Solid-state electrochromic devices based on poly(trimethylene carbonate) and lithium salts

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Abstract

The application of solid polymer electrolytes (SPEs) based on poly(trimethylene carbonate), p(TMC), with lithium perchlorate and lithium tetrafluoroborate as dual-function electrolyte/adhesive components in electrochromic devices and the preliminary characterization of the resulting prototypes is described in this paper. An asymmetric device configuration, represented schematically as glass/ZnO:Ga_2O_3/WO_3/polymer electrolyte/ZnO:Ga_2O_3/glass, was chosen.

Electrolytes with compositions of *n* between 3 and 10, where *n* represents the molar ratio of ((C=O)$OCH_2CH_2CH_2O$) units per guest lithium ion, were prepared by solvent casting. The electrochromic switching performance was characterized as a function of salt type and salt concentration.

The average transmittance in the visible region of the spectrum was above 63% for all the bleached samples characterized. After coloration the structures assembled with both p(TMC)$_n$LiClO$_4$ and p(TMC)$_n$LiBF$_4$ presented an average transmittance in the visible wavelength region above 39%.

Keywords: solid polymer electrolyte, sputtering, electrochromic materials.

1. Introduction

Polymer electrolytes are solvent-free systems in which the ionically-conducting phase is formed by dissolving suitable guest salts in a high molecular weight host matrix [1]. These materials were developed as a result of the pioneering work of Wright and co-workers in 1973 with complexes of (poly(ethylene oxide), designated as PEO, with alkali metal thiocyanates and iodides [2]. This initial study was continued by Armand who suggested that these materials may be developed as a new class of solid electrolyte for application in high energy density batteries, sensors and fuel cells [3]. In the past few decades thin film solid-state ionic materials have been used as components in electrochromic display devices and smart windows, technological applications of considerable commercial impact. The interest in electrochromic devices based on SPEs is motivated by their good optical contrast and memory, flexibility, image stability and capacity to operate over a wide range of temperatures. Polymer electrolytes generally form good interfaces between the active electrochromic layer and the electrolyte component, leading to compact, well-laminated sandwich structures.

One of the pre-requisites of components of electrochromic devices, is that the optical properties must be reversible and continue to function over several thousand cycles under the action of a voltage pulse [4]. Electrochromic phenomena result from the electrochemical insertion/extraction of electrons and ions (singly-charged small ions such as H^+ or Li^+) into inorganic materials. Even after many years of development the main research effort in this domain continues to be focused on using thin tungsten oxide layers as electrochromic components. The favourable characteristics of this material include reversible transmittance modulation when the electric field is established, reversibility to cycle operation and high stability during operation, particularly in devices based on

polymer electrolytes doped with lithium ions [5, 6]. Tungsten oxide can be prepared by different procedures including evaporation, sputtering and both electrochemical and chemical synthesis [5]. Another metal oxide that has recently been the subject of intense research interest is nickel oxide, a material which demonstrates good electrochromic efficiency, cyclic reversibility and high durability [7, 8].

In this paper we describe the assembly of a prototype solid-state electrochromic device based on a four layer sandwich structure with the glass/ZnO:Ga_2O_3/WO_3/polymer electrolyte/ZnO:Ga_2O_3/glass configuration.

2. Experimental

2.1. Materials

High molar mass poly(trimethylene carbonate) (p(TMC) – 3 x 10^5 gmol^{-1}), prepared by catalyzed bulk polymerization and characterized by gel permeation chromatography, was provided by Shell Chemicals, Houston, TX, USA. The transparent elastomeric host polymer was dried before use at 70 °C, under vacuum, for a period of about 7 days. No further purification of the host polymer was carried out.

Lithium perchlorate (LiClO$_4$, Aldrich, 99.99%) was dried under vacuum at 190 ℃ for 7 days and stored in a high-integrity, dry argon-filled glovebox. Lithium tetrafluoroborate (LiBF$_4$, Aldrich, 95%), provided as pure, dry solid, packed under nitrogen, was used as received. All subsequent manipulation of salts, electrolytes and preparations were carried out under a dry argon atmosphere.

2.2. Samples preparation

Preparation of polymer electrolytes:

Homogeneous solutions of p(TMC) and lithium salts in acetonitrile (Aldrich, anhydrous 99.9 %) were prepared by adding known masses of polymer and lithium salt to a small conical flask. A convenient volume of acetonitrile was transferred to the flask and the components were stirred for a period of at least 48 hours within a dry argon-filled preparative glovebox. The resulting homogeneous solutions were cast into glass rings on glass plates and the solvent was evaporated slowly to form films of about 150 μm thickness. These electrolytes films were transferred to a tubular oven and subjected to a drying procedure in which the temperature was raised from 30 to 60 ℃ over a period of 3 days. During this period the oven was periodically evacuated and purged with dry argon. This optimized procedure [9, 10] was used to prepare p(TMC)$_n$LiX compositions with n between 3 and 10. The choice of SPE formulation applied in prototype devices was based on criteria of conductivity and mechanical properties.

Preparation of inorganic thin films

Transparent Conductive Oxide – Gallium-doped zinc oxide films (ZnO:Ga$_2$O$_3$) were deposited on glass substrates by r.f. (13.56 MHz) magnetron sputtering using a ZnO:Ga$_2$O$_3$ ceramic oxide target (95:5 wt%) of 5 cm diameter, (supplied by SCM, Suffern, NY, USA). The sputtering was carried out at room temperature, with an argon flow of 20 sccm and a deposition pressure of 0.11 Pa. The distance between the substrate and the target was 10 cm and the rf power was held constant at 175 W. Further details of the film preparation and the physical properties can be found in reference [11].

Electrochromic film - The tungsten oxide films (WO$_3$) were prepared by thermal evaporation using WO$_3$ pellets (SCM, 99.99% purity). The deposition pressure was 1.2 x10^{-3} Pa with a deposition rate of 1.03 nm/seg.

2.3. Electrochromic cell assembly, Substrate A / p(TMC)$_n$LiX / Substrate B

Electrolyte compositions were prepared and dried to obtain free-standing, transparent films which were located between the $ZnO:Ga_2O_3/WO_3$ and $ZnO:Ga_2O_3$ coated glass plates. The thickness used for each $ZnO:Ga_2O_3$ and WO_3 layer was 200 and 300 nm, respectively. The device assembly was completed simply by removing a suitable section of electrolyte film from cast and dried samples, locating the film section between the coated plates and applying moderate pressure. The assembly procedure described was carried out under a laboratory atmosphere.

3. Results and Discussion

3.1 - Electrochemical behaviour of the p(TMC)$_n$LiX (X = ClO$_4$, BF$_4$) - based devices

SPEs for practical application in commercial devices must support high lithium ion mobility in order to provide rapid response in optical devices. Electrolytes must also be chemically stable to permit devices to attain extensive storage and service lifetimes and in high voltage devices they must be able to withstand the range of potential of the electrode couple. The stability of the electrolyte systems characterized was demonstrated to be adequate for this type of application.

The conductivity behavior of all polymer electrolytes based p(TMC) and lithium perchlorate or lithium tetrafluoroborate was found to show linear log (conductivity) versus 1/T plots with no breaks or inflections. The effects of temperature and salt concentration on p(TMC) electrolytes have been discussed previously. These electrolytes are entirely amorphous, even at very high guest salts compositions [9, 10].

3.2 Electrochromic device structure

The interest in electrochromic devices based on ion-conducting polymers is due their good optical contrast, memory and stability. The color of molybdenum oxide films can be altered by incorporating them in electrochromic "asymmetric" EC devices. In the colored state these devices have a deep blue color. The scheme in Figure 1 shows the prototype device assembly of the electrochemical display characterized in preliminary experiments. The difference in transmittance between the fully colored state and the fully bleached state demonstrates the light modulation capability of the electrochromic devices. The results presented in Figures 2 and 3 report the optical transmittance in the 400-900 nm wavelength range for the electrochromic device using $p(TMC)_n LiClO_4$ and $p(TMC)_n LiBF_4$, respectively. Table 1 summarizes the average transmittance (in the visible part of the spectrum) and optical density exhibited by the electrochromic devices. The average transmittance in the visible region of the spectrum was above 63% for all the bleached samples analyzed. After coloration the structures assembled with $p(TMC)_n LiClO_4$ and $p(TMC)_n LiBF_4$ with compositions of $8 \leq n \leq 10$, present a good color contrast and an optical density above 0.20, providing a good performance in coloring/bleaching process.

The results of the average transmittance for the colored state after 24 hours are also shown in Figures 2 and 3. It is possible to observe a slight shift of the peaks to lower wavelengths, suggesting a partial degradation of the polymer [12].

This study reports a significant improvement in the optical memory relative to devices incorporating immobilized-liquid gel electrolytes, also containing lithium perchlorate [13]. In this respect the results obtained with solvent-cast poly(trimethylene carbonate)-based electrolytes are markedly better.

All the devices incorporating $p(TMC)_n LiClO_4$ electrolytes presented good stability and storage properties under open circuit. The structures assembled with $p(TMC)_n LiBF_4$ however showed marked color degradation after storage for one month.

4. Conclusions

In this paper encouraging results are reported for the preliminary characterization of prototype devices incorporating $p(TMC)_n LiClO_4$ and $p(TMC)_n LiBF_4$ as dual-purpose components. The mechanical properties of these materials contribute an important advance relative to both semi-crystalline or immobilized-liquid gel electrolytes because they provide access to more favourable device architectures.

The use of p(TMC)-based components also improves cycle lifetime and durability of the electrochromic device relative to conventional electrolytes and improves leakage performance, memory effect and humidity resistance.

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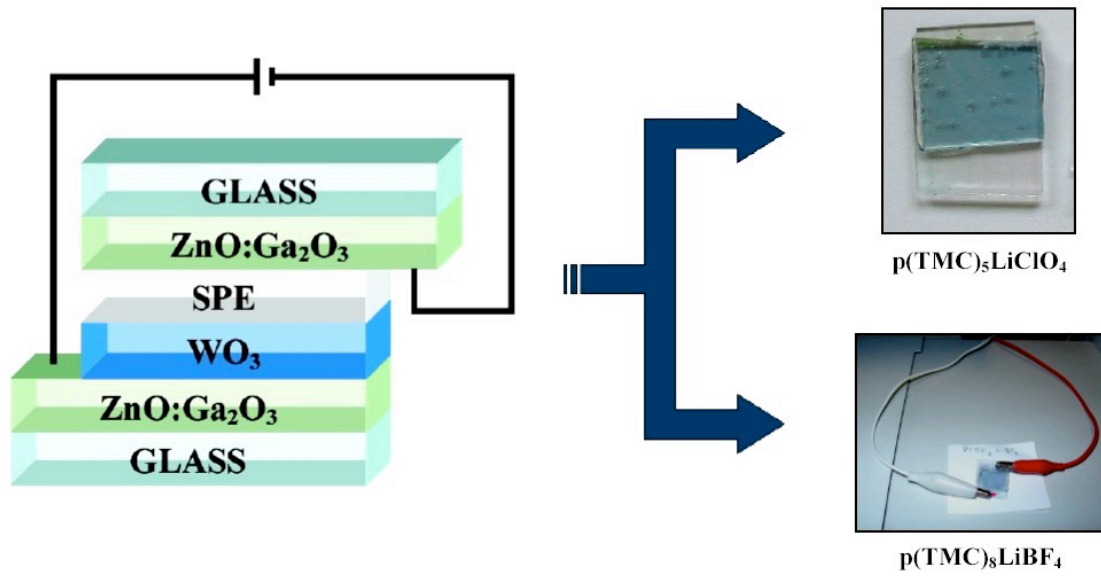
Figure 1 - Schematic illustration of the electrochromic structure device.
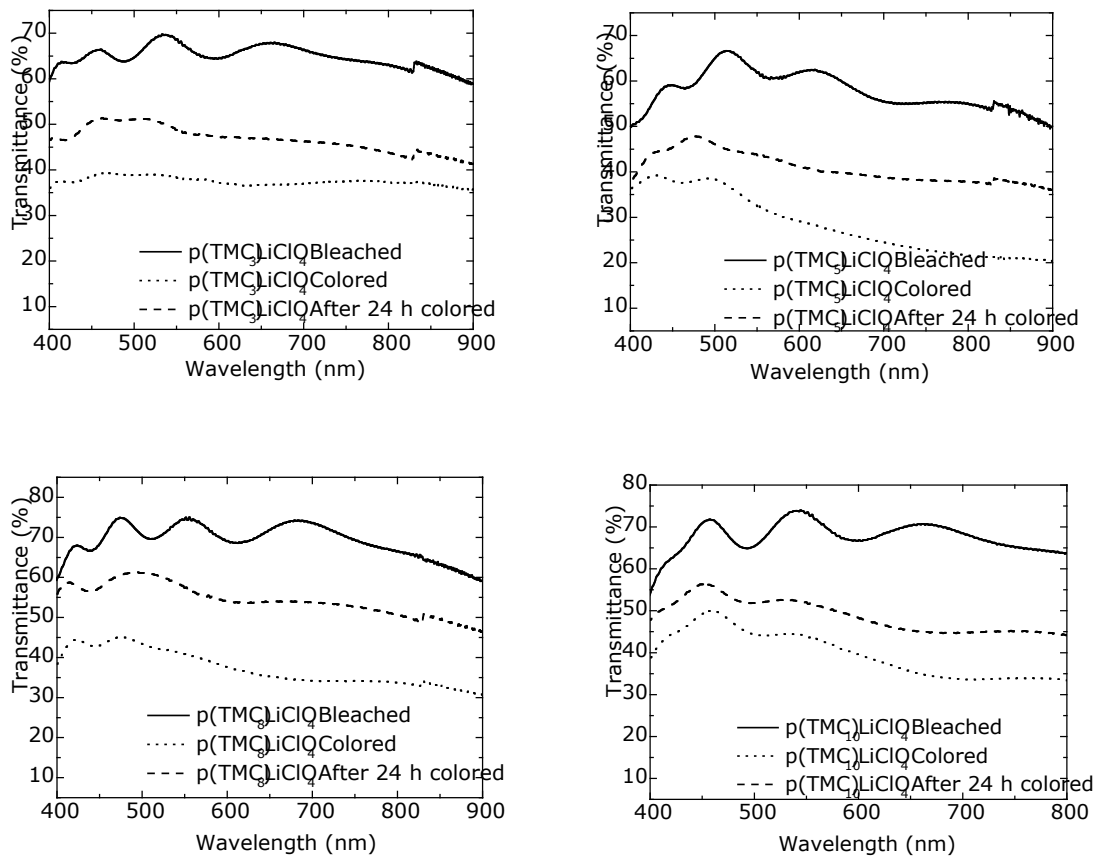
Figure 2 - Optical transmittance as a function of wavelength for the electrochromic device in bleached and colored state using (a) p(TMC)$_3$LiClO$_4$; (b) p(TMC)$_5$LiClO$_4$; (c) p(TMC)$_8$LiClO$_4$; (d) p(TMC)$_{10}$LiClO$_4$.

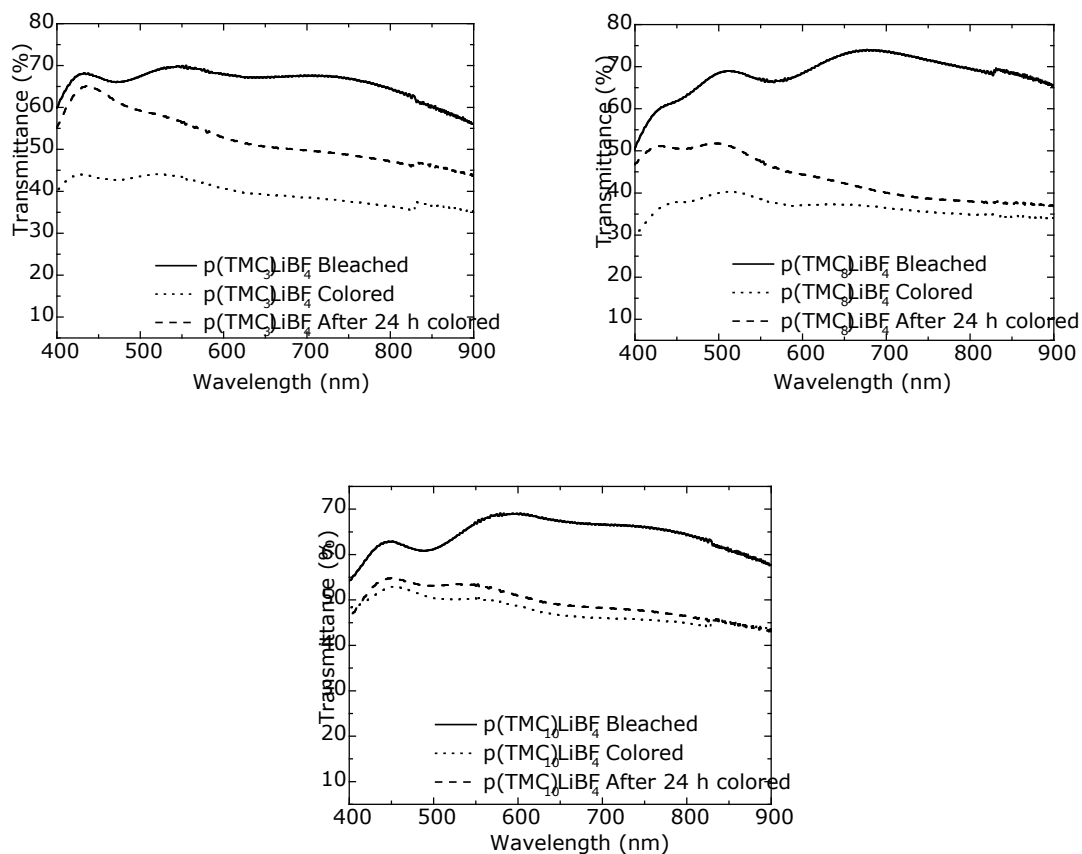Figure 3 - Optical transmittance as a function of wavelength for the electrochromic device in bleached and colored state using (a) $p(TMC)_3LiBF_4$; (b) $p(TMC)_8LiBF_4$; (c) $p(TMC)_{10}LiBF_4$.

Table 1

Average transmittance and optical density exhibited by electrochromic devices.

Sample	Transmittance in bleached state (%)	Transmittance in colored state (%)	Optical density
p(TMC)$_3$LiClO$_4$	66.85	38.40	0.25
p(TMC)$_5$LiClO$_4$	62.72	38.86	0.27
p(TMC)$_8$LiClO$_4$	72.40	44.90	0.26
p(TMC)$_{10}$LiClO$_4$	72.40	47.13	0.22
p(TMC)$_3$LiBF$_4$	69.04	44.29	0.20
p(TMC)$_8$LiBF$_4$	71.40	39.13	0.23
p(TMC)$_{10}$LiBF$_4$	65.95	51.41	0.13