic liquid gel has 78% of the conductivity of the pure EMIBF₄.

The Arrhenius fits of the data in Fig. 3 gives activation energies of 19.2, 20.5, 21.0, 19.1, 27.1, and 37.5 kJ/mol for the conductivities of 100%, 85%, 80%, 75%, 65%, and 50% EMIBF₄, respectively. The activation energy for conduction of EMIBF₄ is essentially unchanged in the single polymer gel down to the 75% ionic liquid. This indicates that the movement of EMIBF₄ in the gels is unimpeded by the polymer up to a certain threshold composition, and that the observed decrease in conductivity appears to be due to the decrease in concentration of ionic species as the polymer content of the gels increases.

Dual Polymer Gel Electrolytes

In an effort to further reduce the total polymer content of our ionic liquid gels, we investigated the addition of a second polymer component, polyacrylic acid (PAA, GC Thorsen). PAA is a highly crosslinked polymer that we hoped would enhance the structural properties of our gels and thus allow us to reduce the total amount of polymer needed. Initial experiments centered around determining the most favorable ratio of PVdF-HFP to PAA. This was done by maintaining the ionic liquid weight percent constant and varying the relative percentages of the two polymer components. From these experiments we found that a 8.5 : 1.5 ratio of PVdF-HFP to PAA gave the gels with the best physical and mechanical properties. Gels with amounts of PAA greater than 1.5% failed to form cohesive composites, most likely due to excessive shrinkage upon curing. Next we investigated the effect of the weight percent of the ionic liquid on the conductivity of the dual polymer gels. Table 1 shows representative data for neat DMPiBF₄ and a series of dual polymer gels. (Similar results were obtained for the other ionic liquids gels studied.) As can be seen in Table 1, we were able to prepare stable gels with up to 90% ionic liquid. As with the single polymer gels, the conductivity of the dual polymer gels improves as the total polymer content decreases. In the case the 90% dual polymer gel, the room temperature conductivity is 77% that of neat DMPiBF₄, and the conductivity at 378 K is 85% that of neat DMPiBF₄. In general, the data for the dual polymer systems exhibited more

Table 1. Conductivity Data for neat DMPiBF₄ and DMPiBF₄ Dual Polymer Gels. The total polymer content was 10%. The Ratio of PVdF-HFP was fixed at 8.5 : 1.5.

Percent ionic liquid	κ (mS/cm), 295 K	κ (mS/cm), κ (mS/cm),	$E_a(\kappa)$, kJ/mol
100%	5.16	45.7	29.2
90%	3.96	38.8	25.1
85%	1.18	23.9	31.3
80%	0.85	10.1	28.8

curved behavior on the $\ln(\kappa)$ vs. T^{-1} (K⁻¹) plots than the single polymer gels. However, attempts to fit these data to other conductivity relationships (e. g., VTF, WLF) failed to produce a more satisfactory result than the simple Arrhenius fit. Consequently, the activation energies generated for these data have a significantly greater error than those generated for the pure ionic liquids and the single polymer gels. However, the data are reasonably self consistent, and these fits can be used to look for noticeable trends. As in the case of the single polymer gels, the activation energies for the dual polymer gels shown in Table 1 remain essentially unchanged as the total polymer content is increased. This again indicates that the polymer component of the gel is not hindering the movement in the ionic liquid.

Ionic Liquids and Gels Containing Lithium Ion

Figure 4 shows the temperature dependent conductivity data for EMiBF₄, DMPiBF₄, and PC containing 0.5 M Li⁺. For comparison purposes, the conductivity data for pure EMiBF₄ are also shown. The conductivity of the lithium ion containing ionic liquids and PC are clearly comparable. However, the PC solution exhibits a stronger temperature dependence than the ionic liquids. The Arrhenius fits of the data in Fig. 4 give activation energies of 19.2, 25.8, 33.1, and 27.8 kJ/mol for the conductivities of pure EMiBF₄, and EMiBF₄, PC, and DMPiBF₄ containing 0.5 M Li⁺, respectively. The data in Fig. 4 clearly demonstrate the significant decrease in conductivity of the ionic liquids upon addition of lithium ion. This loss in conductivity is also accompanied by a noticeable increase in ionic liquid viscosity. These observations, coupled with the observed increase in activation energy for conduction, clearly point to stronger intermolecular interactions in the lithium ion containing melts. The increase in viscosity and resulting decrease in conductivity upon addition of lithium ion to the

ionic liquids has been attributed to the formation of local structure in the ionic liquids due to cation trapping of the small lithium ions [21]. This is shown schematically in Figure 5.

Interestingly, the addition of lithium ion to the ionic liquid gels does not appear to have as significant an impact on the observed physical and chemical properties as it does on the liquid systems. Figure 6 shows the temperature dependent conductivity data for a series of dual polymer gel electrolytes containing 0.5 M Li⁺. This figure clearly illustrates one significant point: The dual polymer ionic liquid gel electrolytes possess ionic conductivities similar to, or better than that observed for a PC based gel. The Arrhenius fits of the data in Fig. 6 give activation energies of 31.3, 28.2, 30.2, and 31.8 kJ/mol for the conductivities of dual polymer gels containing 85% DMPiBF₄, and 85% EMiBF₄, 85% PC, and 85% DMPiBF₄ that were 0.5 M Li⁺, respectively. The differences observed for the lithium ion containing ionic liquids versus the dual polymer gels may indicate some role of the polymer component in restricting the structure formation of the lithium ion.

Conclusion

By using alternate preparation techniques involving sonication, and by addition of a polyacrylic acid, we have demonstrated that it is possible to prepare polymer ionic liquid gel electrolytes of various ionic liquids both with and without lithium. This new preparation enables a significant increase in the amount of molten salt that can be directly incorporated into a polymer composite, allowing for improved physical and electrochemical properties. The high ionic conductivities exhibited by the dual polymer gel electrolytes clearly make the case that these composite electrolytes perform nearly as well as, or in the case of the EMiBF₄ polymer gels, better than, gels prepared from the common nonaqueous electrolyte, propylene carbonate. Activation energy data indicate that the movement of ions in the polymer ionic liquid gel electrolytes is unhindered by the presence of the polymer up a certain threshold polymer content (ca. 25 %). The addition of lithium ion to the ionic liquids results in significant increase in viscosity and corresponding decrease in conductivity. The effect of lithium ion addition on the ionic liquid polymer gel electrolytes is less dramatic and may indicate some role of the polymer in minimizing the structure forming ability

of the lithium cation. Future work will continue to investigate the utility of these novel gel electrolytes as

electrolytes for lithium batteries, as well as the more simple DIME battery systems.

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