Ion transport and storage of ionic liquids in ionic polymer conductor network composites

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We investigate ion transport and storage of ionic liquids in ionic polymer conductor network composite electroactive devices. Specifically, we show that by combining the time domain electric and electromechanical responses, one can gain quantitative information on transport behavior of the two mobile ions in ionic liquids (i.e., cation and anion) in these electroactive devices. By employing a two carrier model, the total excess ions stored and strains generated by the cations and anions, and their transport times in the nanocomposites can be determined, which all depend critically on the morphologies of the conductor network nanocomposites. © 2010 American Institute of Physics. [doi:10.1063/1.3432664]

Ionic liquids (ILs), due to many unique and attractive features as electrolytes, have shown a great promise for applications in energy storage, conversion devices, and other electroactive devices.1–11 For example, the negligible vapor pressure of ILs enables these electroactive devices to operate at ambient atmosphere with long life cycles; the wide electrochemical window allows these devices to work at higher voltage; and the high ion mobility can lead to fast device response time. All of these properties are highly desirable for electroactive devices such as ionic polymer actuators,1–3 supercapacitors,4 batteries,5–8 fuel cells,9 and dye-sensitized solar cells.10 Figure 1 presents schematically a typical device configuration for such an electroactive device, which basically has a three-layer structure. The two porous composite electrodes separated by an ion conducting membrane provide high specific electrode area for ion storage under an applied voltage; and the high ion mobility can lead to fast device response time. All of these properties are highly desirable for electroactive devices such as ionic polymer actuators,1–3 supercapacitors,4 batteries,5–8 fuel cells,9 and dye-sensitized solar cells.10

For the IPCNCs fabricated with the directly assembly method, either the commercial Nafion film NR-211 of thickness 25 µm or Aquivion from Solvay was chosen as the spacer layer in Fig. 1. RuO2/Nafion (or RuO2/Aquivion) composite was fabricated by mixing RuO2 nanoparticles (from Alfa Aesar with 13–19 nm diameter) with 20% Nafion dispersion from Aldrich (or 20% Aquivion dispersion from Solvay). In this study, a CNC layer with 40 vol % of RuO2 nanoparticles was used. IPCNCs fabricated by the LbL method were made by alternately immersing the Nafion film into two aqueous solutions containing the polycation poly(allylamine hydrochloride) (PAH) as the polyanion and polycation and anionic gold nanoparticles (2 nm, from Purest Colloids) or CNT (from Carbon Solutions Inc.).8,14 The LbL CNCs comprise 100 bilayers of PAH/Au and 30 bilayers of PAH/CNT, respectively. The lateral dimensions of the IPC-

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*Schematic of a three layer IPCNC actuator.*

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NCs studied here are 1 × 10 mm². The thickness ranges approximately from 26 μm for LbL IPCNCs to 31 μm for the IPCNCs made from the directly assembly method.

A potentiostat (Princeton Applied Research 2273) was utilized for electrical measurement. In this study, a dc step voltage is applied on the IPCNC samples and the charging current I versus time was recorded and integrated to obtain the stored charge versus time at the CNC electrodes. The time resolved electromechanical response of the actuators was recorded by a probe station (Cascade Microtech M150) equipped with a Leica microscope and a charge-coupled device camera (Pulnix 6740CL). Nuclear magnetic resonance (NMR) provided quantitative measures of self-diffusion coefficients for IL anions (¹⁹F NMR) and cations (¹H NMR) both in pure ILs and in ILs absorbed into ionomers.¹⁵ Ion mobility was calculated from diffusion coefficients using the Einstein relation μ = D/κB T.

Presented in Fig. 2 is the evolution of the bending actuation of the PAH/Au IPCNCs under 4 V step voltage. The actuator initially bends toward the anode and as the time progresses; it reverses the actuation direction and bends toward the cathode. As will be discussed later, this is caused by the two mobile ions in the actuation process. The intrinsic strain S₀ generated in the composite electrode regions. As schematically illustrated in Fig. 2(a), the strain at cathode becomes negative (κ changes sign). Figure 2 also presents the charge density Q versus time for these IPCNCs.

The results in Figs. 2 and 3 can be understood based on a two-carrier model to account for the presence of the mobile cations and anions in the IPCNCs which have different mobility. Using a simplified RC equivalent circuit model for each type of ion (cations and anions) in the IPCNCs lead to Fig. 4(a) where the two branches represent the ion transport of two types of ions. In the figure, the RC transmission line equivalent circuits used in the literature for the porous electrode in each branch are simplified into Rcat and Ccat or Ran andCan, respectively, where the subscripts “cat” and “an” indicate cations and anions.¹⁶ Hence, the charge density Q versus time under a step voltage becomes

\[ Q(t) = Q_0^{\text{cat}}(1 - e^{-t/\tau_{\text{cat}}}) + Q_0^{\text{an}}(1 - e^{-t/\tau_{\text{an}}}), \]

where the time constant \( \tau_{\text{cat}} \) and \( \tau_{\text{an}} \) will depend on the porous electrode morphology as well as the ion mobility (=RC time constant).

The accumulation or depletion of excess ions in the composite electrodes will cause expansion and contraction in the porous electrode regions. As schematically illustrated in Fig. 4(b), in contrast to the conduction current in which the oppositely charged mobile ions add together [Eq. (1)], the strains they generate will have opposite sign and hence will cancel each other. Therefore, the curvature, which is proportional to the net strain in the IPCNCs, follows as:

\[ \kappa(t) = \kappa_0^{\text{cat}}(1 - e^{-t/\tau_{\text{cat}}}) - \kappa_0^{\text{an}}(1 - e^{-t/\tau_{\text{an}}}). \]
Equations (1) and (2) are used to fit the experimental data (solid curves in Fig. 3) and the fitting parameters are summarized in Table I. The fitting results indicate that $r^{\text{an}}$ is smaller than $r^{\text{cat}}$. That is, the cations have fast transport speed compared with the anions, which causes the initial bending actuation from the expansion of cathode and contraction of the anode. As time progresses, the anions will generate strain in the opposite direction and eventually cause the IPCNCs to bend by the coupling between the ions and the composite electrodes. $r^{\text{an}}/r^{\text{cat}}$ for the IPCNCs with RuO$_2$/Nafion ($=4.16$) and RuO$_2$/Aquivion ($=4.6$) are similar. For the IPCNCs with LbL electrode layers, $r^{\text{an}}/r^{\text{cat}}$ is 10.97 for PAH/Au and 2.22 for PAH/CNT, respectively.

For comparison, the diffusion coefficient from the NMR data and the mobility deduced from the Einstein relation for neat ILs and the EMI-Tf IL in Nafion (NR-212) are listed in Table II. Notably, the cation (EMI$^+$) has higher mobility than that of anions (BF$_4^-$ and Tf$^-$), which is consistent with the experimental results presented. The ratio of $\mu_{\text{cat}}/\mu_{\text{an}}$ is 1.27 in neat EMI$^+$BF$_4^-$ and 1.5 in neat EMI$^+$Tf$^-$, which are much smaller than the ratio of $\tau_{\text{an}}/\tau_{\text{cat}}$ from the ion transport in the IPCNCs. These results indicate the crucial role played by the CNC morphology in determining the ion transport in the porous electrodes. Moreover, the large increase in $\tau_{\text{an}}$ compared with $\tau_{\text{cat}}$ suggests the possible large size (ions plus the solvent or aggregation shells) of the anions in the transport process in these composites electrodes.

A comparison of the ratio of $\kappa^{\text{an}}/Q^{\text{an}}$ with $\kappa^{\text{cat}}/Q^{\text{cat}}$ reveals that the anions are more effective in generating strain in these porous electrodes. This again suggests that the anions when they are stored in the porous electrodes have much larger solvent or aggregation shells, or that they associate more strongly with the ionic electrode matrix, resulting in a larger effective ion size and higher strain generated. The results here demonstrate a simple means to compare the effective ion size of the cation and anion of an IL in electro-active devices.

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**Table I. Summary of fitting parameters for the IPCNCs studied.**

<table>
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<tr>
<th></th>
<th>RuO$_2$/Nafion</th>
<th>RuO$_2$/Aquivion</th>
<th>PAH/Au LbL</th>
<th>PAH/CNT LbL</th>
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<tr>
<td>$\tau^{\text{an}}$ (s)</td>
<td>6</td>
<td>7.9</td>
<td>4.83</td>
<td>9</td>
</tr>
<tr>
<td>$\tau^{\text{cat}}$ (s)</td>
<td>25</td>
<td>36.3</td>
<td>53</td>
<td>20</td>
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<tr>
<td>$Q^{\text{an}}$ (C/mm$^2$)</td>
<td>$2.82 \times 10^{-4}$</td>
<td>$8.46 \times 10^{-5}$</td>
<td>$4.28 \times 10^{-4}$</td>
<td>$3.17 \times 10^{-4}$</td>
</tr>
<tr>
<td>$Q^{\text{cat}}$ (C/mm$^2$)</td>
<td>$1.57 \times 10^{-4}$</td>
<td>$9.48 \times 10^{-5}$</td>
<td>$2.91 \times 10^{-4}$</td>
<td>$2.10 \times 10^{-4}$</td>
</tr>
<tr>
<td>$\kappa^{\text{an}}$ (mm$^{-1}$)</td>
<td>1.83</td>
<td>1.29</td>
<td>0.74</td>
<td>2.5</td>
</tr>
<tr>
<td>$\kappa^{\text{cat}}$ (mm$^{-1}$)</td>
<td>2.13</td>
<td>2.62</td>
<td>2.04</td>
<td>3.1</td>
</tr>
</tbody>
</table>

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**Table II. Diffusion coefficients (measured) and electrophoretic mobilities (calculated) from pulsed-gradient NMR for the ILs studied.**

<table>
<thead>
<tr>
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<th>EMIBF$_4$</th>
<th>EMITf</th>
<th>EMITf in Nafion$^*$</th>
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<tr>
<td>$D$ (10$^{-12}$ m$^2$ s$^{-1}$)</td>
<td>43.0</td>
<td>33.7</td>
<td>44.0</td>
</tr>
<tr>
<td>$\mu$ (10$^{-9}$ m$^2$ V$^{-1}$ s$^{-1}$)</td>
<td>1.67</td>
<td>1.31</td>
<td>1.71</td>
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</table>

$^*$32 wt % EMITf in Nafion with 2.1 wt % coexisting water. All data are taken at 25 °C.

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