

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



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Available online 5 April 2007

## Abstract

The application of solid polymer electrolytes as dual-function electrolyte/adhesive components in electrochromic devices and the preliminary characterization of the resulting prototype displays is described in this paper. An asymmetric device configuration, represented schematically as glass/ZnO:Ga<sub>2</sub>O<sub>3</sub>/WO<sub>3</sub>/polymer electrolyte/ZnO:Ga<sub>2</sub>O<sub>3</sub>/glass, was chosen.

Electrolytes with compositions of  $n$  between 3 and 10, where  $n$  represents the molar ratio of poly(trimethylene carbonate), p(TMC), ((C=O)OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O), 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) <sub>$n$</sub> LiClO<sub>4</sub> and p(TMC) <sub>$n$</sub> LiBF<sub>4</sub> presented an average transmittance in the visible wavelength region above 39%. © 2007 Elsevier B.V. All rights reserved.

**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 solid polymer electrolytes (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<sup>+</sup> or Li<sup>+</sup>) 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

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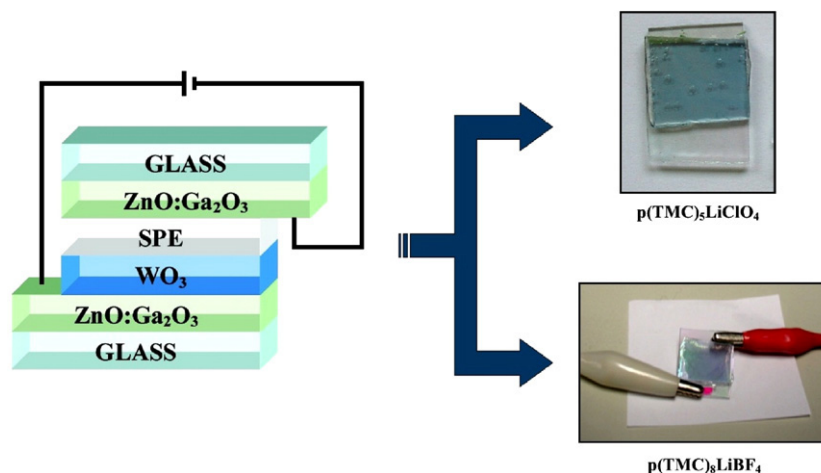


Fig. 1. Schematic illustration of the electrochromic device structure.

structure with the glass/ZnO:Ga<sub>2</sub>O<sub>3</sub>/WO<sub>3</sub>/polymer electrolyte/ZnO:Ga<sub>2</sub>O<sub>3</sub>/glass configuration.

## 2. Experimental

### 2.1. Materials

High molar mass poly(trimethylene carbonate) (p(TMC) —  $3 \times 10^5$  g mol<sup>-1</sup>), 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<sub>4</sub>, Aldrich, 99.99%) was dried under vacuum at 190 °C for 7 days and stored in a high-integrity, dry argon-filled glovebox. Lithium tetrafluoroborate (LiBF<sub>4</sub>, Aldrich, 95%), provided as pure, dry solid, packed

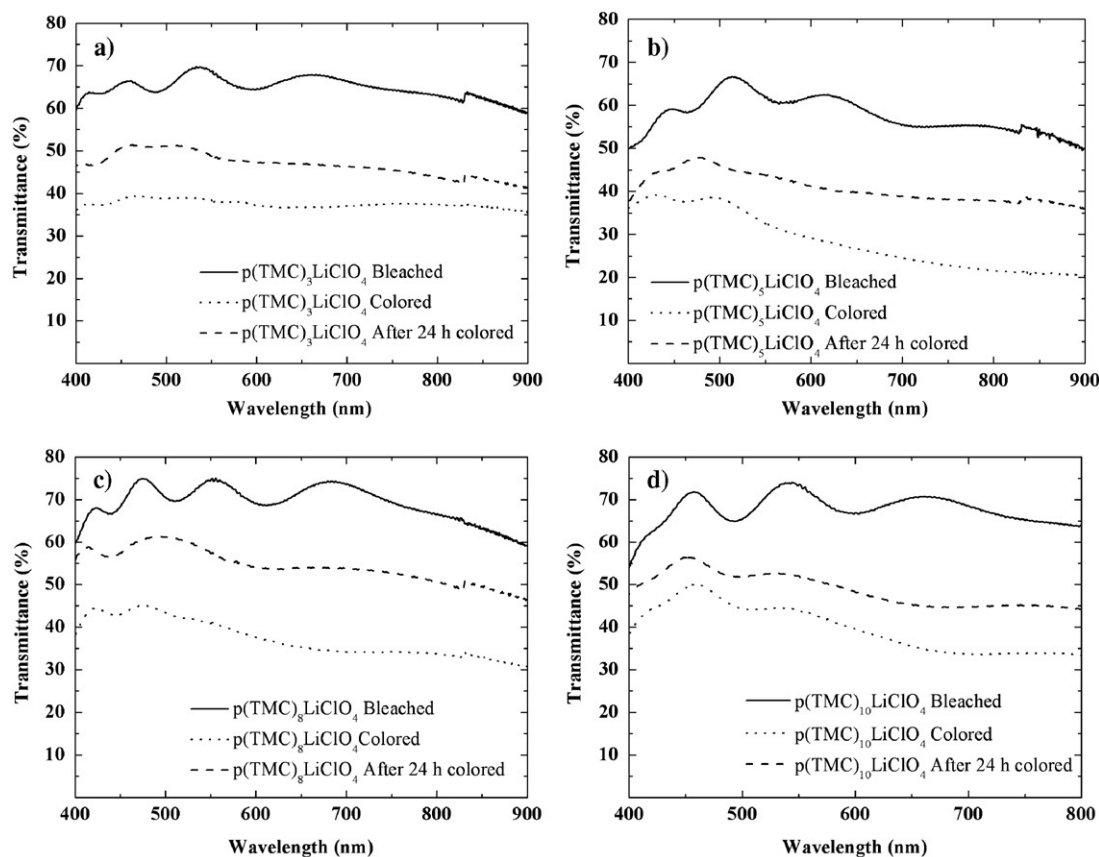


Fig. 2. Optical transmittance as a function of wavelength for the electrochromic device in bleached and colored state using (a) p(TMC)<sub>3</sub>LiClO<sub>4</sub>; (b) p(TMC)<sub>5</sub>LiClO<sub>4</sub>; (c) p(TMC)<sub>8</sub>LiClO<sub>4</sub>; (d) p(TMC)<sub>10</sub>LiClO<sub>4</sub>.

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