Ionic Liquids and Ion Gels -A New Class of Liquids and Polymer Gels-

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Ionic liquids are room temperature molten salts and have many interesting properties as new liquids,\(^1\) such as non-volatility, non-flammability, chemical and thermal stability, and high ionic conductivity. We have directed our attention to the combination of the ionic liquids and network polymers as new polymer gels.\(^2\) \textit{In situ} radical polymerization of common vinyl monomers in these ionic liquids affords compatible combinations of the ionic liquids and the resulting network polymers\(^2\) (Fig. 1). Completely compatible combinations are new polymer gels and named “ion gels”, which exhibit film forming property as well as the characteristics of the ionic liquids. The liquids trapped in the polymer network are non-volatile and thermally stable, which is completely different from conventional polymer gels. Furthermore, the ion gels exhibit an ionic conductivity as high as solution conductivities (ca. 10\(^{-2}\) Scm\(^{-1}\)). The high conductivities are caused by self-dissociating and ion-transporting abilities of the ionic liquids and by the decoupling of the ion transport and polymer segmental motion. If specific properties such as lithium ion conduction and proton conduction are molecularly designed in the ionic liquids, the scope of the utility of ionic liquids and ion gels may greatly expand, as shown in Table 1.\(^3\) In this talk, after reviewing the ionic liquids and ion gels, I will focus on the research on the design of H\(^+\) conducting ionic liquids and ion gels, and the recent progress in our research group will be presented.

We have recently found\(^3b-d\) that novel Bronsted acid-base salts, derived from a simple combination of a wide variety of organic amines with bis(trifluoromethanesulfonyl) amide, form ionic liquids and that they are anhydrous proton conductors and electroactive for H\(_2\) oxidation and O\(_2\) reduction at a Pt electrode under non-humidifying condition, which shows the prospect of the use of the protic ionic liquids as new proton conductors for non-humidifying H\(_2\)/O\(_2\) fuel cells at elevated temperatures.

\textbf{Acknowledgment}

This research was supported in part by Grant-in-Aid for Scientific Research (#404/11167234 and #14350452) from the Japanese Ministry of Education, Science, Sports, and Culture and by NEDO Technology Research Grant.

\textbf{References}


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— A New Class of Liquids and Polymer Gels —

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Outline

1. Introduction
2. Preparation of Ion Gels by In-situ Radical Polymerization
3. Properties of Ion Gels
4. Potentials as New Polymer Gels
EMI cation

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{N} & \quad \text{N} & \quad \text{CH}_2\text{CH}_3 \\
\end{align*}
\]

Counter anion: \( \text{Br}^- \), \( \text{BF}_4^- \), \( \text{N}^-\text{(SO}_2\text{CF}_3)_2 \)

Fig. Difference in appearance of salts at room temperature, depending on the structure of counter anion.
Fig. DSC thermogram of EMITFSI at a heating rate of 10 °C/min.

Fig. TG curve of EMITFSI at a heating rate of 10 °C/min.
Fig. Ion gel obtained by *in situ* polymerization of vinyl monomers in ionic liquid.
<table>
<thead>
<tr>
<th>Monomer</th>
<th>Polymer</th>
</tr>
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<tbody>
<tr>
<td>Methyl methacrylate</td>
<td>○</td>
</tr>
<tr>
<td>Acrylonitrile</td>
<td>○ (phase-separated)</td>
</tr>
<tr>
<td>Vinyl acetate</td>
<td>○ (no polymerization)</td>
</tr>
<tr>
<td>Styrene</td>
<td>○ (phase-separated)</td>
</tr>
<tr>
<td>2-Hydroxyethyl methacrylate</td>
<td>○ (phase-separated)</td>
</tr>
<tr>
<td>Methyl acrylate</td>
<td>○</td>
</tr>
<tr>
<td>Acrylamide</td>
<td>○ (phase-separated)</td>
</tr>
</tbody>
</table>

a) ○: transparent; ×: phase-separated  
b) Ionic liquids and monomers are mixed at 1:1 molar ratio.  
c) Polymerization was carried out in the presence of 2 mol% BPO for monomers at 80 °C for 12 h.
Polymerization at 80 °C for 12 h, and then at 140 °C for 0.5 h

Polymer Electrolyte Film

Measurement

Fig. Procedure for preparation of polymer electrolyte films.
Fig. A photograph of an ion gel.
Fig. DSC thermograms for MMA network polymers with dissolved EMITFSI (composition in molar ratio) at a heating rate 10 °C/min.
Gordon-Taylor equation

\[ T_g = \nu_{\text{EMITFSI}} \cdot T_{g,\text{EMITFSI}} + \nu_{\text{PMMA}} \cdot T_{g,\text{PMMA}} \]

\( \nu_{\text{EMITFSI}} + \nu_{\text{PMMA}} = 1 \); \( \nu \): volume fraction

Fox equation

\[ \frac{1}{T_g} = \frac{w_{\text{EMITFSI}}}{T_{g,\text{EMITFSI}}} + \frac{w_{\text{PMMA}}}{T_{g,\text{PMMA}}} \]

\( w_{\text{EMITFSI}} + w_{\text{PMMA}} = 1 \); \( w \): weight fraction

Fig. Glass transition temperature for MMA network polymers with dissolved EMITFSI as a function of EMITFSI concentration.
Fig. Storage modulus ($E'$), loss modulus ($E''$) and loss tangent ($\tan\delta$) for EMITFSI dissolved in MMA network polymer (EMITFSI:MMA=2:8) as a function of temperature at 1Hz.
Fig. TG curves for MMA network polymers with dissolved EMITFSI (composition in molar ratio) at a heating rate of 10 °C/min.
**Fig.** Arrhenius plots of ionic conductivity for MMA network polymers with dissolved EMITFSI (composition in molar ratio).
Structure of gels is frozen out.

- \( T_g \) from DSC measurements

- \( T_0 \) from conductivity measurements

Ionic motion in gels is frozen out.

\( T_g - T_0 \) is more pronounced when concn. of ionic liquids is low.

**Fig.** Glass transition temperatures (\( T_g \)) and calculated \( T_0 \) in VTF equation for MMA network polymers with dissolved EMITFSI.
Fig. Arrhenius plots of self-diffusion coefficient for EMITFSI dissolved in MMA network polymer (EMITFSI:MMA=7:3).
Fig. The temperature dependence of relaxation time for the ion gel ($\tau_S$: the structural relaxation time, $\tau_\sigma$: the conductivity relaxation time). The conductivity in $T_g$ increases, when the composition of the polymer increases (Decoupling), and temperature dependency of the conductivity approximate to the Arrhenius temperature dependence from the VTF temperature dependence (Fragile $\rightarrow$ Strong).
<table>
<thead>
<tr>
<th>Application Field</th>
<th>Properties to be Utilized</th>
<th>Chemistry to be Pursued</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lithium Polymer Battery</td>
<td>High ionic conductivity, Non-flammability, Non-volatility</td>
<td>Lithium-ionic conductivity</td>
</tr>
<tr>
<td>Double Layer Capacitor</td>
<td>Large double layer capacitance, High temperature stability</td>
<td>Capacity retention at low temperature</td>
</tr>
<tr>
<td>Fuel Cell</td>
<td>New media of proton conduction instead of water</td>
<td>Anhydrous proton-conducting membrane above 100°C</td>
</tr>
<tr>
<td>Solar Cell</td>
<td>Non-volatility, Stability</td>
<td>Ion/electron mixed conduction</td>
</tr>
<tr>
<td>Actuator</td>
<td>Solidification of electrolytes, Non-volatility</td>
<td>Motility by electrochemical reactions</td>
</tr>
<tr>
<td>Electrochromics</td>
<td>Non-volatility, Stability</td>
<td>Reversible and durable electrochromic reactions</td>
</tr>
</tbody>
</table>
Fig. Molecular structures of components of proton conducting ionic liquids.
Anode: $2\text{BI} + \text{H}_2 \rightarrow 2\text{BIH}^+ + 2\text{e}^-$
Cathode: $2\text{BIH}^+ + \frac{1}{2}\text{O}_2 + 2\text{e}^- \rightarrow 2\text{BI} + \text{H}_2\text{O}$
Total: $\text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O}$

Fig. Fuel cell characteristics for BI/HTFSI=5/5, 7/3, and 8/2 under anhydrous condition at 150°C. The cell potential is scanned from open circuit potential to 0 V (vs.RHE) at 1 mV/s.
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TODAY'S HEADLINES
April 17, 2003

Ionic liquids for fuel cells

A novel family of ionic liquids that can serve as electrolytes for hydrogen/oxygen fuel cells operating at elevated temperatures, according to chemistry professor Masahiro Yamasaki and coworkers at Yokohama National University in Japan. They propose a range of halogenated solid-base ionic liquids by combining the superstrong salt bis[trifluoromethanesulfonyl]amide (HTFSI, shown) with a variety of organic anions (Chem. Commun., 2003, 209). The liquids act as electrolytes for hydrogen oxidation at a platinum anode and oxygen reduction at a platinum cathode. The group demonstrated their use in fuel cells with an ionic liquid derived from equimolar amounts of imidazolium and HTFSI. "This is the first evidence of electric power generation by an H\textsubscript{2}/O\textsubscript{2} fuel cell using a Cr rated solid-base ionic liquid as a proton-conducting nonaqueous electrolyte," the authors note. When two of the fuel cells containing the electrolyte were connected in series and H\textsubscript{2} and O\textsubscript{2} gas was bubbled at the electrodes at 130 °C, sufficient power was generated to operate a calculator. The ionic liquids might be used with compatible polymers for the development of solid-state proton conductors and as anhydrous electrolytes in fuel cells that operate at temperatures above 100 °C, the authors suggest.