

Solid hybrid polyelectrolyte with high performance in electrochromic devices: Electrochemical stability and optical study

Flavio L. Souza^{a,*}, Michel A. Aegerter^b, Edson R. Leite^a

^aDepartment of Chemistry, Federal University of São Carlos, 13565-905 São Carlos, SP, Brazil

^bLeibniz—Institut fuer Neue Materialien gGmbH (INM), Im Stadtwald, Gebaude 43, 66123 Saarbruecken, Germany

Received 19 March 2007; accepted 18 June 2007

Available online 31 July 2007

Abstract

This paper presents a high-stability, single-phase hybrid polyelectrolyte (SPHP) applied in a large EC device ($5 \times 10 \text{ cm}^2$) using WO_3 (electrochromic) and $\text{CeO}_2\text{-TiO}_2$ (counter-electrode-ion storage) electrodes, both produced by Leibniz—Institut of New Materials (Leibniz—INM, Germany). The electrochromic device exhibited excellent color and bleach reversibility, high coloration efficiency ($> 35 \text{ cm}^2/\text{C}$) from the first cycle up to more than 60,000 CA cycles, and a maximum constant rate of deintercalation/intercalation ($O_{\text{out}}/Q_{\text{in}} = 1$). Its remarkable behavior and high stability render this material an excellent candidate for application in electrochromic devices. © 2007 Elsevier B.V. All rights reserved.

Keywords: Ionic conductor; Hybrid polyelectrolyte; Sol–gel non-hydrolytic; Electrochromic device; High stability

1. Introduction

An important and relatively recent research area involves hybrid organic–inorganic polymer electrolytes, which are receiving much attention due to their important applications in electrochemical devices such as batteries and electrochromic (EC) windows [1,2]. To a certain extent, these hybrid materials combine the most important properties of their constituents, such as high transparency (glass-like), low processing temperatures (polymer-like), sufficient thermal stability (silicone-like), with high-performance yield and properties not found in either material individually [3–8].

Recently, we described a different class of single-phase hybrid polyelectrolyte (SPHP) in which the ionic conductivity is not coupled to the segmental motion of the polymer chain, i.e., a material in which the ions move independently of viscous flow [9]. The development of a segmental motion-decoupled polymer system is an alternative way to increase ionic conductivity in polymer electrolytes [10]. The material's ionic conductivity showed an Arrhenius-like behavior ($\sigma = 10^{-5} \Omega/\text{cm}$ at room

temperature) as a function of temperature (in the range of temperatures above T_g) and an activation energy of 0.21 eV. These characteristics indicate a fast ion transport mechanism in a segmental motion-decoupled hybrid organic–inorganic polymer. The aforementioned SPHP was synthesized by a derivative *in situ* polymerizable method (a non-hydrolytic sol–gel process) based on the formation of a Si and citric acid (CA) complex subsequently polymerized by means of a polyesterification reaction with ethylene glycol (EG) [11]. The material became ionically conductive when Li_2CO_3 was dissolved in the structure during its synthesis. A transparent, amorphous solid polymer was obtained after elimination of the solvent. The good ionic conductivity allied to the excellent transparency of this SPHP material motivated us to apply it in a classical EC device [12a]. Electrochromism is defined as a persistent but reversible optical change produced electrochemically. A wide range of materials are known today to exhibit reversible coloration through the application of an electric field or, more precisely, by the passage of electric current and ions through them [12b,13]. Solid-state EC devices are of considerable technological and commercial interest in, for example, smart windows, displays and automotive rearview mirrors [14]. To improve the safety of

*Corresponding author.

E-mail address: fleandro@liec.ufscar.br (F.L. Souza).

large devices and avoid the effect of hydrostatic pressure and the need for sealing, the liquid electrolyte can be replaced by solid state electrolyte film. In addition, the main goal in this paper is to analyze the performance of the SPHP material applied in EC devices with dimensions of $5 \times 10 \text{ cm}^2$. The classical EC device was mounted using WO_3 (EC) and $\text{CeO}_2\text{-TiO}_2$ (counter-electrode-ion storage) electrodes, both produced by the Leibniz–Institut of New Materials (Leibniz–INM, Germany) [15], using SPHP as solid state electrolyte.

2. Experimental

2.1. Electrodes

The preparation of the WO_3 , $(\text{CeO}_2)_x(\text{TiO}_2)_{1-x}$ sol–gel layers and of the EC device with SPHP was carried out at the INM [15]. The K-glass substrates (glass-coated with FTO, Pilkington, 17Ω) were washed, dried and heat-treated at 450°C for 15 min. The $(\text{CeO}_2)_x(\text{TiO}_2)_{1-x}$ layers were deposited on these substrates by the dip-coating technique, at a withdrawal rate of 4 mm/s at 21°C and 41% air humidity. The single layers were then heated in air from room temperature to 450°C at a heating rate of 2.5 K/min, held for 15 min at 450°C and cooled to room temperature in the oven in 5 h. The WO_3 layers were deposited in a single coating step on the K-glass, using the same technique and under the same experimental conditions, after which they were heat-treated at 175°C .

2.2. Electrochromic devices

The EC devices (size $5 \times 10 \text{ cm}^2$) of the form K-glass/FTO/ WO_3 /SPHP/ $\text{CeO}_2\text{-TiO}_2$ /FTO/K-glass were fabricated by mounting, in air, a double-sided adhesive tape (thickness 1 mm, 3 M) at the edges of one of the functional coatings and then assembling the two coated substrates. The mounted cells were then filled with hybrid polyelectrolyte (viscous about 30 cps) through a small hole, heated at 60°C for 12 h to solidify the polyelectrolyte (eliminating all the solvents and reaching complete polymerization), and then extra sealed using butyl rubber (3 M) and adhesive tape. The devices were analyzed by electrochemical measurements taken using an EG&G 273A potentiostat. The samples were studied by cyclic chronoamperometry (CA) measurements taken by applying a potential range of $-2.0 \text{ V}/60 \text{ s}$ to $+1.25 \text{ V}/60 \text{ s}$. *In situ* transmittance measurements were carried out with a CARY 5E UV–vis–NIR spectrophotometer. The transmittance of the EC devices was measured against air as reference.

The formation of an absorbing state upon reduction is called cathodic electrochromism, while the formation upon oxidation is called anodic electrochromism. The insertion and extraction of ions is called intercalation (Q_{in}) and deintercalation (Q_{out}). Due to the well-established works done on electrochromism for optical applications, the terms “bleached” and “colored” are often seen. The

operating mode is explained here with an EC window of the configuration glass/FTO/ WO_3 /SPHP/ $\text{CeO}_2\text{-TiO}_2$ /FTO/glass, the configuration used in this work. Initially the system is transparent. After applying a voltage with negative polarization at the WO_3 side, WO_3 is reduced and simultaneously the M^+ ions (M^+ : H^+ , Li^+) stored in the ion-storage layer diffuse through the electrolyte into the WO_3 layer to form a deep blue colored intercalation compound M_xWO_3 . The following reversible coloration and bleaching reactions occur: (transparent) $\text{WO}_3 + x\text{M}^+ + xe^- \leftrightarrow$ (blue state) M_xWO_3 ; WO_3 colors blue in the reduced form and is therefore a cathodic EC material. After reversing the polarization, M_xWO_3 is oxidized and simultaneously the M^+ ions diffuse back to the counter-electrode. The counter-electrode, which was oxidized during the coloration step, will be reduced and the EC device is bleached. The counter electrode layer can be either an ion storage layer (IS layer), which does not change its color during intercalation/deintercalation of the M^+ ions (e.g., cerium oxide–titanium oxide, $\text{CeO}_2\text{-TiO}_2$), or a complementary, anodic EC layer, which colors in the oxidized form (e.g., nickel oxide, NiO) so that the coloration of the EC window can be intensified.

2.3. Single-phase hybrid polyelectrolyte

Following a typical procedure, the SPHP was prepared, with a citric acid/Si (molar) ratio of 2:1 and a Si–citric acid complex/EG mass ratio of 77:23. For the Si–citric acid complex synthesis, TEOS was used as the Si source [9,11a]. The Si–citric acid complex and polymerization reaction were performed in an ethanol solution at 40°C under constant magnetic stirring. The procedure used to obtain SPHP was synthesis by a non-hydrolytic sol–gel process, which seems to derive from an “unpolymerizable method” and has been described in greater detail elsewhere [9]. The ionic conductivity arises from the addition of Li_2CO_3 during the synthesis. As discussed in Ref. [9], only Li^+ is expected to be mobile in the SPHP structure of the polymer. It is believed that the anions are formed from the group present in the polymer network. A transparent solid polymer was obtained after the solvent was eliminated (under vacuum at 60°C). The resulting polymer electrolyte was dried at 60°C for several hours and stored under vacuum for further characterization. The single-phase hybrid polymer was named SPHP. In this work, the lithium concentrations used were 1, 5 and 10 wt% in SPHP systems. The SPHP was characterized structurally by FTIR measurements (Bruker Model EQUINOX 55), which were taken from 400 to 4000 cm^{-1} . The conductivity of the complex was obtained using an HP 4194-A capacitance–voltage meter. The measurements were taken at room temperature, while the frequency ranged from 100 Hz to 15 MHz with a perturbation amplitude voltage of 5 mV. The samples in solid state (water concentration lower than 0.5%) were sandwiched between two platinum blocking electrodes.

Download English Version:

<https://daneshyari.com/en/article/81042>

Download Persian Version:

<https://daneshyari.com/article/81042>

[Daneshyari.com](https://daneshyari.com)