



## Incorporating Ionic Liquid Electrolytes into Polymer Gels for Solid-State Ultracapacitors

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Electrolytes are an important component in determining the performance and cycle life of ultracapacitors. Good electrolytes should have high ionic conductivity, large electrochemical windows, and excellent thermal and chemical stability. Ionic liquids are possibly ideal electrolytes to satisfy these requirements. In the present work, we developed easy-to-use methods to incorporate ionic liquids into a polymer matrix to synthesize gel polymer electrolytes (GPEs). Combining the advantages of both the ionic liquids and the conventional GPEs, the resultant solid-state ionic liquid-incorporated gel polymer electrolytes (ILGPEs) possess better properties than these two components considered individually. Our synthesized ILGPE films are flexible and mechanically strong and have a wide electrochemical window of 4 V, a high ionic conductivity up to 3.5 mS/cm (at room temperature), and a high thermal stability up to 350°C. These ILGPEs have been used to fabricate solid-state ultracapacitors that demonstrate improved performance and cycle life.

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Ultracapacitors (also known as electrochemical capacitors or supercapacitors) are energy storage devices that combine the high energy density of conventional batteries with the high power density of conventional capacitors. Able to store higher energy than conventional capacitors and achieve higher power and longer cycle life than batteries,<sup>1,2</sup> ultracapacitors have been developed to provide peak power pulses for a range of applications such as transportation technology [e.g., hybrid electric vehicles (HEVs)], consumer electronics (e.g., laptops), medical electronics (e.g., portable defibrillators), and military/defense (e.g., missile systems). However, a major obstacle to the application of ultracapacitors to these end-uses is their limited performance, stability, operating windows, and short lifetimes, which are strongly determined by the properties of the currently available aqueous (e.g., H<sub>2</sub>SO<sub>4</sub>, KOH) and organic (e.g., acetonitrile, propylene carbonate) electrolytes.<sup>3</sup> The narrow electrochemical windows (~1.2 V), which are an intrinsic characteristic of aqueous electrolytes, often lead to a small cell voltage and hence low energy/power densities for the ultracapacitor.<sup>2</sup> Organic electrolytes have relatively larger electrochemical windows (2–3 V); however, to develop high-performance ultracapacitors, these electrochemical windows are still limited. In addition, organic electrolytes suffer from serious health and safety problems as they are volatile, flammable, and can be toxic.<sup>4</sup> Ultracapacitors incorporating organic electrolytes can safely work within a rather narrow temperature range and have the potential to explode under certain circumstances (e.g., during car accidents).

Some of the problems of liquid electrolytes discussed above can be overcome by solid-state gel polymer electrolytes (GPEs). Replacing liquid electrolytes with GPEs follows a trend in the commercialization activities of energy storage devices including batteries<sup>5</sup> and ultracapacitors.<sup>6</sup> It has been widely realized that GPEs possess some distinct advantages over their liquid electrolyte counterparts, such as reduced reactivity, reduced leakage, improved safety, better shape flexibility, and better manufacturing integrity. A GPE is usually made from three essential components, a polymer, a salt, and a solvent (or binary/ternary solvent system). Solvents (acting as plasticizers) are usually low-molecular-weight polyethers or other polar organic liquids. It is known that evaporative properties of the organic solvents limit the thermal stability range of GPEs.<sup>7</sup> Moreover, it is believed that the relatively narrow electrochemical windows of these organic solvents are responsible for the electrochemical instability of the resulting GPEs.<sup>8</sup> Therefore, nonvolatile solvents with wider electrochemical windows are sought to fabricate stable GPEs.

Having high ionic conductivity, large electrochemical windows, excellent thermal stability, nonvolatility, nonflammability, and non-toxicity, ionic liquids have been demonstrated to be advantageous as electrolytes for ultracapacitor applications.<sup>9,10</sup> Research on the use of ionic liquid electrolytes in the development of carbon<sup>11,12</sup> and electroactive polymer<sup>13,14</sup>-based ultracapacitors has been reported. These indicate improved performance figures-of-merit and especially longer cycle life, which have been attributed to the unique properties of ionic liquids compared with conventional electrolyte systems. More recently, the development of ionic-liquid-based GPEs has also attracted considerable attention.<sup>12,15,16</sup>

In the present work, we investigated simple approaches of incorporating ionic liquids into polymer matrices to develop solid-state ionic-liquid-incorporated gel polymer electrolytes (ILGPEs). Combining the advantages of both ionic liquids and conventional GPEs, the resulting ILGPEs possess better properties than either component individually. In an ILGPE, the ionic liquid serves as both the solvent and the plasticizer without the addition of any unstable organic solvents/plasticizers, thus promising enhanced stability for ILGPEs. We synthesized free-standing ILGPE films that are flexible and mechanically strong and have a wide electrochemical window up to 4 V, a high ionic conductivity up to 3.5 mS/cm (at room temperature), and a high thermal stability up to 350°C. These ILGPEs have been used to fabricate ultracapacitors with improved performance and cycle life.

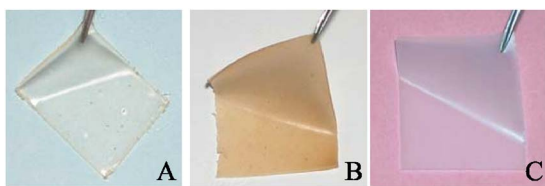
### Experimental

All capacitors were fabricated from carbon/aluminum electrode assemblies provided by W. L. Gore and Associates, Inc. consisting of an activated carbon layer (thickness: ~100 μm, carbon loading or basis weight: 6 mg/cm<sup>2</sup>, and specific surface area: ~2000 m<sup>2</sup>/g) attached onto an aluminum foil current collector. All electrochemical measurements (cyclic voltammetry, ac impedance spectroscopy, and galvanostatic charge/discharge) were performed using an Eco-Chemie Autolab PGSTAT 30 potentiostat. Unless otherwise stated, capacitor performance was based on the mass of the active material (carbon) of the capacitors' electrodes.

*Selection of ionic liquids.*— A range of ionic liquids purchased from Covalent Associates, Inc., Merck, and Sigma-Aldrich were subjected to capacitor performance evaluation using a simple capacitor configuration. Each capacitor consisted of a silicon rubber spacer (thickness: 1 mm, cut-out area: 1.5 × 1.5 cm) sandwiched between two carbon electrodes. Each of the candidate ionic liquids was injected into the capacitor. For comparison purposes, a capacitor using 1 M Et<sub>4</sub>NBF<sub>4</sub>/acetonitrile electrolyte was also fabricated

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**Figure 1.** (Color online) Photographs of ILGPEs prepared by different methods: (A) PVdF-HFP/[EMIM][Tf<sub>2</sub>N] by ionic-liquid-polymer gelation method, (B) PVdF-HFP/[EMIM][Tf<sub>2</sub>N]/zeolite by ionic-liquid-inorganic-polymer composite method, and (C) PTFE/[EMIM][Tf<sub>2</sub>N] by ionic-liquid-polymer membrane method.

and tested. Cyclic voltammetry was used to determine maximum cell voltage, and galvanostatic charge/discharge was used to assess performance.

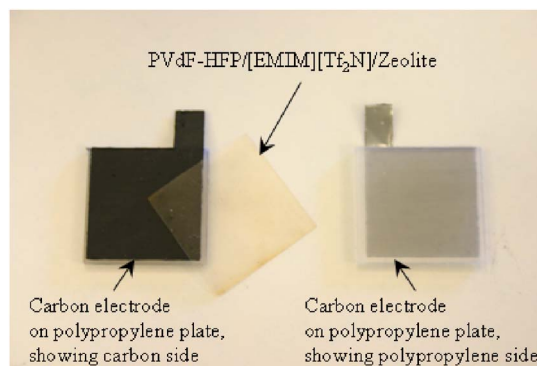
**Synthesis of ILGPEs.**— Ionic liquids 1-ethyl-3-methylimidazolium tetrafluoroborate ([EMIM][BF<sub>4</sub>]) and 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([EMIM][Tf<sub>2</sub>N]) were employed for ILGPE synthesis. Three synthesis approaches were investigated: ionic-liquid-polymer gelation, ionic-liquid-inorganic-polymer composite, and ionic-liquid-polymer membrane.

In the ionic-liquid-polymer gelation method, poly(vinylidene fluoride-co-hexafluoropropylene) (PVdF-HFP) powder was dissolved in 1-methyl-2-pyrrolidone (NMP) under magnetic stirring. The resultant viscous clear polymer solution was then mixed with an ionic liquid for 2 h to complete the polymer gelation with the ionic liquid. The polymer/ionic liquid ratio (by mass) in the resultant solution was 1:2.5. A small amount of this homogeneous polymer-solvent-ionic-liquid mixture was then poured onto a glass slide. Heating this liquid film at 110°C under dynamic (continuously operating pump source) vacuum (22 in. Hg) for 15 h completely evaporated the solvent NMP and formed a uniform and transparent ILGPE film (Fig. 1A). The ILGPE film was easily peeled off from the glass substrate. The thickness of the film was about 50–250 μm depending on the amount of polymer-solvent-ionic-liquid mixture used.

In the ionic-liquid-inorganic-polymer composite method, inorganic particle fillers were introduced to enhance the mechanical strength of the ILGPE system. This was done by modifying the ionic-liquid-polymer gelation method by adding a small amount of zeolite into the polymer/ionic-liquid mixture solution. The zeolite (particle size <45 μm) used was purchased from Sigma-Aldrich. The polymer/ionic liquid/zeolite ratio (by mass) in the resultant solution was about 1:2.5:0.06. Using the same procedure as for the ionic-liquid-polymer gelation method, we obtained composite ILGPE films (Fig. 1B) that were mechanically stronger than the ILGPE without zeolite.

In the ionic-liquid-polymer membrane method, commercially available porous membrane separators purposefully designed for ultracapacitor applications were directly imbibed with ionic liquids. Poly(tetrafluoroethylene) (PTFE) membranes (thickness: 23 μm, pore size: 0.05 μm, porosity: 50–70%) obtained from W. L. Gore and Associates were tested. This was done by soaking a piece of PTFE membrane in a 4 cm diameter aluminum pan containing an ionic liquid, followed by heating the membrane (in the ionic liquid) at 110°C and under dynamic vacuum (22 in. Hg) for 15 h. The ILGPE membrane (Fig. 1C) was then taken out from the ionic liquid and hung to shed the excess ionic liquid.

**Characterization of ILGPEs.**— Electrochemical and thermal properties of ILGPEs were investigated. Electrochemical characterization included measurements of the ionic conductivity and electrochemical windows of ILGPEs using a cell that sandwiched the ILGPE film between two stainless steel electrodes. The cell consisted of two identical stainless steel electrodes (2 × 2 cm for each)



**Figure 2.** (Color online) Photograph of a capacitor before assembly from two carbon electrodes and a PVdF-HFP/[EMIM][Tf<sub>2</sub>N]/zeolite ILGPE. Each carbon electrode was attached on a polypropylene plate on the aluminum foil side.

and a plastic spacer having a circular cut-out area of 0.785 cm<sup>2</sup> and a thickness of 0.0245 cm. Ionic conductivity of ILGPEs was measured by ac impedance spectroscopy with an ac voltage amplitude of 5 mV and a frequency range of 500 kHz–0.1 Hz. The real resistance  $Z'$  at the imaginary resistance  $Z'' = 0$  was used to calculate ionic conductivity of the ILGPE according to  $\sigma = t/(SZ')$  ( $t$  and  $S$  are thickness and area of the electrolyte between the two electrodes). The electrochemical window was measured by linear sweep voltammetry.

Thermal properties of ILGPEs were measured by thermal gravimetric analysis (TGA). TGA was performed using a Sieko TG/DTA200. The purge gas was N<sub>2</sub>, the sample size was ~7–10 mg (Pt pans), and TGA was performed between 30 and 700°C using a 60 min hold at the starting (for baseline stabilization) and end points and a heating rate of 5°C/min.

**Fabrication and testing of ultracapacitors.**— Capacitors were fabricated using a sandwich configuration, sandwiching an ILGPE with two carbon electrodes. Each electrode had a size of 1.5 × 1.5 cm. Prior to use, the aluminum foil current collector of the electrode assembly was attached onto a polypropylene plate with epoxy (Fig. 2). In order to insure good contact and low interfacial resistance between the electrode and the ILGPE, the electrodes were pretreated with ionic liquid ([EMIM][Tf<sub>2</sub>N]) prior to capacitor assembly. This was done by putting a small amount of ([EMIM][Tf<sub>2</sub>N]) on the carbon layer of the electrodes and then placing the ionic-liquid-containing electrodes under dynamic vacuum (22 in. Hg) for 2 h. By doing this, gas bubbles were removed from the electrode interior, allowing the ionic liquid to penetrate into the bulk of the carbon electrode material. Subsequently, the capacitor was assembled by sandwiching an ILGPE separator with these two ionic-liquid-pretreated electrodes, and the edges were sealed with epoxy. For PVdF-HFP/[EMIM][Tf<sub>2</sub>N] and PVdF-HFP/[EMIM][Tf<sub>2</sub>N]/zeolite, one piece of the ILGPE (thickness: ~100 μm) was used directly as a separator for capacitor fabrication. However, four pieces of PTFE/[EMIM][Tf<sub>2</sub>N] (thickness: 23 μm for each) needed to be stacked together to form the capacitor separator for that material. This minimized the difference in separator thickness between different capacitors. Capacitor testing included cyclic voltammetry, ac impedance spectroscopy, and galvanostatic charge/discharge.

## Results and Discussion

**Selection of ionic liquids.**— Prior to the synthesis of ILGPEs, an initial screening of ionic liquids was performed in terms of their ultracapacitor performance relative to the most frequently used conventional organic electrolyte (1 M Et<sub>4</sub>NBF<sub>4</sub>/acetonitrile). Several commercially available ionic liquids covering the imidazolium, phosphonium, ammonium, and pyrrolidinium groups were tested.

**Table I. Properties and capacitor performance of imidazolium ionic liquids and acetonitrile electrolyte.**

Electrolyte	Electrolyte property		Capacitor performance		
	Ionic conductivity (mS/cm)	Viscosity (cp at 20°C)	Maximum cell voltage <sup>a</sup> (V)	Energy density <sup>a</sup> (Wh/kg)	Power density <sup>a</sup> (W/kg)
[EMIM][BF <sub>4</sub> ]	7.6	38	4.0	20	2303
[EMIM][CF <sub>3</sub> SO <sub>3</sub> ]	4.5	43	4.0	10	2108
[EMIM][Tf <sub>2</sub> N]	4.8	28	4.0	28	2317
1 M Et <sub>4</sub> NBF <sub>4</sub> /acetonitrile	15.5	~1	2.3	8	1418

<sup>a</sup> Maximum cell voltage of capacitors was determined by cyclic voltammetry (scan rate: 20 mV/s). Energy and power densities were determined by galvanostatic charge/discharge (current density: 10 mA/cm<sup>2</sup>). Cut-off voltage for charge/discharge: 2.0/4.0 V for ionic liquid capacitors and 1.15/2.3 V for acetonitrile capacitor.

Ionic conductivity of these ionic liquids was measured prior to their capacitor performance evaluation. Our preliminary tests demonstrated that better performance (energy and power densities) was obtained for the imidazolium group, which is believed to be due to their relatively higher ionic conductivity and lower viscosity than other groups.<sup>17</sup> All imidazolium ionic-liquid-incorporated capacitors showed a typical rectangular-shaped cyclic voltammogram (CV) similar to that of the acetonitrile electrolyte-based capacitor. Table I summarizes the electrolyte properties of imidazolium ionic liquids: [EMIM][BF<sub>4</sub>], 1-ethyl-3-methylimidazolium trifluoromethanesulfonate ([EMIM][CF<sub>3</sub>SO<sub>3</sub>]), and [EMIM][Tf<sub>2</sub>N], as well as those of the acetonitrile electrolyte, and the performance of capacitors fabricated from these electrolytes.

The capacitors incorporating imidazolium ionic liquids showed higher performance figures-of-merit than the acetonitrile capacitor. This was mainly due to the wider electrochemical window of the ionic liquids, thus allowing higher cell voltages.<sup>2</sup> Moreover, ionic conductivity and viscosity of the ionic liquids are important factors influencing their capacitor performance. Having the highest ionic conductivity, but also a moderate viscosity in the imidazolium group, [EMIM][BF<sub>4</sub>] exhibited a moderate performance. The highest capacitor performance was achieved for [EMIM][Tf<sub>2</sub>N], the ionic liquid that had the lowest viscosity in the imidazolium group. In spite of its lower ionic conductivity, [EMIM][Tf<sub>2</sub>N] had higher energy and power densities than [EMIM][BF<sub>4</sub>]. It is possible that the negative impact from the lower ionic conductivity of [EMIM][Tf<sub>2</sub>N] may be offset by faster mass-transfer kinetics into the electrodes due to its lower viscosity. As an extreme example, [EMIM][CF<sub>3</sub>SO<sub>3</sub>] showed the poorest capacitor performance and had the lowest ionic conductivity and the highest viscosity. From these observations, it can be seen that high ionic conductivity and low viscosity are the keys for an ionic liquid to be a good electrolyte. Moreover, lower viscosity appears to play a more important role, facilitating the ion transport into and out of the electrical double layer at the electrode surface and thus enhancing the performance for the capacitor. Because of its highest capacitor performance, [EMIM][Tf<sub>2</sub>N] was selected as the primary ionic liquid for the synthesis of ILGPEs. Moreover, combining these electrokinetic attributes with attractive properties, including water immiscibility and high decomposition temperature (400°C),<sup>18</sup> [EMIM][Tf<sub>2</sub>N] promises to be a good electrolyte for ultracapacitor applications.

**Properties of ILGPEs.**— We have identified three simple approaches for the synthesis of ILGPEs with ionic liquids. In addition to the focus on [EMIM][Tf<sub>2</sub>N], another ionic liquid, [EMIM][BF<sub>4</sub>], was also included in this study. Different physical properties (e.g., hydrophilicity/water miscibility) of [EMIM][BF<sub>4</sub>] would give us an opportunity to understand and modify the synthesis conditions to better immobilize the target [EMIM][Tf<sub>2</sub>N] in the polymer matrix. The synthesized ILGPE films are homogeneous and flexible. Figure 1 shows photographs of three [EMIM][Tf<sub>2</sub>N]-incorporated ILGPEs.

In the ionic-liquid-polymer gelation method, we used PVdF-HFP as the polymer host. PVdF-HFP is one of the polymers that has been most frequently used in conventional GPEs<sup>19</sup> due to its relatively high thermal stability. PVdF-based polymer electrolytes are expected to have high anodic stability due to the strong electron-withdrawing functional group -C-F. Furthermore, PVdF copolymerized with hexafluoropropylene (PVdF-HFP) can be used to improve the gel properties of the polymer electrolytes because of its greater solubility in organic solvents, lower crystallinity, and lower glass transition temperature than the PVdF polymer alone.<sup>20</sup> Indeed, PVdF-HFP has been used by Bellcore Technology to manufacture gel polymer electrolytes, consisting of PVdF-HFP, LiPF<sub>6</sub>, and ethylene carbonate/dimethyl carbonate, for their battery products.<sup>21</sup> As discussed in the Experimental section, ILGPEs can be prepared easily using the ionic-liquid-polymer gelation method. The resulting ILGPE films were transparent, flexible, and mechanically strong (Fig. 1A).

In order to improve the mechanical properties for ILGPEs, we developed an ionic-liquid-inorganic-polymer composite approach. In this method, inorganic particulate fillers were introduced into the ILGPE to enhance the mechanical strength of the ILGPE system. Further, introduction of inorganic fillers would disrupt polymer chain packing (and crystallinity) and thus enhance ionic conductivities for the polymer composite electrolytes. Addition of zeolites into a conventional GPE system consisting of polyacrylonitrile, propylene carbonate/ethylene carbonate, and LiAsF<sub>6</sub> resulted in the increase of ionic conductivity from 10<sup>-3</sup> to 10<sup>-2</sup> S/cm,<sup>22</sup> which is the highest so far in the field of polymer electrolytes. To our knowledge, use of zeolite (or other inorganic particulate fillers) in the ionic-liquid-based GPE system has not been reported. In order to synthesize composite ILGPEs, inorganic fillers possessing high surface area and electrochemical inertness, such as ZrO<sub>2</sub>, TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, hydrophobic fumed silica, fiberglass, and zeolites, which have all been employed in conventional GPEs, can be used. For the proof-of-concept, we used zeolites. The synthesized PVdF-HFP/[EMIM][Tf<sub>2</sub>N]/zeolite composite ILGPE was a light-brown, rubbery film (Fig. 1B) and was mechanically stronger than the ILGPE without zeolite. The zeolite was found to be uniformly distributed within the polymer gel. In this fashion, addition of inorganic particulate fillers to improve the mechanical strength of ILGPEs was demonstrated.

In the ionic-liquid-polymer membrane method, commercially available porous membrane separators purposefully designed for energy storage (specifically ultracapacitors) applications were directly swelled/gelled with an ionic liquid to form ILGPEs (Fig. 1C). Previous research showed that ionic liquids could be impregnated into polymer membranes by directly soaking the membrane in an ionic liquid at room temperature.<sup>15</sup> However, the ionic conductivity of the resulting ionic-liquid-impregnated membrane was low (~10<sup>-4</sup> S/cm even at about 50°C). The low ionic conductivity of this polymer membrane electrolyte makes it unattractive for application to electrochemical devices. In our work, we found that incorporation of an

**Table II. Ionic conductivity and electrochemical window of pure ionic liquids and ILGPEs.**

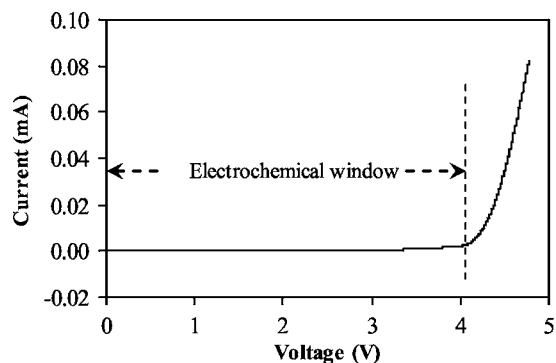
Ionic liquid or corresponding ILGPE	Ionic conductivity (mS/cm)	Electrochemical window (V)
[EMIM][BF <sub>4</sub> ] (pure ionic liquid)	7.6	4.1
PVdF-HFP/[EMIM][BF <sub>4</sub> ] (1:2.5)	3.5	4.0
PVdF-HFP/[EMIM][BF <sub>4</sub> ]/zeolite (1:2.5:0.06)	2.4	4.0
PTFE/[EMIM][BF <sub>4</sub> ]	1.2	4.0
[EMIM][Tf <sub>2</sub> N] (pure ionic liquid)	4.8	4.3
PVdF-HFP/[EMIM][Tf <sub>2</sub> N] (1: 2.5)	1.5	4.1
PVdF-HFP/[EMIM][Tf <sub>2</sub> N]/zeolite (1: 2.5: 0.06)	1.5	4.1
PTFE/[EMIM][Tf <sub>2</sub> N]	1.1	4.2

ionic liquid into the polymer membrane can be improved by imbibing it at elevated temperatures and under reduced pressure. This helps the swelling/gelling of the polymer membrane, enhancing the uptake of ionic liquid into the polymer network and thus increasing ionic conductivity for the resultant ILGPEs. The use of the vacuum can help the penetration of the ionic liquid into the depth of the membrane's pore network and thus enhance ionic conductivity of the resulting ILGPEs. Ionic conductivity of the resultant PVdF-HFP/[EMIM][Tf<sub>2</sub>N] composite membrane was 1.1 mS/cm even at room temperature. This demonstrates the importance of an elevated temperature and reduced pressure in improving the ionic conductivity for ILGPEs fabricated from preformed polymer membranes.

The ionic conductivity of all ILGPEs was measured. The results are summarized in Table II in comparison with those of pure ionic liquids. Ionic conductivity of all ILGPEs is lower than the pure ionic liquids. This is consistent with the relatively slower ion movement in a gel-polymer matrix vs in the bulk liquid form. Nevertheless, all ILGPEs show a reasonable conductivity of >1 mS/cm, which is believed to be sufficient for the fabrication of electrochemical devices. Incorporation of zeolite in the PVdF-HFP/[EMIM][BF<sub>4</sub>] system resulted in a decrease of ionic conductivity for the resultant composite (from 3.5 to 2.4 mS/cm) vs the ILGPE without the zeolite. This was not the case for the PVdF-HFP/[EMIM][Tf<sub>2</sub>N]/zeolite system. In fact, we observed that the PVdF-HFP/[EMIM][BF<sub>4</sub>]/zeolite system was not as homogeneous as the PVdF-HFP/[EMIM][Tf<sub>2</sub>N]/zeolite system. This may reflect a phase separation existing between the hydrophilic ionic liquid ([EMIM][BF<sub>4</sub>]) and the more hydrophobic filler (zeolite), hindering the ion movement and thus decreasing the ionic conductivity. By contrast, both the zeolite and the [EMIM][Tf<sub>2</sub>N] are hydrophobic, which provided greater homogeneity of the mixture, with no significant change in the ionic conductivity (but enhanced the mechanical strength) for the resulting composite ILGPE.

The electrochemical window of these ILGPEs was measured by linear sweep voltammetry. The results are summarized in Table II. Figure 3 shows the voltammogram of PVdF-HFP/[EMIM][Tf<sub>2</sub>N]/zeolite as an example. Upon the voltage scanning from 0 V to a higher value, breakdown of the electrolyte begins at a voltage higher than 4.1 V, indicating an electrochemical window of ~4.1 V for PVdF-HFP/[EMIM][Tf<sub>2</sub>N]/zeolite. All ILGPEs tested have an electrochemical window up to 4 V, showing their high electrochemical stability, which should be attributed to the inherent stability of all components in the ILGPE, i.e., ionic liquids, polymers, and inorganic fillers. This allows the operation of ultracapacitors with a high cell voltage and thus higher energy and power densities.

The thermal stability of ILGPEs was provided by TGA measurements (mass loss resulting from increasing temperature). These indicated three main mass-loss regimes. The first regime was between 200 and 300°C. In this transition, ~0.4 to 5% of mass (depending

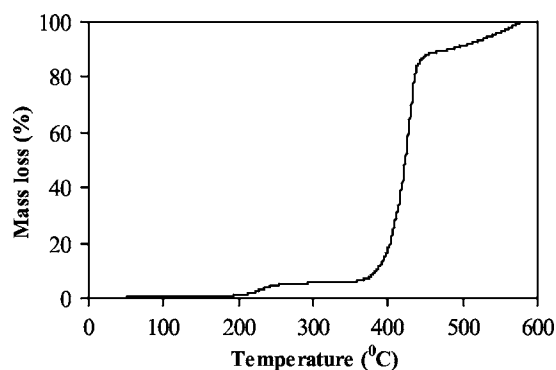
**Figure 3.** Voltammogram of a PVdF-HFP/[EMIM][Tf<sub>2</sub>N]/zeolite film obtained at a scan rate of 20 mV/s.

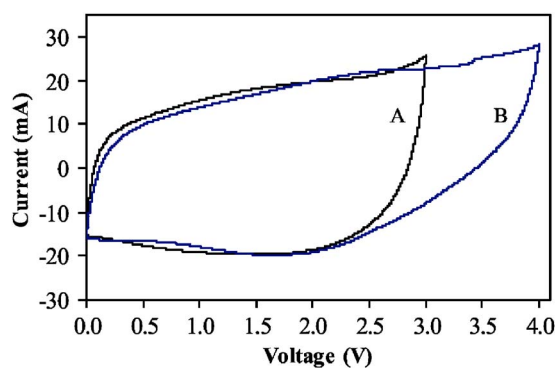
on the specific sample) was lost. This transition is probably the residual NMP solvent. A second regime occurs between 350 and 460°C. In this transition, the majority of mass is lost, with the total mass loss being on the order of 60–85% at this point. This transition is probably the breakdown (pyrolysis) of the ionic liquids in each of the samples. The final regime is >450°C. In this transition, most of the remaining mass is released and is probably due to the breakdown (pyrolysis) of the polymer. Figure 4 shows the TGA result of PVdF-HFP/[EMIM][Tf<sub>2</sub>N]/zeolite as an example.

These results support the contention that ILGPEs, especially [EMIM][Tf<sub>2</sub>N]-containing ILGPEs, have high thermal stability and can be used at an elevated temperature up to 350°C. This insures the longer lifetime and duration of the ILGPE-based ultracapacitors. Considering the commonly used operation temperature of about 60°C for HEVs, these ILGPEs are highly suitable for ultracapacitors for vehicular applications.

*Performance of ultracapacitors.*—ILGPEs synthesized above were employed to fabricate ultracapacitors (as detailed in the Experimental section) with carbon electrodes by sandwiching the ILGPE between two carbon electrodes. A photograph of a capacitor fabricated from a PVdF-HFP/[EMIM][Tf<sub>2</sub>N]/zeolite ILGPE is shown in Fig. 2 as an example.

Preliminary testing demonstrated that capacitors incorporating [EMIM][Tf<sub>2</sub>N]-containing ILGPEs showed better performance than those incorporating [EMIM][BF<sub>4</sub>]-containing ILGPEs, which is consistent with the results observed for capacitors fabricated from the liquid form of ionic liquids (see Table I). For example, using the galvanostatic charge/discharge conditions as for Table I, energy and power densities of a PVdF-HFP/[EMIM][Tf<sub>2</sub>N]/zeolite ILGPE-incorporated capacitor were 20 Wh/kg and 2273 W/kg, respectively, vs 15 Wh/kg and 2259 W/kg for a PVdF-HFP/[EMIM]

**Figure 4.** TGA graph of a PVdF-HFP/[EMIM][Tf<sub>2</sub>N]/zeolite film. The measurement was made in a N<sub>2</sub> purge.

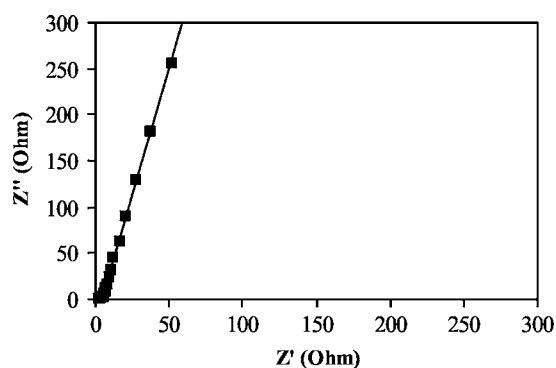


**Figure 5.** (Color online) CVs of a capacitor fabricated from two carbon electrodes and a PVdF-HFP/[EMIM][Tf<sub>2</sub>N]/zeolite ILGPE obtained in the voltage ranges of (A) 0–3 and (B) 0–4 V. Scan rate: 20 mV/s.

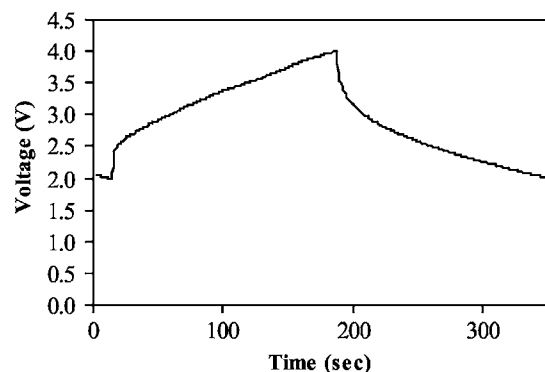
[BF<sub>4</sub>]/zeolite ILGPE-incorporated capacitor. This supports the contention that, within limits, regardless of the form of the electrolyte (either liquid or polymer gel), the viscosity of an ionic liquid plays a more important role than its ionic conductivity in influencing capacitor performance. Having lower viscosity, [EMIM][Tf<sub>2</sub>N]-based ILGPE electrolytes produced higher performance for the capacitors. Therefore, the following more-detailed testing was focused on capacitors fabricated from [EMIM][Tf<sub>2</sub>N]-containing ILGPEs.

The maximum cell voltages of these capacitors were determined to be ~4 V, which is consistent with electrochemical windows of ILGPEs (Table II). These capacitors exhibited typical, well-defined “rectangular-shaped” cyclic voltammograms (for example, Fig. 5). The shape and current’s magnitude for the voltammograms with these ILGPE-incorporated capacitors were similar to those (not shown) of capacitors fabricated from the bulk ionic liquid [EMIM][Tf<sub>2</sub>N], suggesting that the ionic liquid functions well in the polymer network of an ILGPE in the capacitor.

The capacitive behavior of these ILGPE-incorporated capacitors was confirmed by ac impedance spectra (Fig. 6), showing nearly vertical lines at low frequencies, a typical phenomenon for capacitors. Although these capacitors possessed a high cell voltage of 4 V (Fig. 5B), a faster charge/discharge process evidenced by the sharper transient responses at both ends of the cyclic voltammogram was obtained when a smaller voltage was employed (Fig. 5A). The relatively slow charge/discharge process of the capacitors observed at 4 V was believed to be due to the low mesoporosity and poor electrolyte accessibility within the activated carbon electrodes<sup>23</sup> (limiting the mass-transfer kinetics of ionic-liquid ions between the gel and the electrodes’ interior upon charging and discharging the capacitor to a high voltage). Use of carbon nanotubes as electrode



**Figure 6.** AC impedance spectrum of the same capacitor used in Fig. 5. The spectrum was recorded for the capacitor at open circuit using an ac voltage amplitude of 5 mV and a frequency range of 1 mHz–100 kHz.



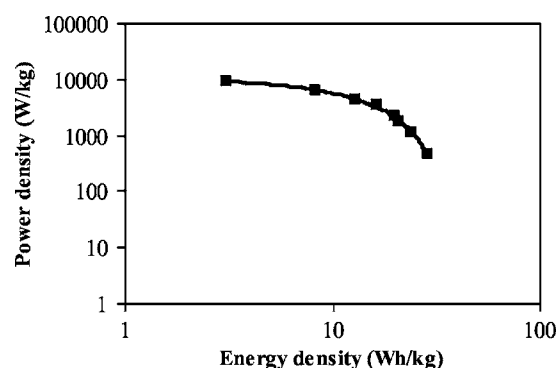
**Figure 7.** Galvanostatic charge/discharge profile of the same capacitor used in Fig. 5. Charge/discharge current density: 10 mA/cm<sup>2</sup>. Cut-off voltage: 2.0/4.0 V.

materials is promising to overcome this problem by providing enhanced surface access and charge transport for the ionic liquids.<sup>24</sup>

Furthermore, these ILGPE-incorporated capacitors were subjected to galvanostatic charge/discharge tests at different current densities of 2–50 mA/cm<sup>2</sup>. Figure 7 shows the charge/discharge curves of the PVdF-HFP/[EMIM][Tf<sub>2</sub>N]/zeolite-based capacitor obtained at a moderate current density of 10 mA/cm<sup>2</sup>. They are similar to that (not shown) of a capacitor fabricated from the liquid form of ionic liquid [EMIM][Tf<sub>2</sub>N] but with relatively lower energy and power densities. This is consistent with the lower ionic conductivity of ILGPEs compared to that of pure ionic liquids (Table II) and the more difficult transport of electrolyte ions within a solid-state polymer network of the ILGPE and/or between the ILGPE and the electrode. Nevertheless, these figures-of-merit are still promising for solid-state-electrolyte-based capacitors, especially when considering the overall advantages of the solid-state electrolytes over liquid ones.

Moreover, further research in our laboratory has demonstrated that carbon nanotubes are superior electrode materials, in conjunction with ionic-liquid electrolytes, for ultracapacitor applications. Their high electrical conductivity, improved charge-transport capability, and excellent mesoporosity and electrolyte accessibility helps overcome mass-transfer bottlenecks at the electrodes by providing enhanced access and charge transport for the ionic liquids.<sup>24</sup> This encourages us to combine ILGPEs developed in the present work with carbon nanotube electrode materials to further improve performances for ultracapacitors in the future.

Ragone plots of ILGPE-incorporated capacitors were obtained using the current densities of 2–50 mA/cm<sup>2</sup>. The typical plot for a PVdF-HFP/[EMIM][Tf<sub>2</sub>N]/zeolite-based capacitor is shown in Fig. 8 as an example. Upon discharge at the highest rate of 50 mA/cm<sup>2</sup>,



**Figure 8.** Ragone plot of the same capacitor used in Fig. 5. Charge/discharge current density: 2–50 mA/cm<sup>2</sup>. Cut-off voltage: 2.0/4.0 V.

Table III. Maximum energy and power densities of ultracapacitors fabricated from ILGPEs.

ILGPE	Maximum energy density (Wh/kg)	Maximum power density (W/kg)	Maximum energy density for packaged cell <sup>a</sup> (Wh/kg)	Maximum power density for packaged cell <sup>a</sup> (W/kg)
PTFE/[EMIM][Tf <sub>2</sub> N]	17	8120	6	2842
PVdF-HFP/[EMIM][Tf <sub>2</sub> N]	15	7000	5	2450
PVdF-HFP/[EMIM][Tf <sub>2</sub> N]/zeolite	20	7791	7	2727

<sup>a</sup> Estimated by multiplying the active-material-based performances by a factor of 0.35.<sup>25</sup>

resulting in a short discharge period of 0.8–1.5 s, high power densities of 9000–9900 W/kg were obtained for these capacitors. Importantly, corresponding to these high power densities, a moderate energy density of 2–4 Wh/kg can still be achieved for capacitors. Practically, regarding the discharge times of 3–30 s (the typical range for HEVs), the maximum energy and power densities were obtained (Table III). The present research was focused on the development of ILGPEs and demonstrating their application in ultracapacitors. Optimization of electrode materials and capacitor packaging materials was not studied. Capacitor performance for the ILGPEs was evaluated based on the mass of the active material (carbon) of electrodes rather than overall mass of the packaged capacitor. Nevertheless, based on a simplified estimation method,<sup>25</sup> the performances for a packaged capacitor can be estimated by multiplying the active-material-based performances by a factor of 0.35 (Table III). The results exceed the performance metrics (4–5 Wh/kg, 1000–1800 W/kg) of currently available ultracapacitors.<sup>26</sup> Again, the wider electrochemical window of ionic liquids over conventional organic electrolytes, and thus the larger maximum cell voltages for such capacitors, is the primary cause for this observation.

Finally, we performed a preliminary cycle life test for an ILGPE-incorporated capacitor. Because the capacitor was fabricated under ambient conditions in air, in order to avoid the possible detrimental affect of oxygen and/or moisture that may exist within the capacitor, a relatively lower cell voltage of 3 V was employed for this preliminary evaluation. Nevertheless, this voltage was still higher than that (~2.3 V) of most current ultracapacitors<sup>26</sup> and would facilitate higher performance figures-of-merit for the capacitor. As shown in Fig. 9, after an initial decrease of ~20% in the first 2000 cycles, the energy remained stable. The power was fairly stable over the entire time tested. The fluctuation in energy and power densities may reflect the effect of environmental conditions (e.g., temperature, humidity, or pressure) on the properties of the ionic liquids during testing, akin to what has been observed for other electrochemical devices incorporating ionic liquids.<sup>27</sup> The test was stopped at the 100,000th cycle. The excellent cycle life achieved indicates the pos-

sibility of even longer cycles for optimized ILGPE-based capacitors. In addition, we expect that more controlled fabrication of capacitors in a dry environment will facilitate their operation at a higher cell voltage of 4 V, allowing realization of higher energy and power densities.

### Conclusions

In this work, easy-to-use methods have been developed to incorporate ionic liquids into a polymer matrix to synthesize solid-state ILGPEs. The ILGPEs were shown to be mechanically strong, electrochemically and thermally stable, and highly conductive. Their application to the fabrication of solid-state ultracapacitors was demonstrated. Large cell voltage, high performance, and long cycle life have been demonstrated for these ultracapacitors.

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### References

1. A. Burke, *J. Power Sources*, **91**, 37 (2000).
2. B. E. Conway, *Electrochemical Supercapacitors: Scientific Fundamentals and Technological Applications*, Kluwer Academic/Plenum Publishers, New York (1999).
3. T. Q. Duong *2003 Annual Progress Report for Energy Storage Research and Development*, FreedomCAR & Vehicle Technologies Program, Energy Storage Research and Development, U.S. Department of Energy (May 2004).
4. L. J. Vimmerstedt and C. J. Hammel, *Current Status of Environmental, Health, and Safety Issues of Electrochemical Capacitors for Advanced Vehicle Applications*, Technical Report, April 1, 1997; <http://www.carttech.doe.gov/pdfs/B/138.pdf>
5. J. Y. Song, Y. Y. Wang, and C. C. Wan, *J. Power Sources*, **77**, 183 (1999).
6. T. Osaka, X. Liu, M. Nojima, and T. Momma, *J. Electrochem. Soc.*, **146**, 1724 (1999).
7. H. Y. Sung, Y. Y. Wang, and C. C. Wan, *J. Electrochem. Soc.*, **145**, 1207 (1998).
8. F. B. Dias, L. Plomp, and J. B. J. Veldhuis, *J. Power Sources*, **88**, 169 (2000).
9. A. B. McEwen, R. Chadha, T. Blakley, and V. R. Koch, in *Electrochemical Capacitors II*, F. M. Delnick, D. Ingersoll, X. Andrieu, and K. Naoi, Editors, PV 96-25, p. 313 The Electrochemical Society Proceeding Series, Pennington, NJ (2006).
10. M. C. Buzzeo, R. G. Evans, and R. G. Compton, *ChemPhysChem*, **5**, 1106 (2004).
11. M. Ue, M. Takeda, T. Takahashi, and M. Takehara, *Electrochem. Solid-State Lett.*, **5**, A119 (2002).
12. J. Fuller, A. C. Breda, and R. T. Carlin, *J. Electrochem. Soc.*, **459**, 29 (1998).
13. W. Lu, B. R. Mattes, and A. G. Fadeev, U.S. Pat. 6,828,062 (2004).
14. J. D. Stenger-Smith, C. K. Webber, N. Anderson, A. P. Chafin, K. Zong, and J. R. Reynolds, *J. Electrochem. Soc.*, **149**, A973 (2002).
15. M. Kinouchi, T. Hirano, and N. Hisano, *Polyelectrolyte membrane and production method*, U.S. Pat. Appl. 20050221193 A1 (2005).
16. M. Freemantle, *Chem. Eng. News*, **82**, 26 (2004).
17. M. Galiński, A. Lewandowski, and I. Stepniak, *Electrochim. Acta*, **51**, 5567 (2006).
18. A. B. McEwen, H. L. Ngo, K. LeCompte, and J. L. Goldman, *J. Electrochem. Soc.*, **146**, 1687 (1999).
19. M. Watanabe, M. Kanba, H. Matsuda, K. Mizoguchi, I. Shinohara, E. Tsuchida, and K. Tsunemi, *Makromol. Chem., Rapid Commun.*, **2**, 741 (1981).
20. A. S. Gozdz, J. M. Tarascon, C. N. Schmutz, P. C. Warren, O. S. Gebizlioglu, and F. Shokoohi, Abstract 117, The Electrochemical Society Extended Abstracts, Vol. 94-2 Miami, FL, Oct 9–14, 1994.
21. J. M. Tarascon, A. S. Gozdz, C. N. Schmutz, F. Shokoohi, and P. C. Warren, *Solid*

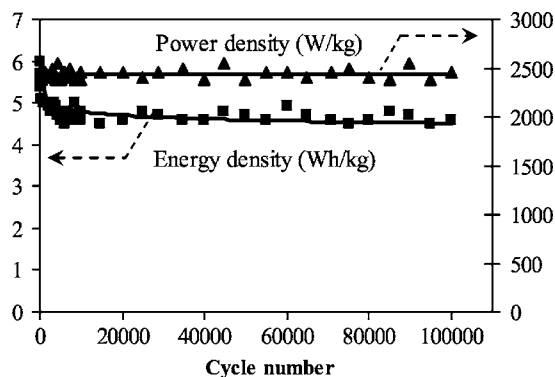


Figure 9. Galvanostatic charge/discharge cycle life test of a capacitor fabricated from a PVdF-HFP[EMIM][Tf<sub>2</sub>N]/zeolite ILGPE and two carbon electrodes. Current density: 20 mA/cm<sup>2</sup>. Cut-off voltage: 1.5/3.0 V.

- State Ionics*, **49**, 86 (1996).
22. S. Slane and M. Salomon, *J. Power Sources*, **55**, 7 (1995).
23. E. Frackowiak and F. Béguin, *Carbon*, **39**, 937 (2001).
24. W. Lu, L. Qu, L. Dai, and K. Henry, Paper 178, presented at the 211th Electrochemical Society Meeting, Chicago, IL, May 6–11, 2007.
25. M. Mastragostino, C. Arbizzani, R. Paraventi, and A. Zanelli, *J. Electrochem. Soc.*, **147**, 407 (2000).
26. A. Burke and M. Arulepp, in *Recent Developments in Carbon-based Electrochemical Capacitors: Status of the Technology and Future Prospects*, PV 2001-21, p. 576, The Electrochemical Society Proceedings Series, Pennington, NJ (2001).
27. W. Lu, A. G. Fadeev, B. Qi, and B. R. Mattes, *J. Electrochem. Soc.*, **151**, H33 (2004).