



1-Ethyl-3-methylimidazolium tetrafluoroborate-doped high ionic conductivity gel electrolytes with reduced anodic reaction potentials for electrochromic devices



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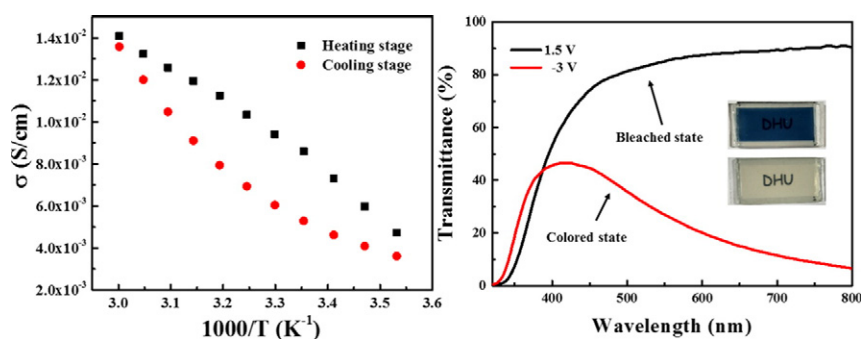
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HIGHLIGHTS

- The gel electrolyte with reduced anodic reaction potential was introduced in electrochromic devices.
- The gel electrolyte exhibits high ionic conductivity due to the addition of charge carriers from ionic liquid.
- Electrochromic devices assembled with the gel electrolyte exhibit higher contrast under small applied potentials.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 29 October 2016

Received in revised form 10 January 2017

Accepted 12 January 2017

Available online 12 January 2017

Keywords:

Ionic liquid

Gel electrolyte

1-Ethyl-3-methylimidazolium tetrafluoroborate

Electrochromic device

ABSTRACT

The electrolyte plays an important role in an electrochromic device (ECD), and an ideal electrolyte can greatly improve the electrochromic performance of the device. Here, we report the preparation of a 1-Ethyl-3-methylimidazolium tetrafluoroborate ([Emim]BF₄)-doped Poly(methyl methacrylate) (PMMA)-based gel electrolyte for electrochromic applications. By the doping of the [Emim]BF₄, the ionic conductivity of the gel electrolyte is improved (2.9×10^{-3} S/cm at room temperature and 10^{-2} S/cm at 40 °C). Most importantly, the addition of the [Emim]BF₄ could reduce the anodic reaction potentials in an ECD, which could enable ECD bleaching at smaller applied voltages and avoid the degradation of optical modulation induced by ion-trapping in tungsten oxide (WO₃) films. This novel electrolyte provides a promising platform for low anodic reaction potential electrochromic devices.

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1. Introduction

The optical properties of electrochromic devices (ECDs) change in response to a small electric potential difference. They are mainly used for information displays, variable reflectance mirrors, supercapacitors,

and smart windows [1–4]. The electrolyte is the most important component in an ECD and is used to conduct ions between two electrodes [5,6]. The electrolytes for ECDs need to meet the following requirements: (i) high ionic conductivity and low electronic conductivity [7]; (ii) high transparency; and (iii) good electrochemical stability [8] and a narrow potential window for inducing a color transition. We have reported ECDs with liquid electrolytes [9,10] but they suffer long-term sealing problems and electrolyte leakage. Much research has therefore focused on the use of gel polymer electrolytes to solve these problems [11,12].

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Gel polymer electrolytes are usually obtained using a polymer as the host and a liquid electrolyte to provide transmission ions. The most commonly used polymer matrices are poly(methyl methacrylate) (PMMA) [13], poly(ethylene oxide) [14,15], poly(acrylonitrile) [16], poly(vinylidene fluoride) [17], and poly(vinylidene fluoride-hexafluoropropylene) (PVDF-HFP) [18]. PMMA is the most used polymer matrix because of its excellent optical properties [19].

The cohesive properties of gel polymer electrolytes can solve sealing problems, but their ionic conductivities are lower than those of liquid electrolytes [20,21]. This problem can be solved by using ionic liquids (ILs) as liquid electrolytes. ILs are room-temperature molten salts, which mostly consist of organic ions, and have almost unlimited structural variations [22]. The ionic nature of ILs effectively reduces evaporation losses and provides high ionic conductivity [23]. ILs are widely used as electrolytes in electrochemical devices such as batteries [24], supercapacitors [25], and solar cells [26], and their use greatly improves the performances of these devices [27]. Most ILs have a high transmittance, therefore they are suitable for use in ECDs. Lu et al. first reported the use of ILs in π -conjugated polymer ECDs [28], and since then ILs have been used to replace lithium salts because they can act as both mobile ions and plasticizers in the electrolyte [29,30]. Lodge et al. reported the use of ion gels consisting of block copolymers and ILs [31–33] as solid-state polymer electrolytes in electrochemical devices such as electrochemiluminescent devices [34,35] and ECDs [4,36].

Low electrochemical reaction potentials are also important for ECDs. A lower electrochemical reaction potential enables completion of the coloring/bleaching process under smaller external voltages, which reduces energy consumption. In WO_3 -based ECDs, the WO_3 films always suffer from ion-trapping-induced degradation of optical modulation [37]. It is therefore desirable to investigate novel gel polymer electrolytes with reduced anodic reaction potentials because this could enable ECD bleaching at smaller applied voltages and avoid the degradation of optical modulation induced by ion trapping. However, to the best of our knowledge, there have been no reports of gel polymer electrolytes with reduced anodic reaction potentials.

In this study, we developed a novel high ionic conductivity gel electrolyte by blending a PMMA/ Li^+ system and 1-Ethyl-3-methylimidazolium tetrafluoroborate ([Emim] BF_4). It has been reported that [Emim] BF_4 has good ionic conductivity at low temperatures [8] and propylene carbonate (PC) in the PMMA/ Li^+ system can serve as a plasticizer, which enhances ion transport. The electrolyte was used in an ECD, i.e., glass/fluorine-doped tin oxide (FTO)/ WO_3 /PMMA-[Emim] BF_4 composite electrolyte/FTO/glass; a WO_3 film was used as the electrochromic layer because WO_3 blocks solar heating caused by transmission of infrared light in the colored state, and acts as a normal window in the bleached state [38]. The ECD based on the PMMA-[Emim] BF_4 composite electrolyte showed a reduced anodic reaction potential, leading to an enhanced electrochromic performance compared with that of an ECD based on a normal PMMA/ Li^+ system electrolyte.

2. Experimental section

WO_3 films were grown on FTO-coated glass as described in our previous report [39]. A PMMA-based electrolyte was prepared by dissolving PMMA (Aldrich, molecular weight ~996,000, previously dried at 80 °C for 12 h, 1 g) and 1 M LiClO_4 (99.9%, anhydrous, Aladdin, 9 g) in PC (CP) and stirring at 70 °C to complete dissolution. A PMMA-[Emim] BF_4 composite electrolyte was prepared by mixing the 1 M LiClO_4 /PC solution, PMMA, and [Emim] BF_4 (99%, Monils Chem. Eng. Sci. & Tech. (Shanghai) Co., Ltd.) at final LiClO_4 /PC:PMMA:[Emim] BF_4 weight ratios of 8.1:0.9:1, and stirred at 70 °C to complete dissolution.

The electrolyte was drop-cast onto WO_3 -coated FTO electrodes and pure FTO surfaces. The two FTO-coated electrodes were pressed together using 50 μm 3 M adhesive tape to prevent electrical short circuiting within the device. The device edges were sealed with UV epoxy glue.

The area of the ECD was 2.5 cm \times 5 cm; the ECD structure is shown in Fig. 1.

3. Characterization

The electrochromic film crystal structure was determined by powder X-ray diffraction (XRD; D/max 2550 V, Rigaku, Tokyo, Japan) using $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) at 40 kV and 300 mA. The morphology of the electrochromic film was examined using field-emission scanning electron microscopy (S-4800, Hitachi, Tokyo, Japan) at 5 kV.

Electrolyte impedance measurements were performed by sandwiching the electrolyte film (4 cm \times 2.5 cm) between two steel electrodes. The thickness of each sample was measured using a screw gauge micrometer. The measurements were performed at room temperature using a Zahner electrochemical workstation (Zennium CIMPS-1). The frequency range was 10^{-1} to 10^5 Hz, amplitude 5 mV. The temperature dependence of the electrolyte conductivity during heating and cooling cycles was investigated by thermal scanning conductometry between 10 and 60 °C using an S230 Seven Compact conductivity meter with an InLab 731-ISM four-electrode conductivity cell (Mettler-Toledo); data were recorded at 5 °C intervals.

Cyclic voltammetry (CV) tests and chronoamperometric (CA) measurements were performed on the ECDs using a CHI760D electrochemical workstation (Shanghai Chenhua Instruments, China). Cyclic voltammograms were recorded by cycling five times between -3 and $+3$ V with electric field scanning steps of 100 mV/s. The CA measurements were performed using voltages stepped between -3 and $+1.5$ V with a delay time at each voltage of 10 s.

The ultraviolet-visible (UV-vis) transmittance spectra, in situ transmittances, and coloration-bleaching times of the electrodes were obtained using a Lambda 950 instrument (Perkin Elmer, Waltham, MA, USA).

4. Results and discussion

4.1. Structural and morphological characterization

Fig. 2(a) shows the XRD patterns of the bare FTO glass and a WO_3 film deposited on an FTO-coated glass substrate. The XRD pattern of the FTO glass can be clearly indexed to tin oxide (JCPDS Card No. 70-4176) and all the peaks in the pattern of the hydrothermally grown film can be indexed to the orthorhombic phase of $\text{WO}_3 \cdot 0.33\text{H}_2\text{O}$ (JCPDS Card No. 54-1012). Fig. 2(b)–(d) show the morphology of the $\text{WO}_3 \cdot 0.33\text{H}_2\text{O}$ electrode. The figure shows that a thin film of large area with a uniform hierarchical nanostructure composed of nest-like nanosheets and nanoribbons was obtained; this facilitates ion insertion/deinsertion into WO_3 . Cross-sectional views of the film (Fig. 2e and f) show that the nanoribbon bundles grew vertically on the

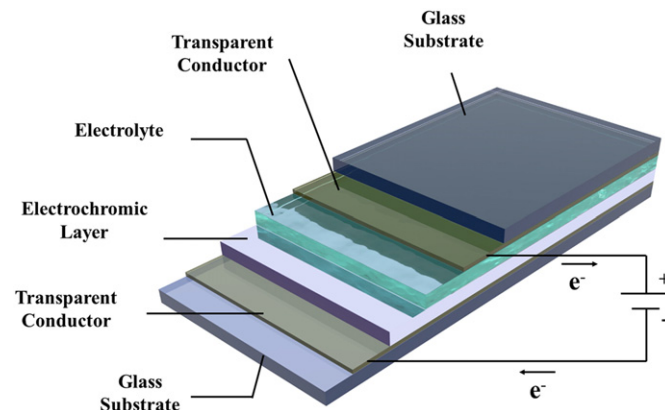


Fig. 1. Schematic diagram of ECD structure.

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