

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

Shahzada Ahmad *, M. Deepa

Electronic Material Division, National Physical Laboratory, Dr. K.S. Krishnan Marg, New Delhi 110012, India

Received 5 February 2007; received in revised form 26 February 2007; accepted 26 February 2007

Available online 1 March 2007

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 ($\sim 10^{-2} \text{ S cm}^{-1}$ 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.

© 2007 Elsevier B.V. All rights reserved.

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].

* Corresponding author. Tel.: +91 11 25742610x2283; fax: +91 11 25726938.

E-mail address: sahmad@mail.nplindia.ernet.in (S. Ahmad).

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-methylimidazolium 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 equimolar 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 WO₃ 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 cm × 4 cm = 34 cm².

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. WO₃ 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 (λ = 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/cm², 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 ΔT_{\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 ΔT_{\max} of 46%, which is indicative of a low resistance to charge transfer at the elec-

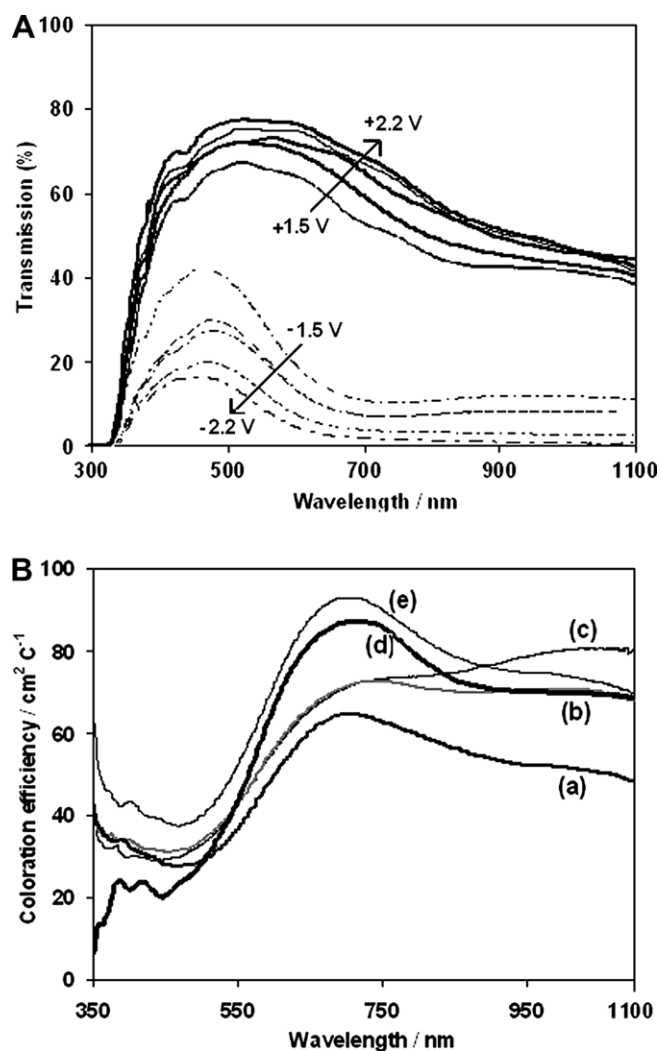


Fig. 1. (A) In situ transmission spectra of electrochromic devices colored (lower set) and bleached (upper set) by 1.5 V, 1.75 V, 1.9 V, 2.0 V, 2.2 V, the arrow denotes increase in voltage and (B) coloration efficiency plots for the devices under applied potentials of (a) ±1.5 V, (b) ±1.75 V, (c) ±1.9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

trode-ionogel interface. That such a low value of external bias (i) brings about an optical contrast (which is sufficient enough for windows applications) and (ii) is beneficial for improving device lifetime is noteworthy. This intimate contact of the ionogels with the electrochromic electrodes and the large ionic conductivity of the electrolyte at room temperature cumulatively act to minimize the ohmic drop across the cell, which effectively translates into a high coloring efficiency for the device. A coloration efficiency (η_{\max}) of $64 \text{ cm}^2/\text{C}$ ($\lambda = 720 \text{ nm}$) is obtained under an external bias of $\pm 1.5 \text{ V}$, and the same device when subjected to a write-erase cycle at 2.2 V shows a η_{\max} of $93 \text{ cm}^2/\text{C}$ ($\lambda = 720 \text{ nm}$) as can be perceived from Fig. 1B. The photodiode response versus time transients recorded for the device under a square wave potential of $\pm 1.5 \text{ V}$, when the frequency was varied between 0.003 Hz and 0.05 Hz , are shown in Fig. 2. The active electrode area of the device

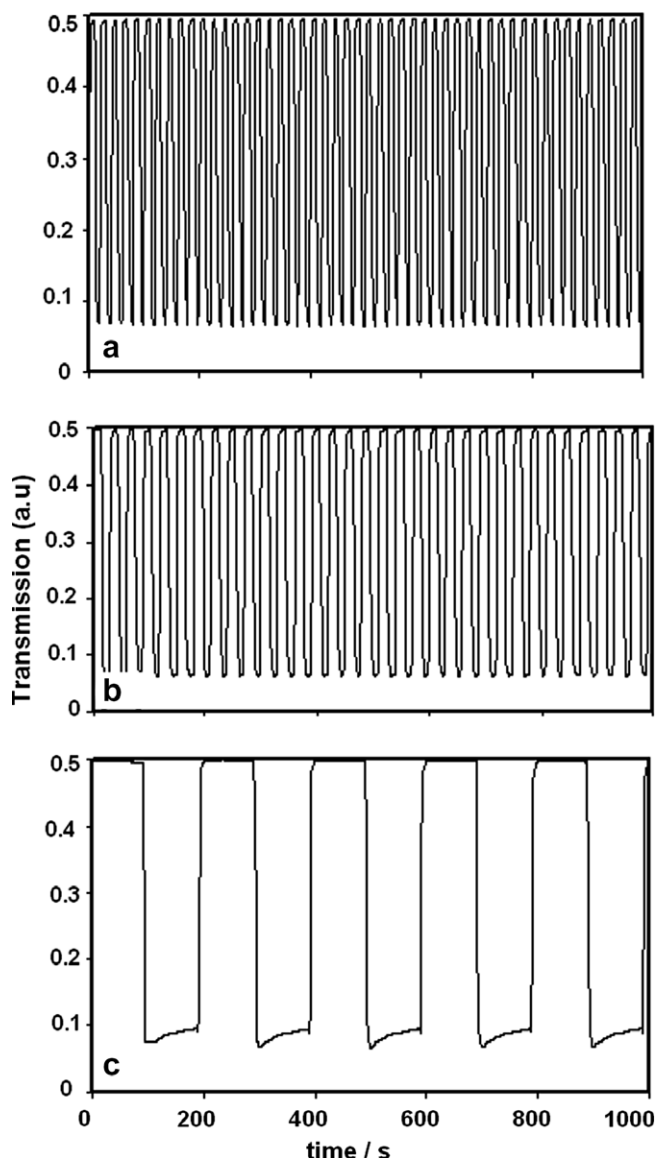


Fig. 2. Color-bleach kinetics of an electrochromic device at 632.8 nm under an applied voltage of $\pm 1.5 \text{ V}$ at (a) 0.05 Hz , (b) 0.005 Hz and (c) 0.003 Hz .

was $4 \text{ cm} \times 8.5 \text{ cm}$. The device colors/undergoes a 90% drop in transmittance in 2 s and bleaches/experiences a 90% enhancement in transmittance in 0.8 s. The rapid color-bleach kinetics shown by the device is attributed to (i) the high liquid like conductivity of the electrolyte which permits an efficient and fast ion transport through the electrochromic films and (ii) the nanostructured morphology of the EC coatings that are endowed with a large number of surface accessible sites, thereby speeding up the W^{6+} to W^{5+} and Fe^{2+} to Fe^{3+} conversions. The mesoporous morphology of the tungsten oxide film along with the pentagonal channels afforded by the tetragonal modification of

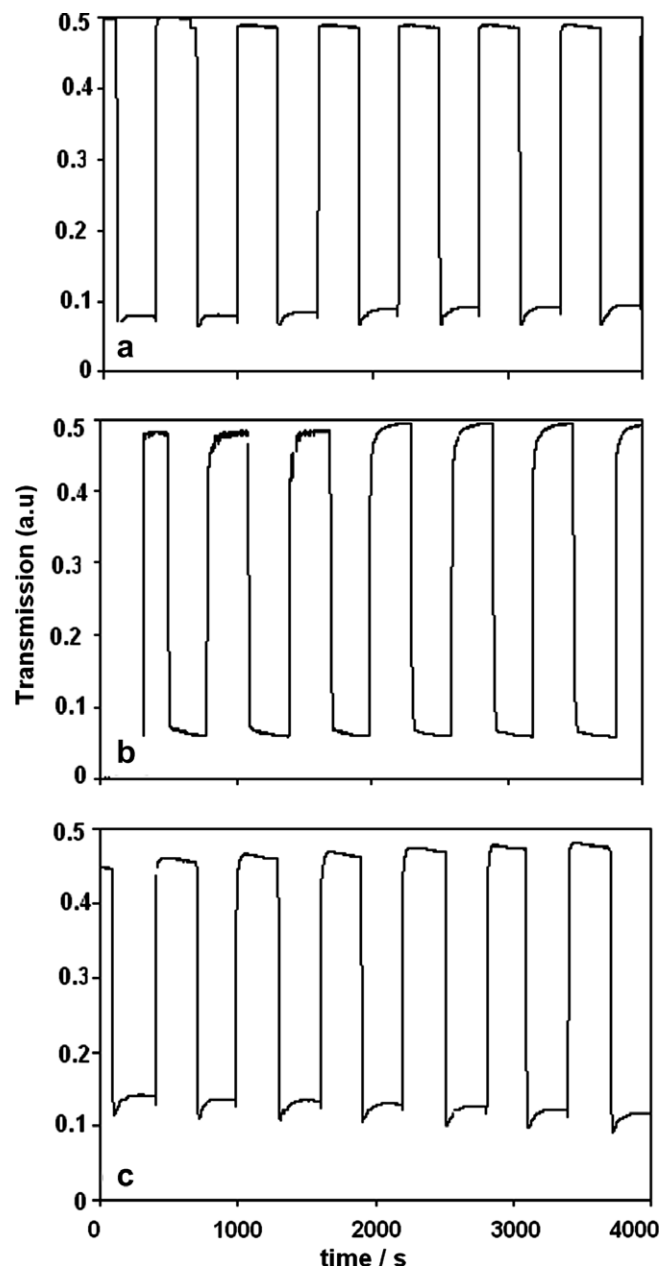


Fig. 3. Color-bleach kinetics of an electrochromic device at 632.8 nm under an applied voltage of $\pm 1.5 \text{ V}$ at 0.0017 Hz after (a) 100, (b) 500 and (c) 1000 cycles.

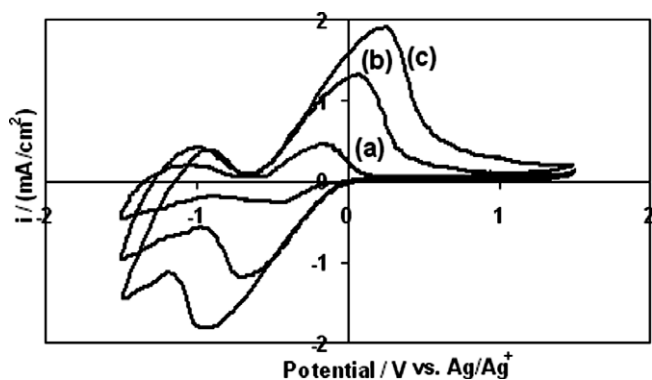


Fig. 4. Cyclic voltammograms of the device in a two electrode configuration under different scan rates of (a) 5 mV/s, (b) 20 mV/s and (c) 50 mV/s.

the films at the lattice scale [17], allow fast diffusion of ions which speed up the bleaching process.

For instance, a proton conducting $\text{WO}_3\text{-PANI-PB}$ device (area: 2 cm^2) showed a $\Delta T \sim 50\%$ (550 nm) and switched from one optical state to the other in 30 s [19]. Usually electrochromic devices based on tungsten oxide as the primary coloring electrode are seldom capable of switching from the clear to dark and vice versa in less than 10 s [20]. The superior performance of the devices with encapsulated ionogels fabricated herein is obvious and more details can be found in the supporting information. Further, the lifetime stability of these ionogels in the devices makes it a potential candidate for practically all solid state electrochromic cells as the span between the colored and bleached states of the device remains remarkably unaltered even after cycling the device 10^3 times (Fig. 3). Experiments are underway to study the durability and environmental stability aspects of these devices.

Fig. 4 illustrates the cyclic voltammograms of the device and also reaffirms the large electrochemical activity of the device and its excellent reversibility for the charge insertion–extraction process. The cyclic voltammograms of the device were recorded at different scan rates of 5, 20 and 50 mV/s when the potential of the device was swept back and forth between $\pm 1.5\text{ V}$. When the device was cathodically polarized it turned blue and when the device was anodically polarized bleaching occurs instantly. The position of the anodic peak current density shifts from 0.3 V (1.89 mA/cm^2) to 0.11 V (0.434 mA/cm^2) on switching the scan rate from 50 to 5 mV/s, a similar change for the cathodic current density peak was observed from 0.96 V (1.82 mA/cm^2) to 0.47 V (0.26 mA/cm^2). About 95% of the charge inserted into electrode during coloration is expunged in the corresponding bleaching cycle, on a repetitive basis which indicates that the structural integrity of

the films is preserved during ionic motion and film microstructure does not allow permanent ion entrapment.

4. Conclusions

In conclusion the synthesized ionogels are transparent, highly conducting, solid like and more importantly exhibit a performance reminiscent of liquid electrolytes thus enabling the realization of leakage free all solid state electrochromic devices with fast kinetics. We believe that this route can be further tuned to binary ionic liquids with additional ionic species for application in a plethora of electrochemical devices.

Acknowledgements

Shahzada Ahmad acknowledges the CSIR for a fellowship, Dr. S.A. Agnihotry and Dr. S.T. LakshmiKumar for all necessary help in carrying out the experiments and discussions. Financial assistance from the DST is gratefully acknowledged.

References

- [1] M. Yoshizawa, H. Ohno, *Chem. Commun.* 16 (2004) 1828.
- [2] Y. He, P.G. Boswell, P. Buhlmann, T.P. Lodge, *J. Phys. Chem. B* (2007), doi:10.1021/jp064574n.
- [3] M.A. Neouze, J.L. Bideau, F. Leroux, A. Vioux, *Chem. Commun.* 8 (2005) 1082.
- [4] S.G. Lee, *Chem. Commun.* 10 (2006) 1049.
- [5] J.H. Shin, W.A. Henderson, S. Passerini, *Electrochem. Commun.* 5 (2003) 1016.
- [6] G. Sonmez, C.K.F. Shen, Y. Rubin, F. Wudl, *Angew. Chem. Int. Ed.* 43 (2004) 1498.
- [7] X. Wei, P.K. Shen, *Electrochem. Commun.* 8 (2006) 293.
- [8] S.K. Deb, *Appl. Opt. (Suppl. 3)* (1969) 192.
- [9] G.A. Niklasson, C.G. Granqvist, *J. Mater. Chem.* 17 (2007) 127.
- [10] M. Deepa, A.G. Joshi, A.K. Srivastava, S.M. Shivaprasad, S.A. Agnihotry, *J. Electrochem. Soc.* 153 (2006) 365.
- [11] S.A. Agnihotry, T.K. Sexana, M. Deepa, A. Verma, Swati, S. Ahmad, *Ionics* 10 (2004) 226.
- [12] S. Ahmad, S. Ahmad, S.A. Agnihotry, *e-Polymers* (2006) 007.
- [13] A. Agrawal, J.P. Cronin, J.L. Tonazzi, B.P. Warner, T.M. McCleskey, A.K. Burrell, *US Patent* (2004) 0257633.
- [14] M.A. Neouze, J.L. Bideau, P. Gaveau, S. Bellayer, A. Vioux, *Chem. Mater.* 18 (2006) 3931.
- [15] M.A. Neouze, J.L. Bideau, A. Vioux, *Prog. Solid State Chem.* 33 (2005) 217.
- [16] M.A.B.H. Susan, T. Kaneko, A. Noda, M. Watanabe, *J. Am. Chem. Soc.* 127 (2005) 4976.
- [17] M. Deepa, A.K. Srivastava, S.A. Agnihotry, *Acta Mater.* 54 (2006) 4583.
- [18] S.A. Agnihotry, P. Singh, A.G. Joshi, D.P. Singh, K.N. Sood, S.M. Shivaprasad, *Electrochim. Acta* 51 (2006) 4291.
- [19] B.P. Jelle, G. Hagen, *Sol. Energy Mater. Sol. Cells* 58 (1999) 277.
- [20] C.G. Granqvist, E. Avendarw, A. Azen, *Thin Solid Films* 42 (2003) 201.