All solid-state electrochromic devices with gelatin-based electrolyte

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Received 15 December 2006; accepted 22 February 2007
Available online 25 September 2007

Abstract

6 × 8 cm\textsuperscript{2} electrochromic devices (ECDs) with the configuration K-glass/EC-layer/electrolyte/ion-storage (IS) layer/K-glass, have been assembled using Nb\textsubscript{2}O\textsubscript{5}:Mo EC layers, a (CeO\textsubscript{2})\textsubscript{0.81–TiO\textsubscript{2}} IS-layer and a new gelatin electrolyte containing Li\textsuperscript{+} ions. The structure of the electrolyte is X-ray amorphous. Its ionic conductivity passed by a maximum of 1.5 \times 10\textsuperscript{-5} S/cm for a lithium concentration of 0.3 g/15 ml. The value increases with temperature and follows an Arrhenius law with an activation energy of 49.5 kJ/mol. All solid-state devices show a reversible gray coloration, a long-term stability of more than 25,000 switching cycles (±2.0 V/90 s), a transmission change at 550 nm between 60% (bleached state) and 40% (colored state) corresponding to a change of the optical density (\textit{DOD} = 0.15) with a coloration efficiency increasing from 10 cm\textsuperscript{2}/C (initial cycle) to 23 cm\textsuperscript{2}/C (25,000th cycle).

Keywords: Solid electrolyte; Gelatin; Electrochromic devices; Nb\textsubscript{2}O\textsubscript{5}:Mo; Ion storage; Thin films; Electrochromic devices

1. Introduction

Electrochromic devices (ECDs) are opto-electrochemical systems that change their optical properties, mainly their transmittance, when a voltage is applied to them. This interesting behavior leads to many applications, such as windows, sunroofs, shades, visor or rear view mirrors for automotive and mass transportation applications, architectural windows, skylight, displays, light filter and screens for light pipes, displays and other electro-optical devices [1,2].

Electrochromic devices may have several configurations and are made using layers of different compositions and this turns their comparison difficult. Nevertheless, the transmittance or reflectance change, the number of stable coloring/bleaching cycles and the switching time are the most important parameters to be considered. Surveys of ECDs investigated between 1998 and 2001 have been presented in recent papers by Granqvist et al. [3] and Heusing and Aegerter [1].

The ionic conductor is an important component in systems such as lithium batteries and ECDs. In contrast to liquid electrolytes, solid-state ones have no or very limited problems with leakage or pressure-related distortions. Solid polymer electrolytes (SPEs) have emerged as important ionic conducting materials due to their good contact with the electrodes, their simple preparation in different forms and good mechanical and adhesive properties [4]. Usually, both crystalline and amorphous phases are present in polymer electrolytes. Since only amorphous phases present high conductivity [5], plasticizers are usually added to enhance the amorphous phase and thus the ionic conductivity [6,7].

Electrochromic devices with solid-state electrochromic thin coatings such as WO\textsubscript{3} or Nb\textsubscript{2}O\textsubscript{5} and counter-electrode such as CeO\textsubscript{2}–TiO\textsubscript{2} have been produced using various electrolytes such as all-inorganic solid-state materials [8], organic compound-based materials [9] or organic–inorganic (ormolite) systems that all contain mobile lithium or proton-charged species. LiClO\textsubscript{4} is the most used salt to get
conducting ions in ionic liquids and organic or polymeric-based electrolytes [10]. The polymeric electrolytes are also very interesting because of their low production cost and better appropriate mechanical properties compared to inorganic materials. Different solid polymeric electrolytes (SPEs) have been proposed, most of them based on poly(ethylene oxide) (PEO) [11,12]. Recent attention has been focused on the use of natural polymers because of their biodegradability, low production cost and good physical and chemical properties. These polymers are usually used in the cosmetic, pharmaceutical and food industries but can also be used to prepare SPEs. This is the case, for instance, of hydroxyethylcellulose (HEC) [13], modified starch [14], chitosan [15] or natural rubber [16]. Li$^+$ ions conductivity values as high as 10$^{-3}$ S/cm at room temperature have been achieved. Small ECDs with good electrochromic properties have already been realized with such SPEs [10,17]. The recent results reported using a gelatin-based polymer electrolyte and an electrochemically deposited bismuth layer [18] have attracted our attention and prompted an investigation on the possibility of using gelatin as polymer electrolyte in other all-solid-state ECDs.

The fabrication of an all-solid-state EC window using Nb$_2$O$_5$:Mo and CeO$_2$–TiO$_2$ as EC layers and a Li ion gelatin electrolyte is reported here. The characterization and the optimization of the electrolyte properties are presented. Electrochemical measurements such as cyclic voltammetry and chronoamperometry (CA) have been used to characterize the devices. The optical density (OD), coloration efficiency (CE) and memory test of the ECDs are also discussed.

2. Experimental

2.1. Solid-state polymeric electrolyte

The electrolyte used for the ECD has been prepared according to the following receipt. Two grams of commercial uncolored gelatin (Oetker) was dispersed in 15 ml of water and heated under magnetic stirring for a few minutes up to 50°C to complete dissolution. Then, 0.3 g of LiClO$_4$, 0.5 g of glycerol as plasticizer and 0.25 g of formaldehyde was added to this solution under stirring. This viscous solution was then cooled down to 30°C and poured on Petri plates to form transparent films or injected into the windows.

2.2. Nb$_2$O$_5$:Mo electrochromic thin film

A Nb$_2$O$_5$:Mo sol was prepared according to an INM receipt [19]. 4.56 g of H$_3$P(Mo$_3$O$_{10}$)$_3$·9H$_2$O (0.12 mol/l Mo) and 27.04 g of NbCl$_5$ (0.4 mol/l Nb) were dissolved separately each in 125 ml of anhydrous ethanol. Next, 30 g of acetic acid (99–100%) (2 mol/l) and the molybdenum solution were added into the niobium chloroethoxide solution under stirring for 5 min. The resulting solution was kept at 20°C in a closed glass recipient for 2 days before deposition. Two layers coatings were deposited on K-glass substrates (float glass coated with transparent conducting layer of SnO$_2$:F, Pilkington, 17Ω/□ washed, dried and heat-treated at 450°C for 15 min) by dripping the substrate into the solution for 30 s and then withdrawing the first layer at a rate of 4 mm/s and the second layer at the rate 2 mm/s. Each layer was heated at 100°C for 30 min. A final heat treatment was performed at 500°C in a hot oven for 30 min, and then cooled down to 30°C. The double-layer coatings were transparent and homogeneous and their total thickness was about 120 nm.

2.3. (CeO$_2$)$_{0.81}$–TiO$_2$ ion-storage thin film

The (CeO$_2$)$_{0.81}$–TiO$_2$ was also prepared according to a receipt of INM, Germany, by dissolving Ce(NO$_3$)$_3$·6H$_2$O (0.056 mol) and Ti(Oct)$_4$ (0.069 mol) in 250 ml ethanol followed by stirring the sol at 30°C for 4 days [20]. The (CeO$_2$)$_{0.81}$–TiO$_2$ layers were deposited on K-glass substrates by the dip-coating technique with a withdrawing rate of 4 mm/s at 20°C with 38% air humidity. The layers were then heated in air from room temperature to up to 550°C with a heating rate of 2.5 K/min, kept for 1 h at 550°C and then cooled down to room temperature in the oven in about 5 h.

2.4. Electrochromic devices

Electrochromic devices having the configuration glass/FTO/Nb$_2$O$_5$:Mo/gelatin/(CeO$_2$)$_{0.81}$–TiO$_2$/FTO/glass and a size of 8 × 6 cm$^2$ were obtained by assembling the two pieces of the coated glasses in the following way. A 1-mm-thick and 5-mm-large spacer were glued on the four edges of one of the functional coatings and 1 cm free space was left for the electrical contact. Then, the other coated substrate was pressed onto the first one in such a way that the two coatings faced each other inside the assembled window. A 1-cm-wide Cu-conducting tape was glued to the free edge of each substrate for electrical connection. The viscous gelatin-based electrolyte was finally injected with a syringe in the mounted cells. The devices were finally sealed with a protective tape.

2.5. Characterization techniques

An X-ray diffraction study of the electrolyte was performed at ambient temperature using a Rigaku Rotaflex RU200B diffractometer with a scan range from 5° to 75° and Cu K$_\alpha$ radiation.

The UV–vis optical spectra of the electrolyte and the ECDs were recorded with a Cary 5E Varian spectrophotometer between 350 and 2000 nm. Impedance spectroscopy measurements were used to determine the electrolyte ionic conductivity and its frequency behavior. A 2-cm-round and 0.5-mm-thick piece of the electrolyte was pressed against two steel electrodes.
The system was installed in a glass cell under vacuum. The measurements were performed with an Autolab instrument equipped with an FRA2 module, applying a voltage of 5 mV rms amplitude in the frequency range 10^6–10 Hz.

Cyclic voltammetry and CA tests of the ECDs were performed with a potentiostat/galvanostat (EG&G model 273A) in the potential range ±2.0 V.

3. Results and discussion

3.1. Solid electrolyte

The ionic conductivity $\sigma$ of the gelatin electrolyte at room temperature is presented as a function of lithium salt amount in Fig. 1. It was calculated using the relation $\sigma = l/R_b A$, where $l$ is the thickness of the electrolyte sample, $A$ is the contact area between the electrolyte and the electrode and $R_b$ is the measured resistance. This value was determined by the intercept of the semicircle with the real axis of the $Z''$ vs $Z'$ Nyquist plot (typical examples are shown in Fig. 2). The ionic conductivity $\sigma$ increases with the amount of LiClO$_4$ to reach a maximum of 1.53 $\times$ 10$^{-5}$ S/cm for a value for 0.3 g of LiClO$_4$ in 15 ml of electrolyte. This is certainly related to the increase in the number of mobile charge carriers. However a decrease of the ionic conductivity is observed for higher amount of LiClO$_4$ salt in the electrolyte, probably due to an incomplete dissociation of the salt [21].

Fig. 2 shows typical impedance plots of the gelatin electrolyte prepared with the optimum concentration of LiClO$_4$ salt measured at various temperatures. The values of the bulk resistance $R_b$ are decreasing with the increase in temperature indicating an increase of the Li$^+$ ions mobility and concentration and the thermal movement of the polymer chain [22]. The progressive disappearance of the high-frequency chord portion with the temperature is a clear indication that capacitive effects are strongly decreasing with the temperature and that a random orientation of dipoles in the side chains of the blend polymer electrolyte became preponderant.

The evolution of the ionic conductivity as a function of temperature in the range 298–353 K is shown in Fig. 3. The value increases from 1.5 $\times$ 10$^{-5}$ S/cm at room temperature to 4.95 $\times$ 10$^{-4}$ S/cm at 80 °C and follows an Arrhenius thermally activated process expressed as $\sigma(T) = \sigma_0 \exp (E_a/kT)$, where $k$ is the Boltzmann constant, $T$ is the temperature and $E_a$ is the activation energy. The value extracted from the data is $E_a = 49.5$ kJ/mol, a value similar to those obtained for polymer electrolytes based on natural polymers [17]. This increase is interpreted as a complex behavior of a hopping mechanism between coordinating sites, local structural relaxations and segmental motions of
the polymer salt complexes. As temperature increases, the polymer chain acquires faster internal modes in which bond rotations produce segmental motion [23]. There is, therefore, no dynamic conformational change in the polymer matrix and the lithium might migrate through the conduction path formed by the lattice structure of the gelatin chains [24].

Fig. 4 shows a typical X-ray diffraction pattern obtained for the best gelatin-based electrolyte measured at room temperature. No crystalline peaks are observed and only a broad weak peak is seen at $2\theta \approx 22^\circ$ with a shoulder at $2\theta \approx 40^\circ$. This means that the electrolyte has an X-ray amorphous structure.

3.2. Electrochromic device

$8 \times 6 \text{cm}^2$ ECDs with the configuration $\text{Nb}_2\text{O}_5$/gelatin electrolyte/$(\text{CeO}_2)_{0.81}\text{–TiO}_2$ were mounted and characterized by cyclic voltammetry (CV). The voltammograms of the first, 5000th, 10,000th and 25,000th cycle are shown in Fig. 5. The first voltammogram shows two peaks: the first is cathodic at $-1.8 \text{~V}$ and is accompanied by the coloring of the device while the other, centered around $\sim 0 \text{~V}$, is anodic and is accompanied by the bleaching of the device. The feature of the voltammograms changes drastically in the first few cycles. The current density decreases sharply, the cathodic peak is shifted to lower negative potentials ($-1.2 \text{~V}$) and two anodic peaks are observed at 0.4 and 1.1 V instead of one. Then, the shape of the cyclic voltammograms does not change drastically by cycling up to 25,000 cycles. These two oxidation processes can be due to the presence of residual water in the electrolyte.

Fig. 6 shows the change of the charge density of the ECD measured by CA ($\pm 2.0 \text{~V}$, 90 s) as a function of the cycle number up to 25,000 cycles. The charge density decreases by cycling—first rapidly (from 10.4 mC/cm$^2$ at the first CA cycle down to 8 mC/cm$^2$ during the first few cycles), then at a lower rate to reach a value of 7.7 mC/cm$^2$ after 6000th cycle and a value $\sim 6 \text{mC/cm}^2$ after 25,000th cycle. It is important to notice that the devices showed a high charge intercalation/deintercalation reversibility and that the ratio of the cathodic to the anodic charge $Q_c/Q_a$ is 1 for all cycles.

The UV–vis–NIR spectra of the ECD measured during the 5000th cycle in the spectral range 300–3000 nm are shown in Fig. 7. The main transmittance variation between the bleached and colored states occurs in the visible range with a maximum $\Delta T = 18\%$ at the wavelength of 550 nm. The transmittance changes drop down to zero for $\lambda > 1400 \text{~nm}$. These results are comparable with ECDs built with starch-based electrolyte containing lithium salt [10] and with ECDs assembled with other polymeric electrolytes listed by Heusing and Aegerter [1].

The time stability of the devices has been tested by cycling them between the colored and bleached states at
potential of \(-2.0\) and \(+2.0\) V (90 s), respectively, up to 25,000 CA cycles. Fig. 8 shows the kinetics of the transmittance variation measured at \(\lambda = 550\) nm during the 5000th CA (\(\pm 2\) V, 90 s) cycle. One observes, as for devices built with other natural polymer electrolytes, that the bleaching process is faster than the coloration ones; the device was fully bleached after 25 s at +2.0 V and this time is similar to that needed to extract the inserted charge completely from a WO\(_3\) layer [17]. The charge density follows the same behavior as the de-insertion process at the positive potential is faster than the insertion process. The transmittance at 550 nm changes between \(T_E = 60\%\) (bleached state) and \(T_E = 42\%\) (colored state) after 2000 cycles, in agreement with the data of Fig. 7. For higher cycle number, the transmittance of the bleached state remains constant (\(T = 61\%\)) and that of the colored state increases slightly by about 3% to a value of \(T = 45\%\) during the 25,000th cycle (Fig. 9). Therefore, the change of transmittance during cycling is rather stable.

Fig. 10 shows the change in the OD of the devices calculated at 550 nm as a function of the number of CA cycles (\(\pm 2.0\) V, 90 s). The \(\Delta OD\) value increases continually during the first 2000 cycles, reaches a maximum value of 0.16 after 2000 cycles and then slightly decreases to a value of 0.13 after 25,000 cycles. A typical time variation of the OD for the 5000th cycle is presented in Fig. 10 (inset).

The coloration efficiency, defined as \(\eta = \Delta OD / Q\), where \(\Delta OD\) is the change in OD at a definite wavelength and \(Q\) is the corresponding charge exchanged during this change, is about \(23\) cm\(^2\)/C.

The investigated ECD with gelatin-lithium based electrolyte was also subjected to a memory test. After polarization at \(-2.0\) V for 90 s, the device, left in open circuit, shows a continuous increase of the transmittance from a value of 42% (colored state) to about 52% in 700 min (Fig. 11). The investigated ECD has, therefore, a good memory and the proposed configuration is promising to be applied for the development of architectural...
applications. Nevertheless, the change of the OD in the visible range measured after a polarization time of 90 s is rather small (0.14). Inspecting the data presented in Fig. 8, longer polarization time should decrease the value of the transmission in the colored state. However, it is believed that the main problem is linked to the too small ionic conductivity of the electrolyte (1.5 \times 10^{-5} S/cm) so that new compositions should be developed in order to improve this value.

4. Conclusions

Gelatin-lithium-based electrolytes are promising materials to be applied in ECDs because the material is available in nature, it is cheap and easy to handle and to prepare. The samples were found predominantly amorphous with ionic conductivity values increasing according to an Arrhenius law as a function of temperature from 1.5 × 10^{-5} S/cm at room temperature to 4.95 × 10^{-4} S/cm at 80 °C.

8 × 6 cm² ECDs were prepared with the configuration Nb₂O₅:Mo/gelatin-LiClO₄ SPE/(CeO₂)₀.₈₁–TiO₂. The ECDs have been characterized by optical and electrochemical measurements. The transmittance change between the colored and transparent states in the vis–NIR range is small and in the range of 18%. The kinetics of the bleaching of the device is faster than the coloration one. The inserted charge density of the devices decreases continuously with cycling from 10.5 mC/cm² (first cycle) down to 5.4 mC/cm² (25,000th cycle), but ΔOD remains rather constant, around 0.13, and the coloration efficiency increases continuously from η = 12.4 cm²/C (first cycle) to 23 cm²/C after 25,000th cycles.

Acknowledgments

The authors are indebted to FAPESP, CNPq, CAPES and PROBAL for the financial support given to this research.

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