

## Fabricating Conducting Polymer Electrochromic Devices Using Ionic Liquids

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## Fabricating Conducting Polymer Electrochromic Devices Using Ionic Liquids

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Electrolytes play an important role in determining the performance of conducting polymer electrochromic devices. Good electrolytes should have high conductivity, large electrochemical windows, excellent thermal and chemical stability, and negligible evaporation. Room-temperature ionic liquids are ideal electrolytes to satisfy these requirements. In the present work, we explored the applications of ionic liquids as electrolytes in electrochemical synthesis of conducting polymers, in electrochemical and electrochromic characterization of both electrochemically and chemically synthesized conducting polymers and in fabrication of conducting polymer electrochromic devices. In ionic liquids, highly stable electroactivity has been obtained for polyaniline in a wide potential range covering its entire redox process of leucoemeraldine  $\leftrightarrow$  emeraldine  $\leftrightarrow$  pernigraniline for  $>1,000,000$  cycles. During the fabrication of electrochromic devices, electrochemically synthesized polymers were employed for displays, while chemically synthesized polymers (via spin-coating) were preferable for large-area electrochromic windows. We have successfully fabricated the prototypes of alphanumeric displays and large-area ( $5 \times 5$  cm) electrochromic windows. High device performance of low operation voltages ( $<1.5$  V), high coloration contrast ( $>50\%$ ), fast coloration speed ( $<100$  ms), and high coulombic efficiency ( $>98\%$ ) has been realized.

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Electrochromic devices are made from electrochromic materials that change color in a persistent but reversible manner by an electrochemical reaction. Electrochromic devices can find applications in a wide range of areas such as in optical and communication industry (optical information displays and storage); building industry (architectural glazing windows for energy control and glare-reduction system for offices); automobile industry (antiglare rear-view mirrors and sun roofs for cars); the military (protective eyewear for soldiers and controllable canopies for aircrafts); and even human daily life (consumer sunglasses). The most successful and frequently used electrochromic materials so far are inorganic compounds (such as  $\text{WO}_3$ ,  $\text{MoO}_3$ ,  $\text{V}_2\text{O}_5$ ). However, these materials are very expensive to process, which inevitably limits their commercial and industrial applications. Therefore, use of organic materials, conducting polymers, has been becoming an attractive topic since their discovery in the middle 1970s.<sup>1</sup> Conducting polymers stand for a family of important electrochromic materials due to their unique advantages over inorganic compounds, such as low cost, good processibility, and flexibility for large-area application, and color tailorability for varying coloration region.<sup>2-4</sup>

Nevertheless, practical applications of conducting polymer electrochromic devices have been limited by their short lifetimes. More broadly, a major obstacle to the commercialization of conducting polymer-based devices is their relatively poor stability,<sup>5</sup> which can be attributed to several degradation mechanisms. Electrolytes play a critical role in determining these problems. Presence of water/moisture in the electrolytes has been found to be a problem in reducing the performance and long-term operation of the devices. Water/moisture could be introduced during the entire fabrication process of devices, including preparation of polymer electrodes, preparation of electrolytes, and assembly of devices. During the electrochemical synthesis of conducting polymers, aqueous or non-aqueous electrolytes can be used. Using aqueous electrolytes, the obtained polymers must be subjected to a drying process (preferably under vacuum) prior to their use in device fabrication. For a particular conducting polymer, polyaniline, the frequently studied electrochromic polymer, other problems have also been realized for its electrochemical synthesis in aqueous electrolyte systems, for example, degradation of polyaniline during polarization<sup>6</sup> and decrease in electroactivity due to nucleophilic attack on the polymer by  $\text{OH}^-$ .<sup>7</sup> Therefore, synthesis of conducting polymers in nonaqueous electrolytes has attracted extensive attention.<sup>8,9</sup> Nevertheless, the ab-

sorption of moisture of these electrolytes would affect the long-term operation of the later-fabricated devices. It is preferable to perform the preparation of conducting polymers in a dry glove box. Furthermore, the water/moisture may also be introduced during the preparation of electrolytes used for device fabrication and during the assembly of devices in air. The operating voltage and lifetime of the resulting devices are affected by the water content of the electrolyte due to the miscibility of the organic solvents employed with water. Thus, lack of miscibility with water is a critical property of electrolytes for the fabrication of durable and stable electrochemical devices.

Use of aqueous electrolytes also affects polymer electrochemical behavior and thus limits their applications in device fabrication. Electrochemical degradation of polyaniline in aqueous electrolytes is a typical example representing the disadvantages of the electrolytes. Typically, polyaniline undergoes two redox processes, *i.e.*, leucoemeraldine  $\leftrightarrow$  emeraldine in the low-potential region and emeraldine  $\leftrightarrow$  pernigraniline in the high-potential region.<sup>10</sup> However, the formation of pernigraniline at high potentials usually leads to polymer degradation in aqueous electrolytes.<sup>11,12</sup> In order to prevent polyaniline degradation in aqueous electrolytes, the applied potential has to be limited in a narrow range, covering only the first redox process leucoemeraldine  $\leftrightarrow$  emeraldine. Unfortunately, this results in low coloration contrast for the polyaniline electrochromic devices.

In this work, we used ionic liquids as electrolytes to overcome these problems and fabricate high-performance and stable conducting polymer electrochromic devices. Due to their unique properties of high conductivity, large electrochemical windows, excellent thermal and chemical stability, and negligible evaporation, ionic liquids have received considerable attention as electrolytes in various electrochemical devices.<sup>13-15</sup> However, use of ionic liquids as electrolytes in the research of conducting polymer electrochemistry is very limited and has not been previously addressed in the development of conducting polymer electrochemical devices. Osteryoung *et al.* have shown that a number of conducting polymers can be prepared in ionic liquids, and the obtained polymer films showed electroactivity in these ionic liquids.<sup>16,17</sup> The research described in these studies was performed using  $\text{AlCl}_3$ -imidazolium chloride systems. It has been stated that a disadvantage of these ionic liquids, and a problem with any ionic liquid containing a strong Lewis acid such as  $\text{AlCl}_3$ , is the liberation of toxic gases when they are exposed to moisture.<sup>18</sup> Additionally, the highly reactive nature of Lewis acids used to form ionic liquids limits the use of these ionic liquids due to their incompatibility with many materials. Therefore, in the present work, we

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focused on the use of non-Lewis-acid ionic liquids that are liquids at room temperature and are stable upon exposure in air. More specifically, we explored the applications of ionic liquids as electrolytes in electrochemical synthesis of conducting polymers, in electrochemical and electrochromic characterization of both electrochemically and chemically synthesized conducting polymers, and in fabrication of conducting polymer electrochromic devices.

### Experimental

**Reagents.**—All reagents were AR grade. Pyrrole, 3,4-ethylenedioxythiophene, and aniline were purchased from Aldrich and distilled prior to use. Poly(3-octylthiophene) was purchased from Aldrich and used without further purification.

**Synthesis of ionic liquids.**—Ionic liquid, 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF<sub>4</sub>]), was synthesized according to the methods described elsewhere.<sup>19,20</sup> Precursor 1-butyl-3-methylimidazolium chloride ([BMIM][Cl]) was prepared according to procedure described by Wilkes *et al.* 1-methylimidazole (82 g) was mixed with chlorobutane (139 g) in a round bottom 1 L flask. The flask was attached to a rotary evaporator and the reaction was carried out by refluxing the mixture under vacuum at 60–70°C for 8–36 h. The product of the reaction phase separated from the reaction mixture, which accumulated at the bottom of the flask as a clear viscous liquid ([BMIM][Cl]). The unreacted reagents were decanted and the hot product was washed ten times with 200 mL aliquots of ethyl acetate. The final product was dried at 70°C under dynamic vacuum for 24 h. [BMIM][BF<sub>4</sub>] was prepared using the method developed by Bonhote for other ionic liquids.<sup>20</sup> An aqueous solution of HBF<sub>4</sub> (50 wt %), in the amount of 152 g, was slowly added to 150 g of [BMIM][Cl] that had been previously dissolved in 500 mL of water. The produced [BMIM] × [BF<sub>4</sub>] was extracted from the mixture with dichloromethane. The solvent was removed by vacuum distillation and [BMIM] × [BF<sub>4</sub>] was dried at 70°C under dynamic vacuum.

**Measurements of electrochemical windows of ionic liquids.**—Electrochemical windows of ionic liquids were measured using an EcoChemie Autolab PGSTAT 30 potentiostat with a three-electrode electrochemical cell consisting of a 0.25 mm Pt wire working electrode, a 1.5 mm Pt wire counter electrode, and a 1.0 mm Ag wire quasi-reference electrode.

**Electrochemical synthesis of conducting polymers in ionic liquids.**—Electrochemical synthesis of conducting polymers was carried out using the potentiostat with a three-electrode electrochemical cell. Based on different purposes, different substrate electrodes were employed as the working electrodes. Three typical electrochemical methods, namely, voltammetric, potentiostatic, and galvanostatic, were investigated for polymer synthesis and deposition. Polymerization solutions used for electrochemical synthesis of polymers were 0.1 M pyrrole in [BMIM][BF<sub>4</sub>] for polypyrrole (PPy), 0.1 M 3,4-ethylenedioxythiophene in [BMIM][BF<sub>4</sub>] for poly(3,4-ethylenedioxythiophene) (PEDOT), and 0.5 M aniline and 2 M CF<sub>3</sub>COOH in [BMIM][BF<sub>4</sub>] for polyaniline (PANI). The resulting polymer-coated electrodes were rinsed with [BMIM][BF<sub>4</sub>] three times prior to their use in further measurements or device fabrication. For electrochemical and electrochromic characterization, polymers were deposited on indium tin oxide (ITO) glass electrodes (0.7 × 4.2 cm) by cyclic voltammetry (CV) at 50 mV/s. The potential ranges and cycling numbers were –0.5 to 0.9 V for 20 cycles for PEDOT, –0.8 to 0.8 V for 12 cycles for PPy, and –0.2 to 1.2 V for 15 cycles for PANI, respectively. For the fabrication of electrochromic displays, PANI and PEDOT were deposited on patterned ITO glass electrodes galvanostatically at a current density of 0.5 mA/cm<sup>2</sup>. The patterned ITO glass electrode contained seven pixels with the size of 0.25 × 1.7 cm for each pixel. PEDOT was deposited onto seven pixels of an ITO glass electrode altogether, while PANI was deposited onto each pixel of another ITO glass

electrode separately. The times used to deposit PEDOT and PANI were 40 and 120 s, respectively. For the fabrication of PEDOT/POT composite polymer involved display, PEDOT was coated onto the top of a poly(3-octylthiophene) (POT) precoated ITO glass electrode that was prepared by spin-coating.

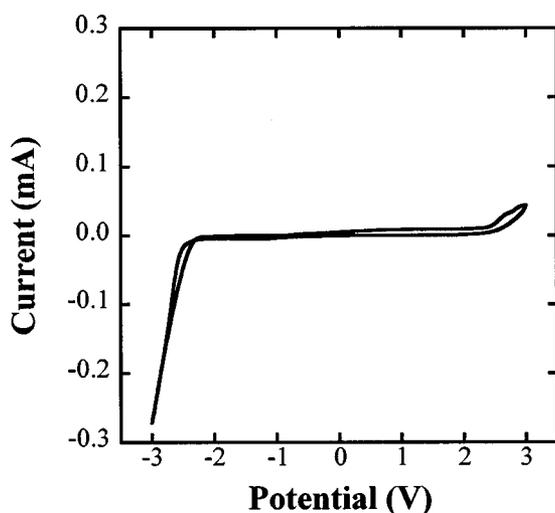
**Spin-coating of conducting polymers onto ITO glass electrodes.**—Chemically synthesized conducting polymers were dissolved in the appropriate solvents and the obtained solutions were used for polymer coating on ITO glass electrodes by means of spin-coating. POT was coated at 11,000 rpm from a solution of 1 wt % POT dissolved in CHCl<sub>3</sub>, resulting in a ~0.2 μm thick POT film. PANI was coated at 11,000 rpm from a solution of 4% emeraldine base dissolved in a mixture of 80 wt % formic acid and 20 wt % dichloroacetic acid, resulting in a ~0.5 μm thick PANI film. The obtained polymer coatings were dried under dynamic vacuum for 24 h prior to their further use. For electrochemical and electrochromic characterization, POT was coated onto a 0.7 × 4.2 cm ITO glass electrode. For the fabrication of PEDOT/POT composite polymer involved display, POT was coated onto a patterned ITO glass electrode prior to the electrochemical deposition of PEDOT. For the fabrication of large-area electrochromic windows, both PANI and POT were coated onto two ITO glass electrodes (5 × 5 cm), respectively.

**Electrochemical and electrochromic characterization of conducting polymers.**—Electrochemical measurements of conducting polymers were performed using the potentiostat with a three-electrode electrochemical cell. Polymer-coated electrodes were used as the working electrodes. Electrochromic measurements of conducting polymers were carried out by combining the potentiostat with a Varian Cary 500 UV-visible (UV-vis) near-infrared spectrophotometer. A three-electrode electrochemical cell made from a quartz cuvette cell was used for electrochromic measurements. Polymer-coated ITO glass electrodes were used as the working electrodes.

**Fabrication of electrochromic devices.**—Electrochromic devices (windows and displays) were fabricated by sandwiching a thin layer of [BMIM][BF<sub>4</sub>] between two polymer-coated ITO glass electrodes with the polymer films facing the inside of the device. Edges of the device were sealed with epoxy resin. Electrical contact for each ITO glass electrode was made by attaching a metal wire using silver paint. For displays, two ITO glass electrodes were used. ITO layer on the electrode used for PANI coating was cut to divide the electrode into seven electrically independent electrodes (Fig. 7c), while the electrode used for PEDOT (or PEDOT/POT) coating was not cut (Fig. 7b). Each ITO glass electrode was then masked with a Scotch tape to pattern seven pixels. After device assembly, electrolyte in each pixel was limited within the space defined by the two Scotch tapes and thus could not contact with the electrolyte in other pixels. Consequently, all seven pixels of the PEDOT (or PEDOT/POT) coated ITO glass electrode were used as one counter electrode, while each pixel of the PANI-coated glass electrode was used as an independent working electrode. This allowed an independent voltage applied on each pixel. During operation, the display was operated by a controller. Therefore, the ON and OFF of color change could be switched among these seven pixels by the controller to display alphanumeric numbers. In order to evaluate the electrochemical and electrochromic performance of the display, any pair consisting of a pixel of PANI-coated ITO glass working electrode and the joined PEDOT (or PEDOT/POT) coated ITO glass counter electrode of the display could be used.

### Results and Discussion

**Synthesis and electrochemical quality control of ionic liquids.**—In this work we referred to the procedures reported elsewhere<sup>19,20</sup> for the synthesis of ionic liquid [BMIM][BF<sub>4</sub>] and its precursor [BMIM][Cl]. In addition to the routine quality evaluation of ionic liquids by ionic conductivity and UV-vis spectrophotometry,

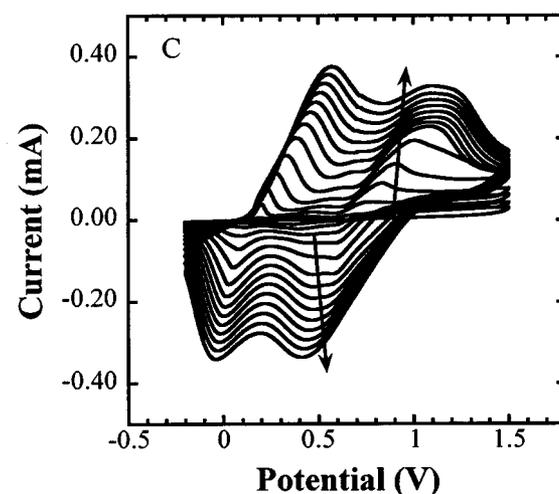
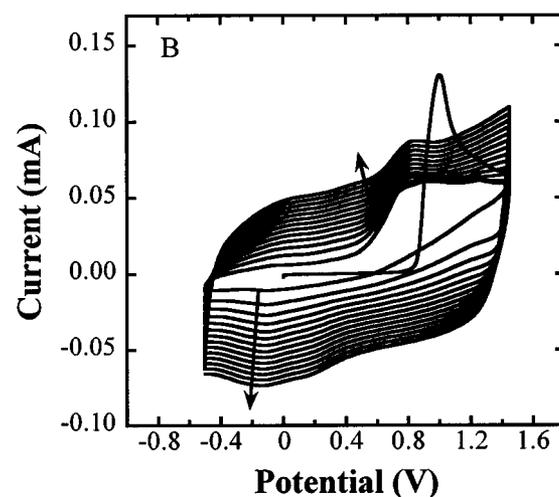
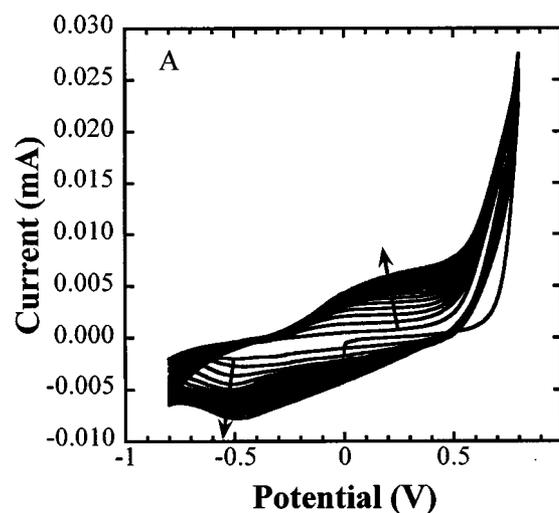


**Figure 1.** CV obtained at a Pt wire electrodes ( $S = 0.016 \text{ cm}^2$ ) for ionic liquid-[BMIM][BF<sub>4</sub>] synthesized from precursor [BMIM][Cl]. Scan rate 50 mV/s.

we also performed the electrochemical characterization of ionic liquids. To be good electrolytes, the electrochemical windows over which the electrolyte is neither reduced nor oxidized at an electrode should be determined prior to their use in device fabrication. Using CV, we were able to measure the electrochemical windows of ionic liquids. Over a large potential range ( $-3$  to  $+3$  V), a typical electrochemical window of ionic liquid [BMIM][BF<sub>4</sub>] was obtained and is shown in Fig. 1. As can be seen, [BMIM][BF<sub>4</sub>] displays a wide electrochemical window ( $-2.5$  to  $+2.5$  V) over which the ionic liquid can be used safely without decomposition. This clearly demonstrates the large electrochemical windows of ionic liquids, which are a promising property for the fabrication of stable and durable electrochemical devices.

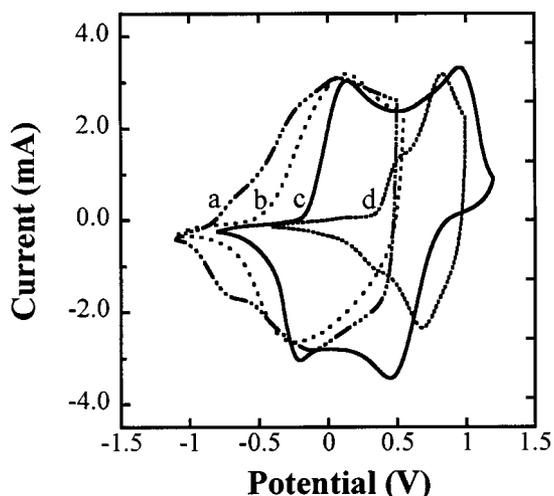
*Electrochemical synthesis of conducting polymers in ionic liquids.*—Subsequently, we investigated the feasibility of electrochemically synthesizing conducting polymers in ionic liquid [BMIM][BF<sub>4</sub>]. PPy, PEDOT, and PANI were selected as the representative polymers. It is well known that an ionic liquid is either a pure solvent or a pure salt. Thus, without the addition of any other salts, we tried to synthesize these polymers from a pure ionic liquid containing only the corresponding monomers. This is different from a conventional synthesis route using an aqueous (or organic) electrolyte, where a salt is usually dissolved in a solvent to obtain the electrolyte and the resulting electrolyte is then mixed with a monomer to prepare the polymerization solution. In the present method, the ionic liquid played the role of both supporting electrolyte and dopant source. We found that similar to other electrolyte systems, PPy or PEDOT could be synthesized from a polymerization solution obtained by dissolving the monomer in the ionic liquid. However, for the synthesis of PANI, another acid was needed as the proton source to ensure the polymer deposition and the electroactivity of the resulting polymer, which is similar to the electrochemical synthesis of PANI in other organic electrolyte systems.<sup>8</sup> In order to ensure the exclusion of water, we used organic acids (such as CF<sub>3</sub>COOH) rather than aqueous ones.

These polymers could be deposited onto different substrate electrodes including metal electrodes (such as Pt, Au) and ITO-coated electrodes. Oxidation potentials of the monomers of these polymers at a Pt electrode in [BMIM][BF<sub>4</sub>], as shown in Fig. 2, were determined to be 0.5 V for pyrrole, 0.8 V for 3,4-ethylenedioxythiophene, and 0.8 V for aniline. These are reasonably low values and are similar to those reported in other electrolyte systems.



**Figure 2.** CVs obtained at a Pt disk electrode ( $S = 0.018 \text{ cm}^2$ ) in (A) 0.1 M pyrrole in [BMIM][BF<sub>4</sub>], (B) 0.1 M 3,4-ethylenedioxythiophene in [BMIM][BF<sub>4</sub>], and (C) 0.5 M aniline and 2 M CF<sub>3</sub>COOH in [BMIM][BF<sub>4</sub>]. Scan rate 50 mV/s.

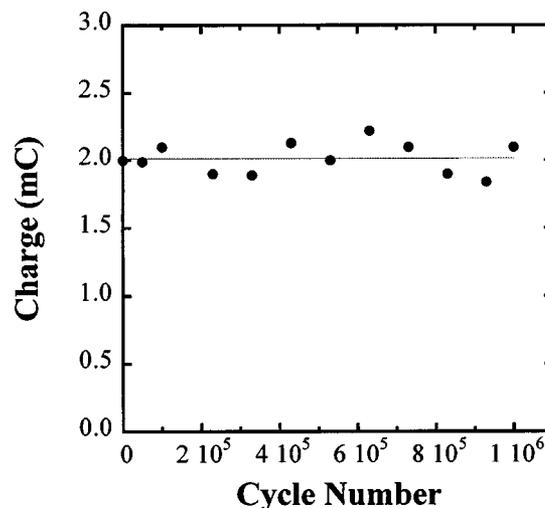
Electrochemical synthesis of these polymers in ionic liquids could be achieved by three typical electrochemical methods, namely,



**Figure 3.** CVs of (a) PEDOT, (b) PPy, (c) PANI, and (d) POT-coated ITO glass electrodes ( $0.7 \times 4.2$  cm) obtained in  $[\text{BMIM}][\text{BF}_4]$ . Scan rate 50 mV/s. PEDOT, PPy, and PANI were prepared electrochemically and POT was prepared by spin-coating as described in the Experimental section.

voltammetric, potentiostatic, and galvanostatic. Figure 2 represents the results obtained by using voltammetry. During the anodic scan, monomers were oxidized and polymerized at the electrodes. The resulting polymers then displayed reduction and oxidation peaks upon potential cycling. The increased currents as shown by arrows indicate the deposition of electroactive polymers onto the substrate electrodes. During the synthesis of PANI (Fig. 2C), only two pairs of peaks, typical redox process of leucoemeraldine  $\leftrightarrow$  emeraldine  $\leftrightarrow$  pernigraniline of PANI, were obtained. The absence of a so-called middle peak indicates the absence of PANI degradation during the synthesis step, which has been observed in aqueous electrolytes.<sup>6</sup> In the latter case, a low potential was always needed to prevent the formation of pernigraniline and thus to avoid polymer degradation. This problem was overcome in ionic liquids in our work. Using the galvanostatic method, we tested the polymerization of these polymers at ITO glass electrodes. The chronopotentiograms (not shown) obtained at an applied current density of  $0.5 \text{ mA/cm}^2$  show that low and constant potentials of 0.80 V for PPy, 1.05 V for PEDOT, and 0.70 V for PANI were observed at a certain period of time after the current was applied, indicating the deposition of electroactive polymers onto the substrate ITO glass electrodes.

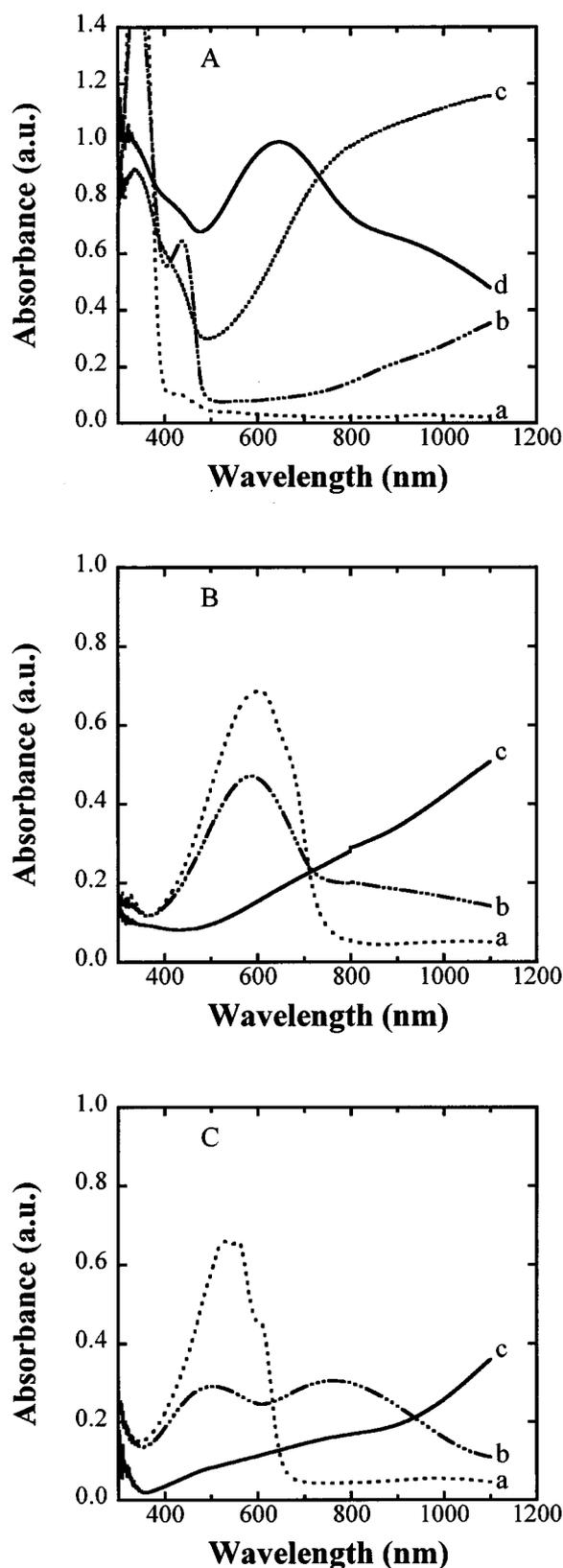
**Electroactivity and electrochromism of conducting polymers in ionic liquids.**—We investigated the electroactivity and electrochromism of conducting polymers, which were electrochemically synthesized from ionic liquids and coated on ITO glass electrodes as discussed previously, in ionic liquid  $[\text{BMIM}][\text{BF}_4]$ . Also, to investigate the feasibility of the use of chemically synthesized conducting polymers in the fabrication of electrochromic devices with ionic liquids, we involved chemically synthesized POT as an example. All polymers showed well-defined CVs in  $[\text{BMIM}][\text{BF}_4]$  (Fig. 3), which were similar to those reported in other electrolyte systems. For polythiophene derivatives, PEDOT and POT, the former showed the redox peaks in a lower potential region than the latter. Higher electron density of repeating units contributed by the 3, 4-fused dioxane ring and the lower polymer bandgap of PEDOT<sup>2</sup> should be responsible for this observation. Once again, only two pairs of peaks were obtained for PANI in  $[\text{BMIM}][\text{BF}_4]$ , which can be assigned to the entire redox process of PANI, *i.e.*, leucoemeraldine  $\leftrightarrow$  emeraldine in the low-potential region and emeraldine  $\leftrightarrow$  pernigraniline in the high-potential region.<sup>10</sup> The absence of the so-called middle peak, which is related to PANI degradation in aqueous electrolytes,<sup>11,12</sup> indicates that the PANI film was



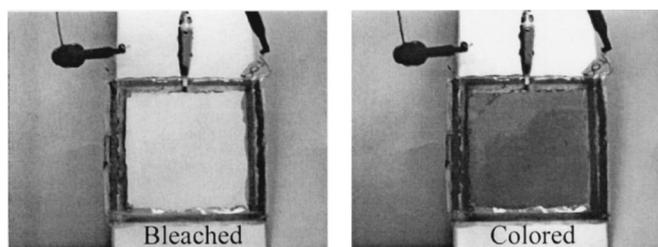
**Figure 4.** Oxidation charge observed at different cycles in  $[\text{BMIM}][\text{BF}_4]$  upon potential pulsing for a PANI-coated ITO glass electrode prepared as in Fig. 3. Potential pulsing was performed between  $-0.6$  and  $+1.1$  V with the pulse width of 0.5 s for  $1 \times 10^6$  cycles.

electrochemically stable in the ionic liquid. During the fabrication of PANI electrochromic devices, this is especially important because the ability to access the entire redox process of PANI would induce high coloration contrast for the devices. To further demonstrate the excellent electrochemical stability of PANI, we cycled a PANI-coated ITO glass electrode by potential pulsing between its leucoemeraldine and pernigraniline under ambient conditions. Using the charge that could be injected into the polymer upon PANI oxidation as an indicator, we found that the PANI film did not degrade in electroactivity in the ionic liquid for 1,000,000 cycles (Fig. 4), except the scattering of the data, which has been confirmed to be associated with the environmental behavior of the ionic liquid  $[\text{BMIM}][\text{BF}_4]$  under ambient conditions (*e.g.*, humidity, temperature, or pressure) during the test. It can be anticipated that use of environmentally more stable ionic liquids (*i.e.*,  $[\text{BMIM}][\text{PF}_6]$ ,  $[\text{BMIM}][(\text{CF}_3\text{SO}_2)_2\text{N}]$ ) could further improve the polymer electrochemical stability.

The *in situ* UV-vis spectra of these polymers at different potentials were obtained in  $[\text{BMIM}][\text{BF}_4]$  and are shown in Fig. 5. As a typical anodically coloring polymer, PANI showed the enhanced absorption as its oxidation level increased. Multiple color change of PANI observed in ionic liquids in the present work is similar to that reported previously in other nonaqueous electrolytes.<sup>21</sup> In the fully reduced leucoemeraldine state at  $-0.6$  V (Fig. 5Aa), the two low-wavelength spectra bands can be assigned to an aromatic  $\pi$ - $\pi^*$  transition (337 nm) related to the extent of conjugation between the adjacent rings in the polymer chain and to radical cations formed in the polymer matrix (437 nm). Due to the presence of the small peak of 437 nm in the visible region, the leucoemeraldine state appeared very light transparent yellow (almost colorless). Intensity of this color was strongly dependent on the thickness of the PANI film. As the potential and thus the oxidation level of PANI was increased, the 337 nm band absorption decreased and the 437 nm band absorption increased, accompanied by the appearance of transparent yellow color for the partially oxidized PANI (between leucoemeraldine and emeraldine), as shown in Fig. 5Ab. Meanwhile, as the potentials were increased, the 437 nm band decreased and a broad free carrier electron band at  $>800$  nm was introduced, indicating the formation of the conducting state of the polymer. In the most conductive state (emeraldine) of PANI at 0.5 V, this broad free carrier electron band became most apparent (Fig. 5Ac). In the form of emeraldine, PANI film showed green color. Further oxidation beyond emeraldine resulted in the decrease of polymer conductivity and hence, the disap-



**Figure 5.** *In situ* UV-vis spectra of polymer-coated ITO glass electrodes ( $0.7 \times 4.2$  cm) obtained in  $[\text{BMIM}][\text{BF}_4]$  at different potentials. (A) PANI: (a)  $-0.6$ , (b)  $+0.1$ , (c)  $+0.5$ , and (d)  $+1.25$  V. (B) PEDOT: (a)  $-1.1$ , (b)  $-0.25$ , and (c)  $+0.5$  V. (C) POT: (a)  $-0.4$ , (b)  $+0.7$ , and (c)  $+1.5$  V. Polymer-coated ITO glass electrodes were prepared as in Fig. 3.



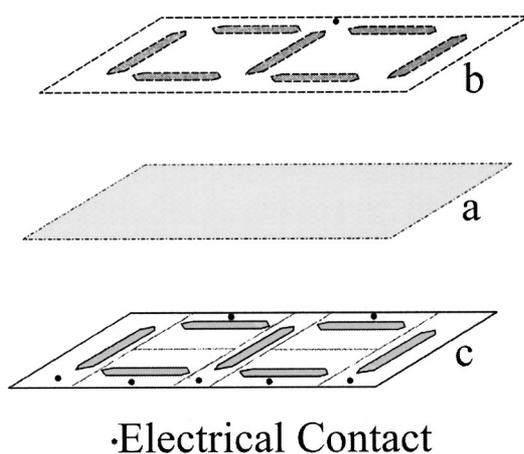
**Figure 6.** Photographs of the large-area PANI/ $[\text{BMIM}][\text{BF}_4]$ /POT electrochromic window ( $5 \times 5$  cm) showing the bleached and colored states.

pearance of the broad free carrier electron band for the fully oxidized state of PANI, pernigraniline (Fig. 5Ad). In the form of pernigraniline, PANI film showed dark blue color with a maximum absorption centered at 645 nm.

In contrast to PANI, PEDOT and POT behaved as the typical cathodically coloring polymers,<sup>2</sup> showing the dark color in the reduced rather than the oxidized states. As shown in Fig. 5Ba, in its fully reduced state at  $-1.1$  V, PEDOT was dark opaque blue with the maximum absorption at 600 nm, which can be assigned to the  $\pi$ - $\pi^*$  transition. This absorption decreased as the potential and thus polymer oxidation level increased (Fig. 5Bb) and finally disappeared for the fully oxidized state of PEDOT at 0.5 V (Fig. 5Bc). Fully oxidized PEDOT was very transmissive light blue and displayed a broad free carrier electron band in the high-wavelength region, indicating its highly conducting state, which is the same observation for the emeraldine form of PANI (Fig. 5Ac). Similar electrochromic behavior was obtained for POT (Fig. 5C), except that its color change took place at higher potentials, which coincides with its higher redox potentials as shown in Fig. 3. Compared to PEDOT, the maximum absorption of POT in its fully reduced state (Fig. 5Ca) shifted to low-wavelength region (540 nm) due to its larger bandgap, resulting in a dark purple color for the polymer.

*Fabrication and performance of electrochromic devices.*—Using ionic liquid  $[\text{BMIM}][\text{BF}_4]$  as electrolyte, we have realized conducting polymer electrochromic devices in two typical modes, *i.e.*, windows and displays, with more efforts on the latter. Both chemically synthesized (via spin-coating) and electrochemically synthesized (from ionic liquids) polymers could be used to fabricate the devices. The opposite electrochromic behavior of polymers as discussed previously, *i.e.*, anodically coloring for PANI and cathodically coloring for PEDOT and POT, allowed us to achieve complementary coloration for all-polymer devices fabricated from these polymers without the introduction of any other inorganic compounds.

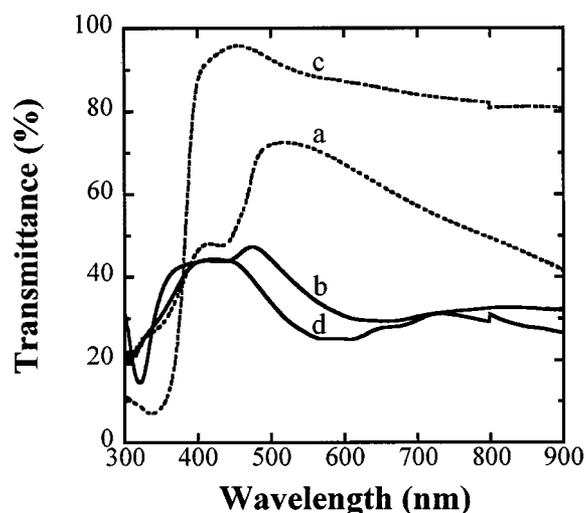
To realize large-area electrochromic windows, at least two factors should be taken into account. One is the uniform coating of conducting polymers in large area, and the other is the well-defined electroactivity and electrochromism of the resulting polymer films in the electrolytes used. Chemically synthesized conducting polymers are preferable for the coating in large scale to realize large-area electrochromic windows. In the present work, we used chemically synthesized PANI and POT as anodically coloring and cathodically coloring polymers, respectively. They were spin-coated onto large-area ITO glass electrodes ( $5 \times 5$  cm). The resulting polymer films showed well-defined CVs (not shown) in  $[\text{BMIM}][\text{BF}_4]$ . Generally, CV peaks become ill-defined as the surface area of the electrode increases. This results in slow and nonuniform coloration of the device. In contrast, in the ionic liquid systems employed in this work, typical CV peaks of PANI and POT were obtained even over a large area. This is the basis for the fabrication of large-area electrochromic windows. A moderate maximum transmittance ( $\sim 30\%$ ) but uniform and fast coloration ( $\sim 1$  s) were realized for a large area PANI/ $[\text{BMIM}][\text{BF}_4]$ /POT electrochromic window fabricated from PANI, POT, and  $[\text{BMIM}][\text{BF}_4]$  in this work. Photographs of the device in the bleached and colored states are shown in Fig. 6.



**Figure 7.** Construction of a seven-pixel alphanumeric display. The device was fabricated from two patterned ITO glass electrodes. One electrode (b) was electrically joined together, the other (c) was electrically independent, allowing each pixel to be addressed individually. A thin layer (a) of  $[\text{BMIM}][\text{BF}_4]$  formed by capillary action was sandwiched between (b) a PEDOT (or PEDOT\_POT)-coated ITO glass electrode and (c) a PANI-coated ITO glass electrode.

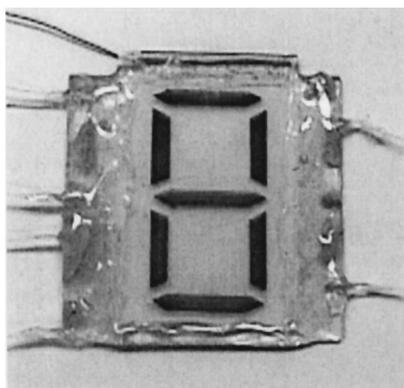
For the fabrication of electrochromic displays, we used PANI as the anodically coloring polymer and polythiophene derivative (PEDOT or POT) as the cathodically coloring polymer. PANI and PEDOT were electrochemically deposited from  $[\text{BMIM}][\text{BF}_4]$  and POT was spin-coated using chemically synthesized polymer. The construction of a seven-pixel alphanumeric display is shown in Fig. 7. In the preliminary work, we fabricated a display with PANI and PEDOT-coated patterned ITO glass electrodes and  $[\text{BMIM}][\text{BF}_4]$ , *i.e.*, PANI/ $[\text{BMIM}][\text{BF}_4]$ /PEDOT. The maximum transmittance was found to be 35% (Fig. 8a and b), which is slightly higher than that of a similar electrochromic device fabricated from the same polymers.<sup>22</sup> Referring to the CVs of polymers in  $[\text{BMIM}][\text{BF}_4]$  (Fig. 3), low coloration contrast of the PANI/ $[\text{BMIM}][\text{BF}_4]$ /PEDOT device can be interpreted by the electrochemical behavior of the couple of PANI and PEDOT. In the colored state of the device, PEDOT was in its fully reduced state, while PANI was in its fully oxidized state (pernigraniline). This made the device display a very dark color. Upon bleaching the device, PEDOT was oxidized to its oxidation state. However, during this process, PANI could be reduced from the pernigraniline to the intermediate oxidation state (emeraldine), not to the fully reduced state (leucoemeraldine). Thus, the green color of emeraldine state (Fig. 5Ac) of PANI would induce some absorbance for the bleached state of the device, resulting in low coloration contrast for the device (Fig. 8a and b). Accordingly, in order to improve the coloration contrast for the device, PANI needs to be reduced to its fully reduced state, leucoemeraldine, upon bleaching the device. We found that POT could satisfy this requirement due to its higher redox potential than that of PEDOT. In fact, PANI can be electrochemically switched between pernigraniline and emeraldine states in the pair of PANI and PEDOT and between emeraldine and leucoemeraldine in the pair of PANI and POT according to their different potentials, as shown in Fig. 3. Therefore, the entire redox process of PANI, leucoemeraldine  $\leftrightarrow$  emeraldine  $\leftrightarrow$  pernigraniline, would be accessible by a PEDOT\_POT composite polymer.

We obtained the PEDOT\_POT composite polymer by electrochemically depositing PEDOT from  $[\text{BMIM}][\text{BF}_4]$  onto the top of a POT pre-coated ITO glass electrode that was prepared by spin-coating from chemically synthesized POT. Using the PEDOT\_POT composite polymer as the cathodically coloring polymer to couple with PANI, the resulting display device PANI/ $[\text{BMIM}][\text{BF}_4]$ /PEDOT\_POT showed well-defined electroactivity between



**Figure 8.** UV-vis spectra of one pixel obtained for a PANI/ $[\text{BMIM}][\text{BF}_4]$ /PEDOT display between (a) bleached ( $-1.3$  V) and (b) colored ( $+1.4$  V) states and for a PANI/ $[\text{BMIM}][\text{BF}_4]$ /PEDOT\_POT display between (c) bleached ( $-1.5$  V) and (d) colored ( $+1.5$  V) states. Details of polymer preparation and device fabrication are described in the Experimental section.

$-1.5$  and  $+1.5$  V. Within this voltage window, PANI could be switched over its entire redox process by the PEDOT\_POT composite polymer so that the improved coloration contrast was achieved for the device as expected. As can be seen, the colored state of the device PANI/ $[\text{BMIM}][\text{BF}_4]$ /PEDOT\_POT (Fig. 8d) was similar to that of the device PANI/ $[\text{BMIM}][\text{BF}_4]$ /PEDOT (Fig. 8b), indicating that PANI was oxidized (by PEDOT) to pernigraniline upon coloring in both cases. However, during bleaching, PANI was reduced all the way from pernigraniline to leucoemeraldine by the PEDOT\_POT composite polymer in the device PANI/ $[\text{BMIM}][\text{BF}_4]$ /PEDOT\_POT, resulting in a more bleached state (Fig. 8c) by about 30% in comparison to that of the device PANI/ $[\text{BMIM}][\text{BF}_4]$ /PEDOT (Fig. 8a). Therefore, a higher maximum transmittance difference of up to 63% (at 560 nm) was observed for the composite polymer-incorporated display device. This satisfies the requirement for a good display.<sup>2</sup> Using voltage pulsing between  $-1.5$  and  $+1.5$  V, we observed a fast coloration speed for the device PANI/ $[\text{BMIM}][\text{BF}_4]$ /PEDOT\_POT, which should be because a significant amount of charge (68% as compared with the maximum charge addressable in 1 s) can be injected into and removed from the device within 100 ms. This speed is comparable to good inorganic-based electrochromic displays.<sup>23</sup> We also obtained a high coulombic efficiency (98%), defined by the ratio of the injected charge at  $+1.5$  V to the removed charge at  $-1.5$  V for this device. This indicates the high redox reversibility and thus helps ensure long-term operation of the device. Obviously, this high electrochemical reversibility of the device is determined by the reversibility of each polymer used in the device. As shown in Fig. 3, all polymers (PANI, PEDOT, and POT) involved in the device are highly electrochemically reversible in the ionic liquid. PANI can be reversibly accessed across its entire redox process (leucoemeraldine  $\leftrightarrow$  emeraldine  $\leftrightarrow$  pernigraniline) in the ionic liquid without degradation. This is the basis of fabricating high-contrast electrochromic devices based on PANI. Furthermore, its excellent electrochemical stability (Fig. 4) upon switching between the fully reduced state (transparent yellow) and the fully oxidized state (dark blue) ensures the long-term operation of the PANI-based electrochromic devices. Finally, this PANI/ $[\text{BMIM}][\text{BF}_4]$ /PEDOT\_POT display device was operated by a controller system, where numeric information was sent by a signal generator through control logic to the driver which sends  $\pm$  voltage signals to drive the redox reaction at the pixel level of the display. Due to



**Figure 9.** Photograph of the PANI/[BMIM][BF<sub>4</sub>]/PEDOT\_POT display (6 × 6 cm) showing the number 8.

the independent electrical contact on each PANI pixel, the voltage level of each pixel can be independently controlled to address the different pixels to display numbers between 0 and 9. A photograph of the display showing the number 8 is shown in Fig. 9 as the example.

### Conclusion

In this work we investigated the applications of ionic liquids as electrolytes in electrochemical synthesis of conducting polymers, in electrochemical and electrochromic characterization of both electrochemically and chemically synthesized conducting polymers, and in fabrication of conducting polymer electrochromic devices. We obtained highly stable electroactivity for PANI in a wide potential range covering its entire redox process for >1,000,000 cycles in [BMIM][BF<sub>4</sub>]. Using [BMIM][BF<sub>4</sub>] as electrolyte, we successfully fabricated the prototypes of alphanumeric displays and large-area electrochromic windows. High device performance of low operation voltages, high coloration contrast, fast coloration speed, and high coulombic efficiency has been realized.

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