Performance of a single-phase hybrid and nanocomposite polyelectrolyte in classical electrochromic devices

Flavio L. Souzaa, Michel A. Aegerterb, Edson R. Leitea,*

a Department of Materials Science and Engineering, Federal University of São Carlos, São Carlos 13565-905, SP, Brazil
b Leibniz-Institut für Neue Materialien gGmbH-INM, Im Stadtwald, Gebäude 43, 66123 Saarbruecken, Germany

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Abstract

In this paper, we discuss the high stability of a single-phase hybrid polyelectrolyte (SPHP) and nanocomposite hybrid polyelectrolyte (NHP) in a large electrochromic (EC) device (5 cm × 10 cm) mounted with different electrodes. The electrochromic device (K-glass/FTO/WO3/SPHP/CeO2–TiO2/FTO/K-glass—ECI, K-glass/FTO/WO3/NHP/CeO2–TiO2/FTO/K-glass—ECII,) exhibited excellent color and bleach reversibility, high coloration efficiency (CE) (>35 cm²/C) from the first cycle up to more than 60,000 CA cycles, and a maximum constant rate of deintercalation/intercalation (Qout/Qin = 1). Also, the life time of the EC device with Nb2O5:Mo (K-glass/FTO/Nb2O5:O/SPHP/CeO2–TiO2/FTO/K-glass—ECIII) was prolonged to up to more than 10,000 cycles with a fairly stable coloration efficiency (around 19 cm²/C) and Qout/Qin = 1. The SPHP and NHP were tested in a large EC device with different configurations to evaluate its successful performance. In conclusion, its remarkable behavior and high stability render this material an excellent candidate for application in EC devices.

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1. Introduction

Electrochromism is defined as a persistent but reversible optical change produced electrochemically [1]. 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 [1,2]. Large electrochromic glazing can be used for architectural and automotive applications in order to control the entry of solar radiation into buildings and automobile to save air-conditioning costs in summer and heating costs in winter [3,4].

A critical component in electrochromic (EC) devices is the ion-conducting electrolyte. The ions should move rapidly from the EC-layers through the electrolyte and, in battery-type EC-devices, to the complementary EC-layer or the ion-storage (IS) layer [5,6]. The electrolyte may be a liquid, a polymer, a gel or a thin film electrolyte. Liquid electrolytes are not useful for large area applications because of buckling of the glass and the risk of leakage. To improve the safety of large devices and avoid the effect of hydrostatic pressure and the need for sealing, the liquid electrolyte can be replaced by a solid-state electrolyte film. The literature on ionic conductors is vast and several reviews on inorganic ion conductors suitable for EC devices and other applications can be found in Refs. [7–9]. Most of the research in this field has been done on H⁺ and Li⁺ conductive coatings, the latter being the one used in this work.

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 windows [10,11]. To a certain extent, these hybrid materials combine the most important properties of their constituents, such as high transparency (glasslike), low processing temperatures (polymer-like), sufficient thermal stability (silicone-like), and high-performance yield and properties not found in either material individually [12–17].

Recently, we described a different class of single-phase hybrid polyelectrolyte in which the ionic conductivity is not

* Corresponding author.
E-mail address: derl@power.ufscar.br (E.R. Leite).

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coupled to the segmental motion of the polymer chain, i.e., a material in which the ions move independently of viscous flow [18]. The development of a segmental motion-decoupled polymer system is an alternative way to increase ionic conductivity in polymer electrolytes [19–21]. The material’s ionic conductivity \( (\sigma = 10^{-5} \Omega^{-1} \text{cm}^{-1}) \) at room temperature showed an Arrhenius-like behavior as a function of temperature (in the range of temperatures above \( T_g \)) and an activation energy of 0.23 eV. These characteristics indicate a rapid ion transport mechanism in a segmental motion-decoupled hybrid organic–inorganic polymer. The aforementioned single-phase hybrid polyelectrolyte (SPHP) was synthesized by a derivative in situ polymerizable method (a nonhydrolytic sol–gel process) based on the formation of a Si and citric acid complex subsequently polymerized by means of a polyesterification reaction with ethylene glycol (EG) [22,23]. The material became ionically conductive when \( \text{Li}_2\text{CO}_3 \) was dissolved in the structure during its synthesis. A transparent, amorphous solid polymer was obtained after elimination of the solvent. The good ionic conductivity alluded to the excellent transparency of this SPHP material motivated us to apply it in a classical electrochromic (EC) device [24–26]. In a recent communication, we discussed the high stability of the single-phase hybrid polyelectrolyte (SPHP) applied in an electrochromic device (5 cm \( \times \) 10 cm) using \( \text{WO}_3 \) (electrochromic) and \( \text{CeO}_2–\text{TiO}_2 \) (counter-electrode–ion storage) electrodes, both produced by the Leibniz Institute of New Materials (Leibniz-INM, Germany). The electrochromic device exhibited excellent color and bleach reversibility, high coloration efficiency (>35 cm\(^2\)/C) from the first cycle up to more than 60,000 CA cycles, and a maximum constant rate of deintercalation/intercalation \((Q_{\text{out}}/Q_{\text{in}} = 1)\). Its remarkable behavior and high stability render this material an excellent candidate for application in electrochromic devices.

The main purpose of this paper is to analyze the electrochemical performance of the single-phase hybrid polyelectrolyte (SPHP) and nanocomposite hybrid polyelectrolyte (NHP, with nanoparticles of \( \text{SiO}_2 \)) materials applied in EC devices with dimensions of 5 cm \( \times \) 10 cm. The classical EC device was mounted using two different configurations: \( \text{WO}_3 \) (electrochromic layer) or \( \text{Nb}_2\text{O}_5:\text{Mo} \) (electrochromic layer) and \( \text{CeO}_2–\text{TiO}_2 \) (counter-electrode–ion storage) electrodes, all produced by the Leibniz Institute of New Materials (Leibniz-INM, Germany) [27–30], using SPHP and NHP as solid-state electrolytes. Fig. 1a and b depicts the solid-state electrochromic (EC) device studied here in the bleached and colored states.

2. Experimental

2.1. Polyelectrolyte

The chemical synthesis and other features (such as reproducibility) of this polyelectrolyte are presented elsewhere [22]. Basically, the single-phase hybrid polyelectrolytes (SPHP) and the nanocomposite hybrid polyelectrolyte (NHP) were synthesized by a nonhydrolytic sol–gel process involving an organic–inorganic polymeric glass network, apparently deriving from an “unpolymerizable method” [23]. The ionic conductivity arises from the addition of \( \text{Li}_2\text{CO}_3 \) during the synthesis. As discussed in Ref. [22], only \( \text{Li}^+ \) is expected to be mobile in the inorganic–organic hybrid structure of the polyelectrolyte. As a consequence, the SPHP and NHP are single ion conductors [22]. The anions are believed to form from the carboxyl group (~COO~) that is present in the polymer network. It is important to point out that the SPHP and NHP are fully amorphous at room temperature. Following a typical procedure, the both polymers were prepared with a citric acid/Si (molar) ratio of 2:1 and a Si–citric acid complex/EG mass ratio of 77:23. TEOS was used.

Fig. 1. (a) Picture of 5 cm \( \times \) 10 cm blue-colored EC device after galvanostatic coloring and bleached for 120 s. The configuration is K-glass/\( \text{WO}_3/\text{SPHP/\text{CeO}_2–\text{TiO}_2/\text{K-glass} \), potential used was \(-2.0 \text{~V}, 60 \text{~s}+1.25 \text{~V}, 60 \text{~s} \) and working more than 60,000 CA cycles, (b) Picture of 5 cm \( \times \) 10 cm gray-colored EC device after galvanostatic coloring and bleached for 180 s. The configuration is K-glass/\( \text{Nb}_2\text{O}_5:\text{Mo}/\text{SPHP/\text{CeO}_2–\text{TiO}_2/K-glass} \), potential used was \(-2.0 \text{~V}, 90 \text{~s}+2.0 \text{~V}, 90 \text{~s} \) and after 15,000 CA cycles the cell destroyed. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)
as the Si source in the synthesis of the Si–citric acid complex. The Si–citric acid complex and polymerization reaction were carried out in an ethanol solution at 40 °C under constant magnetic stirring. The preparation of the polymer electrolyte included the addition of Li2CO3 (10% in mol) during the synthesis. In order to obtain the nanocomposite material (NHP), an extra step is necessary. After polymerization reaction, were added 10 wt% SiO2 nanoparticles (Cabot, CAB-O-SIL with mean particle size of 5 nm) [22]. The lithium concentration used here was 10 wt% in the SPHP and NHP systems.

2.2. WO3, Nb2O5:Mo, (CeO2)x(TiO2)1−x sol–gel layers

The preparation of the WO3, Nb2O5:Mo, (CeO2)x(TiO2)1−x sol–gel layers and of the EC device with single-phase hybrid polyelectrolyte (SPHP) was carried out by INM. The K-glass substrates (glass coated with FTO, Pilkington, 17 Ω), were washed, dried and heat-treated at 450 °C for 15 min. The (CeO2)x(TiO2)1−x layers were deposited on these substrates by the dip-coating technique at a withdrawal rate of 4 mm/s at 21 °C with 41% air humidity. The single layers were then heated in air from room temperature up to 450 °C at a heating rate of 2.5 K/min, held for 15 min at 450 °C and cooled to room temperature inside the oven within 5h. The (CeO2)x(TiO2)1−x system was produced by the Leibniz-INM and the layers also were deposited following the steps created by the same group. Thus, the (CeO2)x(TiO2)1−x layers were used as obtained, i.e., the electrode was not pre-reduced or any other kind of treatment by us. The WO3 layers were deposited in single coating steps on the K-glass by the same technique under the same experimental conditions and then heat-treated at 175 °C. The parameters used in the WO3 layer deposition was indicated by the INM researchers in order to obtain a stable coating. Nb2O5:Mo layers were deposited in two layers by the same technique (dip coating). For the first layer, the substrate was dipped in the solution for 30 s, withdrawn at a rate of 4 mm/s (at 21 °C and 30% air humidity), and heated at 100 °C for 30 min. For the second layer, the substrate was again dipped in the solution for 30 s, withdrawn at a rate of 2 mm/s (at 21 °C and 30% air humidity), and then heated at 100 °C for 30 min. The substrate coated with two layers was then placed directly in a hot oven preheated to 500 °C for 30 min, after which the oven was allowed to cool down to 30 °C. The double layers were homogeneous, with a thickness of ~120 nm.

2.3. EC device

The EC devices (size 5 cm × 10 cm) made of K-glass /FTO/Nb2O5:Mo or WO3/SPHP or NHP/CeO2–TiO2/FTO/K-glass were prepared by mounting, in air, a double sided adhesive tape (thickness 1 mm, 3M) 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 (highly viscous liquid) through a small hole, heated at 80 °C for 12 h to solidify the polyelectrolyte, and then extra sealed using butyl rubber (3 M) and adhesive tape. The electrochemical measurements were taken using an EG&G 273A potentiostat.

The samples were studied by cyclic Chronoamperometric (CA) measurements were taken by applying a potential range of −2.0 to +1.25 V 120 s to the EC device/WO3 and −2.0 to +2.0 V for 180 s to the EC device/Nb2O5:Mo. 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 a reference.

3. Results and discussion

Three different configurations were studied: K-glass /FTO/WO3/SPHP/CeO2–TiO2/FTO/K-glass (ECI), K-glass /FTO/WO3/NHP/CeO2–TiO2/FTO/K-glass (ECII) and K-glass /FTO/Nb2O5:Mo/SPHP/CeO2–TiO2/FTO/K-glass (ECIII). Fig. 1a and b illustrates solid-state electrochromic (EC) devices in the bleached and colored state after galvanostatic coloring and bleaching with ±135 μA/cm² for 2 min, using a safety voltage limit of ±2.5 V.

3.1. Tungsten oxide (WO3)

The transmittance spectra of the ECI (with SPHP) and ECII (with NHP) devices can be observed by the evolution of transmittance variations (λ = 550 nm) in the bleached (Tb) and colored (Tc) states as a function of the number of CA cycles (Fig. 2). The transmittance of the bleached state (EC with SPHP, Tb = 74%) remained constant throughout the 60,000 cycles. On the other hand, a slow increase in the transmittance was observed in the colored state (Tc) up to 30,000 cycles, after which it remained practically constant. Initially, the transmittance varied little (about 10%), increasing continuously to about 30% and 25% up to 30,000 cycles, thereafter declining slightly. Finally, the device continued to work at a constant rate from the 40,000th to the 60,000th cycle, with no apparent sign of degradation or delamination of the polyelectrolyte. Although the ECII displayed a slightly stronger colored state than the ECI, the variation in trans-

![Fig. 2. Transmittance (Tb and Tc) of the ECI and ECII devices at λ = 550 nm as a function of the CA cycle number (−2.0 V, 60 s/+1.25 V, 60 s) with single-phase hydrid and nanocomposite polyelectrolyte (SPHP and NHP).](image-url)
mittance ($\Delta T = T_b - T_c$) of the ECII was slower. This was due to the slight reduction in the transmittance of the bleached state after the 10,000th cycle. We believe that the behavior of the ECII after 25,000 cycles was attributable to an increase in the carrier number, probably because of the contribution of $H^+$. This effect can be explained by the features of the SiO$_2$ nanoparticle surface, which is usually hydrated. Therefore, if the SiO$_2$ nanoparticles are dispersed in the hybrid organic–inorganic polyelectrolyte during synthesis in an acid environment, the following reaction may occur:

$$\equiv \text{SiOH} + H^+ \leftrightarrow \text{SiOH}_2^+$$  \hspace{1cm} (1)

which explains the increase in the transference number charge and, in consequence, we observed a change in the behavior of the ECII device.

The coloration efficiency (CE), defined as the ratio of optical density ($\Delta OD = \log_{10}(T_{\text{bleached}}/T_{\text{colored}})$) to $(Q_{\text{in}})$ intercalated charge, was calculated at 550 nm (Fig. 2), based on the results of 2-min chronoamperometric (CA) cycles (Fig. 3). For the ECI and ECII device studied here with SPHP and NHP, the CE values increased from the 1st cycle up to and beyond the 25,000th cycle (about 30–45 cm$^2$/C), thereafter declining slightly in the 30,000th cycle and remaining practically constant up to 60,000th cycle (about 35 cm$^2$/C). This finding is also in agreement with the change of transmittance in the colored state, which, after 30,000 cycles, declined slightly (5% of the original value), remaining practically constant up to the 60,000th cycle. This effect is probably due to the charge ($\text{Li}^+$) arrest in the counter-electrode. All our results lead us to this conclusion. The electrochromic electrode WO$_3$ was not responsible for retaining Li$^+$ since, throughout the experiment, we observed no variation in the bleached state, as clearly indicated in Fig. 2. Another critical component possibly associated with charge arrest is the electrolyte. However, after 60,000 cycles, a constant ratio ($Q_{\text{out}}/Q_{\text{in}} \approx 1$) of deintercalated/intercalated charge was observed, as shown in Fig. 4, suggesting no charge accumulated in the solid electrolyte (SPHP and NHP). Thus, all the intercalated charge was deintercalated through the electrolyte, precluding this component’s possible inefficiency. On the other hand, a reduction was noted in the value of the intercalated charge ($Q_{\text{in}}$), as illustrated in Fig. 5. This reduction must relate to the counter electrode (CeO$_2$–TiO$_2$), which is responsible for charge storage. The charge arrest in the counter-electrode explains the reduction in the transmittance of the colored state and coloration efficiency, as is clearly indicated in Figs. 2 and 3.

Although the overall behavior of the transmittance spectra did not change, the EC device with SPHP did not present a deeper colored state after a 1 min of switching time. One minute was probably insufficient for full coloration, but this time was applied in order to switch the devices within a reasonable time up to 60,000 cycles. However, one minute sufficed for the devices to reach a completely bleached state. Another good explanation for this is the performance of the WO$_3$ layer. The EC device with SPHP and NHP was not equipped with an electrochromic ele-
trode (WO3) processed in the optimum condition, which could explain why the EC device did not reach coloration stronger or greater than 30%. Sun et al. [28] reported that WO3 layers obtained by heat treatment at 240 °C are still X-ray amorphous and show a better long-term stability and lower change of optical density $\Delta OD = \log_{10}(T_{\text{bleached}}/T_{\text{colored}})$ than layers heat-treated at lower temperatures. Thus, the short switching time and inappropriate thermal treatment of the WO3 layer can help explain why we did not observe better (or deep blue) results of transmittance (colored state). In addition, the low heat treatment applied during preparation of the WO3 layer may also explain the charge created ($Q_{\text{out}} > Q_{\text{in}}$) during the cycles.

Fig. 4 shows that the $Q_{\text{out}}/Q_{\text{in}}$ ratio of the deintercalated to the intercalated charge remained constant from cycle 1 through 60,000, indicating good reversibility of the ionic charge exchange with the electrolyte. The ratio showed a value higher than 1. This effect was associated with the charge created during the operation, probably water dissociation or some organic component of the WO3 layer (ECI with SPHP). In the case of ECII with NHP, there was probably also a contribution of the dissociation of $H^+$ encountered in the surface charge of the SiO2 nanoparticles.

After 60,000 cycles, chronopotentiometry measurements ($\pm 2.5$ V, 60 min and current density $\pm 130$ μA/cm$^2$) were taken, the results of which confirmed that the switching time used here was inappropriate. The evolution of the transmittance (bleached and colored state) and charge density showed a continual increase until the maximum values in both devices were attained. We found that, with a higher potential and a long switching time between intercalated/deintercalated, all the parameters improved significantly. Table 1 summarizes the values of $T_c$, $T_b$, CE and $\Delta OD$ (after 60,000 cycles).

However, these experiments confirmed our expectation that one way to improve EC devices (without having an electrochromic electrode in optimum condition) is to change some of the kinetic parameters, such as switching time (intercalation/deintercalation) and/or higher potential. On the other hand, the concentration of salt in the hybrid polyelectrolyte was still not optimized when a large content was synthesized. Therefore, we know that a greater number of transfers could obviate the need for a higher potential or a longer switching time.

The use of SPHP and NHP in large EC devices was highly successful in the kinetic process during deintercalation/intercalation. These results are presented in Figs. 2 and 4, which show that the cell’s bleached state was recovered and all the intercalated charge was deintercalated during all the cycles. Another excellent result achieved with the EC device studied here is illustrated in Fig. 1a. After 60,000 cycles, no evidence of degradation was found, i.e., the EC device with the SPHP and NHP presented excellent stability.

Table 1

<table>
<thead>
<tr>
<th>ECI device (WO3 layer)</th>
<th>Size (cm$^2$)</th>
<th>$T_b$ (%)</th>
<th>$T_c$ (%)</th>
<th>$\Delta OD$</th>
<th>Number of CA cycles</th>
<th>CE (cm$^2$/C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>K-glass/WO3/SPHP/CeO2–TiO2/K-glass</td>
<td>5 × 10</td>
<td>74</td>
<td>20</td>
<td>0.56</td>
<td>60,000$^a$</td>
<td>47</td>
</tr>
</tbody>
</table>

$^a$ Still working.
optical density ($\Delta OD = \log_{10}(T_{\text{bleached}}/T_{\text{colored}})$) depends on the variation in transmittance ($\Delta T$), and the values of $\Delta T$ obtained here were low.

Another important result was the coloration efficiency, which was calculated from the optical density/intercalated charge ($\Delta OD/Q_{\text{in}}$) ratio, as illustrated in Fig. 9. The coloration efficiency increased continually, reaching a maximum value of $\sim 19$ cm$^2$/C (150,000 cycles), followed by complete degradation of the device. This low CE value was expected due to the minor variation in transmittance ($\Delta T = T_b - T_c = 12\%$) obtained throughout the experiments. Therefore, the low value of the ECIII when compared with the ECII (WO$_3$ and SPHP) was not due to a kinetic effect, as in the case of the ECI and ECII devices (low intercalated charge, Fig. 10, and/or short time for intercalation charge). In fact, after 60 min at an applied voltage of $\pm 2.5$ V, the results were not relevant compared with the devices built with WO$_3$. Nonetheless, we found that the intercalated charge increased to about twice the initial value (12 mC/cm$^2$), while the values of transmittance variation ($\Delta T$), optical density ($\Delta OD$) and coloration efficiency (CE) did not undergo significant alterations, as indicated in Table 2. This fact, allied with the results obtained for the ECI and ECII (also after 60 min of applied voltage of $\pm 2.5$ V) leads us to believe that the reason (for the ECIII) is not due to the effect of kinetics but probably due to the fact that the electrochromic electrode (Nb$_2$O$_5$:Mo) was not properly optimized.

Schmitt et al. [31,32] showed that changes occur during the initial cycles in $T_b$, $T_c$, $\Delta OD$ and that, after 15,000 chronoamperometric cycles, these values change drastically and worsen in a dry composite electrolyte in which the cells are destroyed. The cells presented a low $\Delta OD$ (about 0.1) during the initial cycles, increasing continually to about 0.33 up to 700 cycles, and then decreasing to 0.1 after about 14,000 cycles, when the cell was destroyed. The conditions applied in their study were $+2.5$ V, 2 min/$-2.5$ V, 2 min. In our study, the potential and time
employed were lower, i.e., +2.0 V, 1.5 min/−2.0 V, 1.5 min, but our results were almost identical to those reported by Schmitt.

Although the ECIII device (with Nb2O5:Mo) did not present a marked behavior in terms of coloration and bleaching, it performed its role as an electrolyte successfully (Fig. 11). The main goal of an electrolyte is to transport charge. In this study (Fig. 11), we found that the SPHP presented a maximum intercalated/deintercalated charge of about ∼1, at 15,000 chronoamperometric cycles. During the 15,000 cycles and in the chronopotentiometric test, we found that all the intercalated charge in the electrochromic electrode, 90 seg and/or 60 min, was deintercalated and led to the electrode-counter (ion storage electrode), indicating a totally reversible process. Other important characteristics of the performance of the SPHP were the excellent adhesion of the electrodes, the high fill factor, absence of shortcircuit and bubbles, which eliminates possible interface problems. Fig. 1b illustrates the homogeneity (ECIII with SPHP) achieved in the colored state (gray) and the total recovery of the bleached state. Thus, for the ECI and ECII (with WO3), the use of SPHP in large EC devices (with Nb2O5:Mo) was highly successful in the kinetic process during deintercalation/intercalation, as shown in Figs. 1a and b and 11.

4. Conclusions

In summary, the hybrid SPHP or NHP polyelectrolytes (with SiO2 nanoparticles) both tested entirely successfully in EC devices (5 cm × 10 cm size) using different configurations. The lifetime of the ECI and ECII device were prolonged to over 60,000 cycles with the single-phase hybrid polyelectrolyte (SPHP). Long-term stability and high coloration efficiency (CE) were achieved. The single-phase hybrid polyelectrolyte (with and without nanoparticles) showed excellent charge transport performance throughout all the cycles tested (over 60,000 cycles ECI, ECII and 10,000 cycles for ECIII), with a maximum constant rate of deintercalation/intercalation (Qout/Qin = 1). The development and improvement of hybrid polyelectrolytes with decoupled behavior can lead to the development of large solid EC devices with high stability performance. Further studies aimed at achieving even better results with this and other configurations are under way.

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