Use of polymer/ionic liquid plasticizers as gel electrolytes in electrochromic devices

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Abstract. The dual polymer configuration is commonly used when constructing electrochromic devices (ECDs) due to the expected electrochemical stability and enhanced optical properties. In this configuration, two different polymers are used which are optically complementary. Herein we report the construction and characterization of dual-type ECDs using poly(3,4-ethylenedioxythiophene) (PEDOT) and poly[3,6-bis(2-(3,4-ethylenedioxy)thienyl)-N-methylcarbazole] (PBEDOT-NMCz) as the two complementary electrochromic polymers for the device. A variety of gel electrolyte solutions were prepared and evaluated for these devices. The use of ionic liquids within these gels imparted interesting properties, including long lifetimes, and thermal stability of devices. Switching speeds for the various devices, as well as optical contrasts, were also obtained for the gel electrolytes containing different amounts of ionic liquid as plasticizer.

1. Introduction

Possibly the most widespread application of electrochromic materials is as components of “smart windows” or other such devices such as antiglare rearview mirrors, and electronic paper that pursue the control of transmitted light for variable transmission devices [1-6]. Materials which can reversibly change from a transmissive clear state to an absorbent dark state are the ideal candidates for this purpose. The use of poly(3,4-ethylenedioxythiophene) (PEDOT) as one of these materials is widespread. Its incorporation into electrochromic devices (ECDs) in both the five-layer single polymer ECD and seven-layer dual-polymer ECD configurations has also been accomplished [7-9]. Electrochromic devices are electrochemical cells composed of two electrodes and an electrolytic medium. For dual polymer configurations, two different materials, each coated on one of the electrodes, with the correct optical properties are used to construct the cell using the same electrochemical reaction to promote color changes in both materials and therefore increasing the efficiency of the device. Electrochemical switching of a dual-type electrochromic device involves complementary color change of the constituent polymers. PEDOT, a cathodically coloring polymer, has been used in conjunction with an anodically coloring polymer, such as PBEDOT-NMCz [7-8]. The oxidized form of PEDOT and the reduced form of PBEDOT-NMCz constitute the bleached state. Both neutral PEDOT and oxidized PBEDOT-NMCz show dark blue color, thus increasing the optical density of the electrochromic device in the colored state.

Among the possible electrolytes that can be used for these devices, liquid electrolytes can be undesirable for two main reasons: safety issues related to possible eye damage if they are to be used in eyewear application and potential evaporation of solvent which would lead to device malfunction. The use of ionic
liquids in different electrochemical devices has been reported, showing enhanced lifetimes [10]. The use of ionic liquids is an elegant solution to avoid organic solvents and prevent evaporation, although its liquid nature could still be a safety concern. In this study, we propose their inclusion as part of a solid gel electrolyte as a plasticizer for polyethylene oxide based polymers, expecting to add the benefits of solid electrolytes to those of the ionic liquids. Typical polyelectrolytes include a solid salt in a polymer matrix with solvent to plasticize such that there is higher mobility of ions in the matrix. The ionic liquid in the polymer matrix serves the purpose of both plasticizer and salt.

Although the results presented correspond to variable transmission devices, the possible advances from this approach can be applied in any other electrochromic device showing different color transitions. The potential use of electrochromic materials in chameleonic devices is but one of the many applications expected. The development of optical camouflage requires a variety of colors produced over short periods of time, and the wealth of electrochromic materials makes it easy to envision such a system. Further, applications of ECDs include smart windows, which can not only provide shade for an office or home, but can also reduce energy expenditures from air conditioning by allowing less heat to enter the building during the warmer months. Such systems can be employed on much smaller scales as well, in areas such as eyeglass manufacturing. Achieving a simple way to mimic the full color gamut of human vision remains a challenge for the electrochromic field, but one which is exciting and could be fruitful.

2. Experimental

2.1. Materials
3,6-dibromocarbazole and 3,4-ethylenedioxythiophene (EDOT), and propylene carbonate (PC) were purchased from Sigma-Aldrich. EDOT was distilled under reduced pressure before its use, resulting in a clear, colorless liquid. Bis(3,4-ethylenedioxythiophene)-N-methylcarbazole (BEDOT-NMCz) was synthesized via the reported procedure [11]. Reactions were also run on longer timescales (approx. 12 hrs), resulting in quantitative yields for 3,6-Dibromo-N-methylcarbazole at room temperature. Acetonitrile (ACN) was procured from Fisher Scientific and distilled over calcium hydride (from ACROS). Poly(ethylene glycol) ethyl ether methacrylate (MA), lithium trifluoromethanesulfonate (LITRIF), poly(ethylene glycol) diacrylate (DA) and 2,2-dimethoxy-2-phenyl-acetophenone (DMPAP) were purchased from Aldrich and used as received. Glass beads (50-100 μm diameter) were purchased from Polysciences Inc. 75 x 75 x 0.7 mm indium doped tin oxide (ITO) coated glass with a nominal surface resistance of 15-25 Ω/sq, 7 x 50 x 0.7 mm ITO coated unpolished float glass cuvette slides with nominal surface resistance of 15-25 Ω/sq, and ITO coated polyethylene terephthalate with a nominal resistance of 40-60 Ω/sq were purchased from Delta Technologies. The ionic liquids (ILs), 1-butyl-3-methylimidazolium hexafluorophosphate (BMIMPF₆) and 1-butyl-3-methylimidazolium tetrafluoroborate (BMIMBF₄), were obtained from Fluka.

2.2. Instruments
CH Instruments CHI 400 and CHI 660A potentiostats were used both for the electrochemical polymerization of EDOT and BEDOT-NMCz as well as the study of the ECDs. A Perkin-Elmer UV-Vis-NIR Lambda 900 spectrophotometer was used for optical studies. Thermal stability studies were carried out with a TA Instruments Hi-Res TGA 2950. Differential Scanning Calorimetry (DSC) studies were performed on either a TA Q100 or DSC-2920. DSC was performed in platinum pans up to 700°C at a rate of 10°C/min.

2.3. Electrochemical polymerization
A special cell was fabricated for the electrochemical polymerization of EDOT and BEDOT-NMCz onto 56 cm² ITO coated substrates. Approximately 30 cm² were coated with the electrochromic polymers using this cell configuration. PEDOT was deposited electrochemically onto the glass/ITO substrate from an acetonitrile solution containing 20 mM EDOT and 0.1 M BMIMPF₆ or BMIMBF₄ at 1.2 V (vs. a non-aqueous Ag/Ag⁺ reference, 0.456 V vs. NHE). PBEDOT-NMCz was deposited onto PET/ITO from a 1 mM BEDOT-NMCz solution containing 0.1 M BMIMPF₆ or BMIMBF₄ at 0.7 V (vs. Ag/Ag⁺) and further reduced to the pale yellow neutral form at -0.8 V (vs. Ag/Ag⁺). Both polymers were washed with acetonitrile, dried, and stored in a desiccator until the device was prepared. The structures of these polymers are shown in Figure 1.

![PEDOT and PBEDOT-NMCz structures](image)

**Figure 1**: Structures of cathodically coloring PEDOT and anodically coloring PBEDOT-NMCz electrochromic polymers

2.4. Device Construction

The gel electrolyte was composed of a poly(ethylene glycol) based acrylate macromonomer, photoinitiator, ionic liquid as plasticizer, glass beads. Ionic liquids were used in place of a typical salt, such as LITRIF, and it had the same plasticizing effect as the material which is typically used for these devices, propylene carbonate. Approximately 0.5 mL of the gel electrolyte solution was poured onto the PEDOT coated ITO glass and the PBEDOT-NMCz coated PET-ITO was placed over it, with the conducting surfaces facing each other. The glass beads are present as a spacer in order to prevent electrical shorting between ITO layers. The two electrodes were hand pressed together to remove any air-bubbles within the device and to remove excess macromonomer solution. Polymerization of the macromonomer in the presence of photoinitiator DMPAP, was carried out under UV light [365 nm, 5.8 mW/cm²] for 15 minutes.

3. Results and Discussion

3.1. Electrochromic Device Background

A typical dual-polymer electrochromic device consists of seven layers: a glass or plastic (or other clear, insulating material) substrate, a conducting layer, a polymer layer, an electrolyte layer (liquid or gel; used for ion transport), the complementary polymer layer, another conducting surface, and another insulating substrate. The “sandwich” device is typically hermetically sealed for longevity. This is particularly necessary for any liquid electrolyte, where solvent evaporation or leakage is an issue.
For gel electrolytes, a UV-curable resin is used allowing the medium to crosslink and seal itself. In our system, the application of ionic liquids replaces the propylene carbonate plasticizer and the electrolyte portion of the gel matrix. A representation of a typical device is shown in Figure 2.

![Figure 2: Schematic Architecture of a Seven-Layer ECD (Dual-Polymer Device)](image)

### 3.2. Thermal Evaluation of Ionic Liquids and ECDs with IL-based Gel Electrolytes

DSC was performed on a variety of gel electrolyte compositions. The glass transition temperature ($T_g$) of the gel electrolyte was evaluated, using various weight percentages of propylene carbonate (PC) and poly(ethylene glycol) diacrylate (PEG-DA) as well as several weight percentages of ionic liquid and poly(ethylene glycol) monoacrylate (PEG-MA). A summary of this data appears in Table 1. The Fox equation has been used to estimate the glass transition temperature, and these predictions agree reasonably well with the observed values. In both cases, there is a decrease in the $T_g$ corresponding to increasing concentrations of PC or IL. In the case of ionic liquid, $T_g$s were significantly lower indicating that gel compositions using ionic liquids could have reasonable switching speeds down to these temperatures.

| Wt.% IL / PEG-MA | Est. $T_g$ (°C) (Fox) | $T_g$ (°C) | Wt.% PC / PEG-DA | $T_g$ (°C) |
|------------------|-----------------------|------------|------------------|------------|
| 20% / 80%        | -55.00                | -53.63     | 10% / 90%        | -33.44     |
| 40% / 60%        | -58.8                 | -56.93     | 20% / 80%        | -36.38     |
| 60% / 40%        | -64                   | -59.12     | 30% / 70%        | -36.34     |
| 80% / 20%        | -69.90                | -72.01     | 40% / 60%        | -44.48     |
| 100% PEG-MA (w/ LITRIF) | N/A | -37.43 | 100% PEG-DA (w/ LITRIF) | N/A |

**TABLE 1:** Glass transition temperatures for a variety of gel electrolyte compositions and their estimated values when using the Fox Equation.

Further, compositions of both BMIMPF$_6$ and BMIMBF$_4$ with PEG-DA have been evaluated for their thermal decomposition ($T_{decomp}$). Onsets for the degradation of the device, since degradation of the electrolyte will lead directly to device failure, are reported. An advantage observed with this data is the increase of temperature tolerance with increasing percent composition of IL. In the case of BMIMPF$_6$, a four-fold increase, 20% to 80% IL vs. PEG-DA, resulted in a 21.09°C increase in degradation onset temperature. For BMIMBF$_4$, the same four-fold increase resulted in a 9.12°C increase in tolerance (Table 2). The mass percentage of gel electrolyte remaining at 350°C was over 90% for all cases, retaining as much as 97.62% of its mass for 40% BMIMBF$_4$ / 60% PEG-DA.

| Wt.% IL / PEG-DA | Est. $T_g$ (°C) (Fox) | $T_g$ (°C) | Onset for $T_{decomp}$ (°C) |
|------------------|-----------------------|------------|----------------------------|

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3.3. Electrochromic Evaluation of ECDs With Ionic Liquid-based Gel Electrolytes

The dual-polymer electrochromic devices comprised of PEDOT and PBEDOT-NMCz switched between a dark blue state at an applied voltage of 1.4V and a yellow, transparent state at an applied potential of -1.0 V. An ECD in the colored and bleached states is shown in Figure 3. The device is stable in both states under open circuit.

![Figure 3: (left) Bleached state consisting of oxidized PEDOT and reduced PBEDOT-NMCz (right) Colored state consisting of reduced PEDOT and oxidized PBEDOT-NMCz](image)

The 30cm² dual-polymer devices were also evaluated for lifetime (i.e. the number of switching cycles it can sustain without an appreciable loss of contrast) as well as switching speed. The switching speeds from both colored to bleached states, as well as the reverse process, have been measured by calculating the time taken for the device to achieve a 90% change in photopic transmittance. Chronocoulometry is applied to the device from -1 V to 1.4 V with the PEDOT coated electrode acting as counter and reference electrode, which is colored to bleached. The reverse case is also evaluated. The speeds (Table 3) show a trend of faster switching speeds for BMIMBF₄ versus BMIMPF₆ for all compositions, and a general increase in switching time for a general increase in ionic liquid content of the gel electrolyte.

| Wt.% IL / PEG-DA | Switching Speed (s) | Switching Speed (s) |
|------------------|---------------------|---------------------|
|                  | Colored → Bleached  | Bleached → Colored  |
| 20% BMIMPF₆ / 80%| 0.9                 | 1.4                 |
| 40% BMIMPF₆ / 60%| 0.6                 | 0.7                 |
| 60% BMIMPF₆ / 40%| 0.6                 | 0.8                 |

**TABLE 2:** DSC (T_g) and TGA (T_{decomp}) data for the gel electrolyte compositions
80% BMIMPF$_6$ / 20% 1.1 0.7

| Electrolyte Composition | Switching Speed (s) | Optical Contrast |
|-------------------------|---------------------|-----------------|
| 20% BMIMBF$_4$ / 80%    | 0.5                 | 0.9             |
| 40% BMIMBF$_4$ / 60%    | 0.5                 | 0.6             |
| 60% BMIMBF$_4$ / 40%    | 0.4                 | 0.5             |
| 80% BMIMBF$_4$ / 20%    | 0.5                 | 0.6             |

**TABLE 3**: Switching speeds for Dual-Type ECDs with varying gel electrolyte compositions

The transmittance values were observed at 555 nm. The device was observed to have a 35-40% optical contrast. The absorbance spectrum corresponding to the contrast data for the fresh device appears in Figure 4.

![Graph showing optical contrast](image)

**Figure 4**: Optical Contrast for a PEDOT / PBEDOT-NMCz Dual-Type ECD

4. Conclusions

Dual polymer PEDOT/ PBEDOT-NMCz electrochromic devices were evaluated. Inclusion of ionic liquids in the composition of a UV-curable gel electrolyte resulted in enhanced thermal stability of the resulting gel. All of the devices with different ionic liquid compositions have shown switching speeds of ca. 1 second. These initial results are encouraging for the replacement of volatile organic solvents with ionic liquids in the gel electrolyte matrix. It is clear that there is a future for devices which can deliver high optical contrasts, high thermal stability, low energy consumption, fast switching speeds, long lifetimes, and a wide variety of colored states. Electrochromic materials and their corresponding electrochromic devices are constantly improving in each of these areas, and their performance can benefit from the use of ionic liquids.
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