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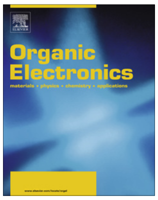

Electrochromic properties as a function of electrolyte on the performance of electrochromic devices consisting of a single-layer polymer

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ABSTRACT

Herein, a study on varying salts and their composition used in the gel electrolyte for a one-step lamination assembly procedure for electrochromic devices was carried out to explore their effects on various electrochromic performance parameters, such as color uniformity, photopic contrast, switching speed, and optical memory. Electrochromic polymers formed in different gel electrolyte compositions are highly dependent on the type, amount, and composition of salt used. The following groups of salts were investigated: ionic liquids, ammonium salts, and lithium salts. The lithium salts yielded devices with the best color uniformity, photopic contrast as high as 48%, and switching response speeds as low as 1 s for 5.5 cm^2 devices using the electroactive monomer 2,2-dimethyl-3,4-propylenedioxythiophene (ProDOT-Me_2) to generate the electrochromic polymer. Hermetically sealed electrochromic devices exhibited optical memory of 27 h for a 2% photopic transmittance loss under normal laboratory conditions, and a 171 cm^2 electrochromic device was demonstrated.

1. Introduction

Electrochromism (EC) is a color change in response to an applied electrical charge [1,2]. Among the numerous types of electrochromic materials ranging from the inorganic such as tungsten oxide (WO_3) and nickel oxide (NiO), organic small molecules like bipyridiliums (viologens) to conjugated polymers, conjugated polymers are of interest due to their color variety and variability, rapid response time, open air processing, high optical contrast, relatively low cost, and light weight [3,4]. Recent advances in viologen and tungsten oxide electrochromic materials have led to commercialization in rearview mirrors, smart windows, electro-transparent panoramic sunroofs, and more [5–10]. Some high profile examples are the Boeing 787 Dreamliner's windows eliminating the need for manual shades. Also, Maybach has incorporated the use of electrochromics into their roofs, called electro-transparent panoramic glass roof, allowing an open driving experience [11].

Traditionally, electrochromic polymers are prepared via electrochemical deposition, in which monomers are

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polymerized onto an electrode surface from an electrolyte bath [6,12]. However, due to the nucleation and growth nature of electropolymerization, this method is very sensitive to the substrate surface and any defect will ultimately lead to a defect in the polymer film. Moreover, a sizeable amount of waste is generated due to leftover monomers and byproducts that are generated during the polymerization that limit the recyclability for further polymerization is a major cost impediment for commercialization.

We previously reported a one-step method to make electrochromic devices, called the *in situ* approach [13]. In this method, a liquid monomer electrolyte is first prepared by dissolving electroactive monomers into a liquid electrolyte composed of salt, solvent, low molecular weight PEG with acrylate end functional groups, and a photoinitiator. The liquid monomer electrolyte is then sandwiched between two electrodes with subsequent photopolymerization of the acrylate end groups under UV light forming a cross-linked gel matrix. Electrochemical conversion of monomer to electrochromic polymer takes place inside the solid gel electrolyte using a potential sufficient to oxidize the monomer. This results in an electrochromic polymer/gel electrolyte composite layer in close proximity to the working electrode rather than a electrochromic polymer film. For simplicity, the electrochromic polymer/gel layer is referred to as a “film” throughout this study. This one-step *in situ* procedure eliminates the need for an electrolyte bath, and all the electrolyte material is used for the device. A variety of thiophene-based monomers, such as 3,4-ethylenedioxythiophene, 2,2-disubstituted 3,4-propylenedioxythiophenes, and 1,3-disubstituted 3,4-propylenedioxythiophenes have been reported to be viable monomers for *in situ* polymerization. Previously, we reported a high-throughput screening method using the *in situ* procedure for several ProDOT monomers within a single electrochromic device (ECD), resulting in a continuum of copolymer compositions that exhibited the full spectral range of subtractive colors [14].

To be useful in eyewear and rearview dimming mirror applications, EC materials must possess color uniformity, greater than 50% photopic contrast, switch speed of less than 1 to 5 s, high coloration efficiency, optical memory, and long-term stability greater than 10,000 cycles. Here, the salts used in the gel electrolyte were varied to determine which will give optimum device performance keeping the monomer 2,2-dimethyl-3,4-propylenedioxythiophene (ProDOT-Me_2) constant, poly(2,2-dimethyl-3,4-propylenedioxythiophene) (PProDOT-Me_2) switches between purple in the neutral state and colorless in the oxidized state, and yields a higher photopic contrast than other PProDOT derivatives and PEDOT [12,15]. Commonly used salts in the gel polymer electrolyte were chosen for the study such as lithium trifluoromethansulfonate (LiTRIF), lithium bis(trifluoromethane)sulfonamide (LiTFSI), lithium tetrafluoroborate ($LiBF_4$), tetrabutylammonium hexafluorophosphate ($TBAPF_6$), tetrabutylammonium tetrafluoroborate ($TBABF_4$) and the ionic liquids: 1-butyl-3-methylimidazolium tetrafluoroborate (BMIM BF_4), and 1-butyl-3-methylimidazolium hexafluorophosphate (BMIM PF_6). Chemical structures for the salts and monomers are shown in Fig. 1.

2. Experimental

2.1. Materials

All aforementioned salts and ionic liquids, propylene carbonate, poly (ethylene glycol) diacrylate ($M_n = 700$ g/mol) and dimethoxyphenylacetophenone (DMPAP) were purchased from Sigma–Aldrich and used as received. Indium Tin Oxide (ITO) coated glass (sheet resistance 8∼12 Ohms/sq) and ITO coated polyethylene terephthalate (PET) substrates (sheet resistance 60 Ohms/sq) were purchased from Delta Tech Inc. and Bayview Optics Inc., respectively and were cleaned by rinsing with acetone prior to use. UV-sealant (UVS 91) glue was purchased from Norland Products, and a two-component epoxy adhesive (EP41S-1ND) was purchased from Master Bond Products. 2,2-dimethyl-3,4-propylenedioxythiophene (ProDOT-Me_2) was synthesized according to the reported procedure [15]. 3,4-ethylenedioxythiophene (EDOT) was purchased from Heraeus Clevios GmbH and distilled under reduced pressure before use.

2.2. Liquid monomer electrolyte

5 g of propylene carbonate, 5 g of poly (ethylene glycol) diacrylate, 17.5 mg of photo-initiator, DMPAP and varying amounts of salts as required for this study were added together and sonicated for 10 min until all solids were dissolved. Monomer was then added at 2.5 wt% with respect to the weight of all other components and sonicated for 30 s.

2.3. Electrochromic device assembly

ITO coated glass (1.91×5.1 cm^2) was used as the working electrode and its perimeter was covered with a silicon rubber gasket (0.79 mm) to give an active device area of 5.5 cm^2. The liquid monomer electrolyte was then drop cast onto this active area and ITO coated PET (1.91×5.1 cm^2) was placed atop as the counter electrode. The device was then placed inside a UV crosslinker to cure the gel electrolyte under 365 nm UV light for 5 min at 5.8 mW/cm^2 and sealed with UV curable glue. Under a constant potential of +3 V, the monomer was converted to electrochromic polymer for an appropriate conversion time commensurable with our study. Larger devices (9×19 cm^2 active area) were fabricated by injecting monomer electrolyte into a preassembled device frame (10.3 cm × 20.3 cm) hermetically sealed with Masterbond epoxy adhesive, UV cured and the monomer was converted to electrochromic polymer as stated above. All electrochromic devices were cycled between their bleached and colored states at ±2 V (pulse width = 2 s) five times before data was recorded.

2.4. Instrumentation

All electrochemistry was performed using a CHI 700 potentiostat. A UVP CL-1000 Crosslinker (365 nm) was used to cure the liquid monomer electrolyte. Ionic