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Ionogels encompassing ionic liquid with liquid like performance preferable for fast solid state electrochromic devices

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Abstract

Novel ionogels encompassing an ionic liquid encaged in an inorganic matrix were synthesized by sol–gel chemistry. The ability of these highly conducting ionogels ($\sim 10^{-2}$ S cm^{-1} at 25 °C) to act as liquid electrolytes in spite of their solid form has been exploited in inorganic electrochromic devices based on tungsten oxide and Prussian blue electrodes. These devices exhibit extremely fast switching kinetics and make it the best and only candidate for the realization of fast all solid state electrochromic devices.

Keywords: Ionic liquids; Sol–gel; Electrochromic devices; Electrolytes; Fast kinetics ECD

1. Introduction

Inherent difficulties in synthesizing solid electrolytes, ubiquitous in all electrochemical devices with outstanding performance characteristics are a major hindrance in the development of many of our technologies that cater to the need of our society [1,2]. Many of the earlier issues such as low ionic conductivity, electrochemical stability, corrosion, thermal stability and low vapor pressure have been resolved by ionic liquids, which have attracted the attention of both academia and industries [3–5]. Room temperature ionic liquids, which have recently aroused a surge of interest as electrolytes, are in the forefront area of chemical research. Furthermore, with the revival of commercial interest in the development of optical switching devices for the dynamic (controllable and switchable) modulation of visible and near infra-red (NIR) radiation, electrochromic technology is being touted as a forerunner among the several existing energy efficient technologies for energy efficiency [6,7].

One of the earliest electrochromic (EC) materials tungsten trioxide (WO_3) was brought to public attention some 38 years ago, thanks to the seminal work by Deb [8], and continues to be the material of choice due to its superior stability compared to organic or polymeric electrochromes and a high contrast ratio despite slow switching times [9,10]. The sluggish device kinetics can be accelerated but at the cost of durability of the device. The electrochromic film/device shows fast switching times in liquid electrolytes but fails to retain its switching behavior in a polymer electrolyte system [10–13]. Formation of a durable, leakage free and a high shelf life device entails the use of a solid polymeric material. From here stems the need to immobilize liquid electrolytes in a solid matrix that will warrant their use not only in all solid state EC devices, but also in other electrochemical cells.

Here, we report an alternative method based on sol–gel chemistry wherein an ionic liquid is ensconced in a solid matrix composed of inorganic materials, without compromising on its electrochemical and thermal properties. The ensuing ionogels or electrolytes are full of ions and have been prepared by a simple non-hydrolytic sol–gel [14], route involving ionic liquids, which is a variant of the strategy proposed by Neouze et al. [15].

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2. Experimental

1-Methylimidazole was obtained from HiMedia, India, while ethyl bromide and cyclohexane used were of reagent grade; formic acid, ethyl acetate and isopropyl alcohol were used as received from Merck India Ltd. Tetraethyl orthosilicate (TEOS) was obtained from Aldrich while Lithium bis(perfluoroethylsulfonylimide) [LiPFSI] salt was kindly supplied by 3M, USA, and the latter was vacuum dried at 120 °C overnight. 1-Ethyl-3-methylimidazolium bis(perfluoroethylsulfonyl)imide [EMIPFSI] was prepared by a slight modification of a previously reported method and was obtained as a transparent liquid [16]. 1-Ethyl-3-methyl imidazolium bromide [EMIBr] was first prepared by a metathesis reaction and reacting 1-methylimidazole with ethyl bromide and it was recrystallized twice. The anion exchange reaction was carried out from Br^- to bis(perfluoroethylsulfonyl)imide by heating an eqimolar mixture of EMIBr and LiPFSI and finally filtered through activated alumina to give an anhydrous, highly pure, colorless liquid of EMIPFSI.

Tetraethyl orthosilicate (TEOS) was mixed with formic acid (FA) in EMIPFSI. The molar ratio was kept constant (TEOS:FA:EMIPFSI: 1:7.8:0.5); further 0.1 M LiPFSI was added to the solution mixture and was stirred for a few minutes. The solution was then injected into a cavity with a syringe in a pre-assembled electrochromic device. The device was fabricated with WO_3 as the primary electrode and Prussian blue as the counter electrode as they are complementary electrochromic materials and deposition of these coatings is summarized elsewhere [17,18]. The films were separated by an acrylic tape of 250 μm thickness and the edges were sealed with an epoxy sealant and the area of the device was $8.5\ \text{cm} \times 4\ \text{cm} = 34\ \text{cm}^2$.

Five devices of the same dimensions and configuration were made under similar experimental conditions and tested for their electrochromic response. The filled device was then ultrasonicated for 30 min to enable gelation. The resulting device contained a transparent electrolyte solidified in situ at ambient temperature and suffers from absolutely no shrinkage. Fabrication of devices with polymeric electrolytes and free of shrinkage is not generally easily accomplished.

UV–Vis Perkin–Elmer Lambda 25 spectrophotometer was used for recording in situ transmission spectra while cyclic voltammetry of devices was performed on a microprocessor controlled Omni 90 Potentiostat, Cypress systems Inc. USA in a two-electrode set up under different scan rates. WO_3 formed the working electrode while Prussian blue, the counter electrode (shorted with the reference electrode) was the other electrode. A custom made set up consisting of a He–Ne laser ($\lambda = 632.8$ nm), a Si photodetector with the help of a microprocessor controlled versatile automation unit was used to record the optical response versus time plots for devices [17]. The unit supplied a square wave potential of any desired value (±10 V range) at any specific frequency (between 0.001 Hz and 1 Hz) for activating the device.

3. Results and discussion

The ionic conductivity of the ionogel was 1.2×10^{-2} S/cm at 25 °C. UV–Visible spectra of the device colored by d.c potential that was varied from 1.5 to 2.2 V and bleached under the same potential with reverse polarity are shown in Fig. 1A. With increase in applied potential, the cation intercalation level in the cathodic tungsten oxide layer enhanced from 8 to 22 mC/cm^2, while the color of the device intensifies from colorless to dark blue. The offered transmission modulation of the device, irrespective of the magnitude of the applied voltage, shows a peak value at about 621 nm and then declines monotonically. It is established that the optical modulation increases with increasing voltage and here the highest $\Delta T_{\max}$ of ~72% is observed under a potential of ±2.2 V. Even at a lower applied potential of ±1.5 V, the device exhibits a $\Delta T_{\max}$ of 46%, which is indicative of a low resistance to charge transfer at the elec-

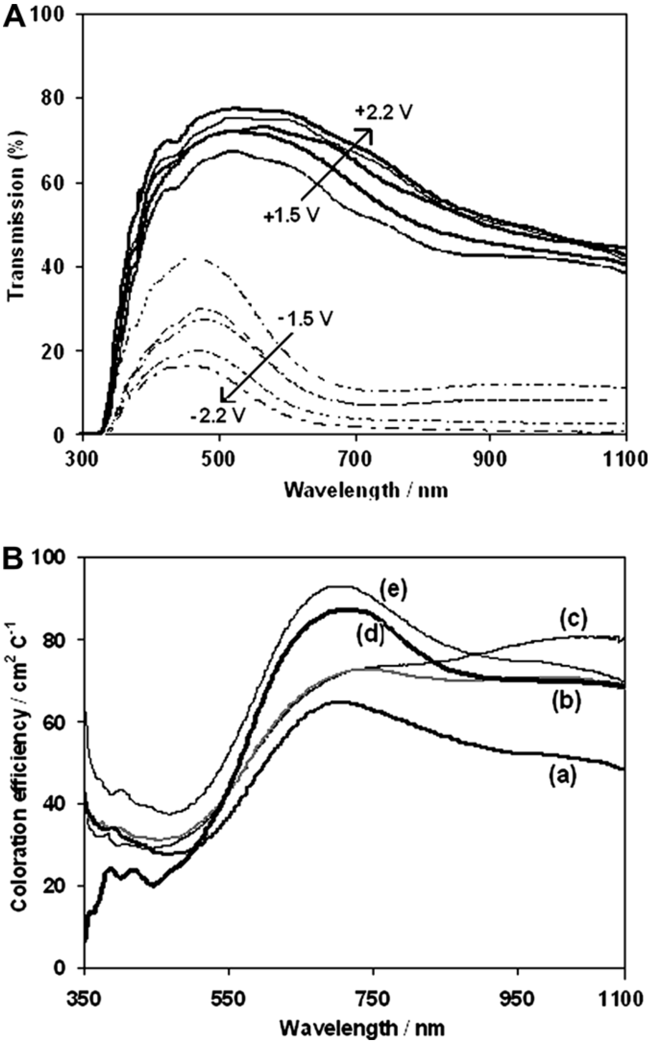

Fig. 1. (A) In situ transmission spectra of electrochromic devices colored (lower set) and bleached (upper set) by 1.5 V, 1.75 V, 1.9 V, 2.0 V, 2.2 V, the arrow denotes increase in voltage and (B) coloration efficiency plots for the devices under applied potentials of (a) ±1.5 V, (b) ±1.75 V, (c) ±1.9 V, (d) ±2.0 V and (e) ±2.2 V.