



Enhanced Reliability of Electrochromic Devices with a LiPON Protective Layer

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The electrochromic properties of WO₃ thin films with a LiPON (lithium phosphorous oxynitride) protective layer and of an electrochromic device composed of WO₃ and V₂O₅ with a LiPON protective layer prepared by radio-frequency magnetron sputtering were investigated. The WO₃ film and the electrochromic devices (glass/ITO/V₂O₅/LiPON/electrolyte/LiPON/WO₃/ITO/glass) with a protective layer not only showed improved durability with continuous potential cycling, but also demonstrated faster bleaching-coloring response rates and a higher coloration efficiency. Our results demonstrated that LiPON layers are electrochemically stable, enhance the electrochromic properties of Li ion-conducting electrolytes, and can be used as a protective layer for electrochromic devices.

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The development of energy efficient windows which make use of the phenomenon of electrochromism, wherein the color changes depending on the potential of an applied electric field, can contribute to reducing the emissions from fossil fuels and providing energy savings through the utilization of alternative energy sources, while helping to preserve the global environment.^{1,2} Also, because the development of this new concept of windows allows an increase in the quality of life by improving the residential and office environment, many studies on these windows are currently being conducted.³ Electrochromism can be applied to spectacles, mirrors, windows, smart cards, price labels, and displays such as mobile phones.⁴⁻⁹ Electrochromic (EC) devices have components similar to those of battery cells and comprise thin layers, consisting of an EC layer (positive electrode)/electrolyte (Li⁺, H⁺)/counter electrode layer (negative electrode).¹⁰ A brief explanation of the principle of electrochromism is as follows. When cations and electrons, such as Li⁺ or H⁺,^{4,11} are injected into an EC layer made of a reducing coloration material (e.g. W_xO_y, Mo_xO_y, etc.), the layer will be colorized, and when the cations are released, the layer will become transparent.^{1,2} On the other hand, when cations and electrons, such as Li⁺ or H⁺, are released from a counter electrode layer made of an oxidative coloration material (e.g. V_xO_y, Ni_xO_y, etc.), the counter electrode layer will be colorized, and when the cations are injected, the counter electrode layer will become transparent. Conventional EC devices comprise a glass substrate, and a transparent electrode layer, a counter electrode layer, an electrolyte layer, an EC layer and a transparent electrode layer, which are sequentially formed on a glass substrate. However, these conventional EC devices have a stability problem, because the reversibility of the intercalation and deintercalation of the ions (H⁺, Li⁺, etc.) is broken, due to the contact between the EC or counter electrode layer and the electrolyte layer.¹²⁻¹⁷

Tungsten oxides, which have been widely studied as EC materials, can cause an irreversible chemical reaction with the lithium ions intercalated in an electrochromic device, so that the lithium ions will be trapped in each layer of the device. Consequently, each layer of the EC device will be degraded and cleaved into thin layers, thus leading to the deterioration of the properties of the device, with the result that the material either can no longer perform electrochromism rapidly or loses its function as an EC device altogether due to electrical leakage.¹⁵⁻¹⁹

As described above, conventional EC devices have the drawbacks of a short lifecycle and irreversible electrochemical reaction

and, consequently, there is an urgent need for the development of novel EC devices having high durability and excellent electrochromic properties.

It has been found in our previous study⁷ that an inorganic solid electrolyte (LiPON, lithium phosphorous oxynitride)²⁰ thin film plays a role in protecting the EC matrix in the Li ion-conducting electrolytes. The LiPON deposited WO₃ and V₂O₅ films showed greater stability against EC coloring/bleaching, a higher response time and a higher coloration efficiency (CE). However, if the inorganic solid electrolyte layer has a thickness less than a specific thickness (diffusion thickness, etc.), it will have a very insignificant effect on the improvement of durability. If it has a thickness over a specific thickness, it will provide an improvement of durability, but cause significant reduction in bleaching response time and coloring response time, which are important properties in electrochromic devices. Accordingly, in this work, we investigated whether it is possible to realize fast bleaching response and coloring response rates and an increase in the durability of the electrochromic device simultaneously by forming the inorganic solid electrolyte layer in the thickness within the above-specified range.

Experimental

We used glass substrates each having a transparent electrode [indium tin oxide (ITO) with a resistivity of 15–18 Ω/□] coated on them, with a 30 nm thick layer of silicon oxide (SiO₂) interposed between the substrate and the electrode. WO₃ was deposited on the transparent electrode (ITO) in a vacuum of 10 × 10⁻³ Torr at room temperature under an argon atmosphere at an rf power of 150 W for 52 min. The deposition rate of the tungsten oxide was 7.7 nm/min. WO₃ was deposited to a thickness of about 400 nm. Then, LiPON [Li_{3.3}PO_{3.8}N_{0.22}, United Vacuum & Materials (UVM)] was deposited on the WO₃ layer. A LiPON target was used as an inorganic solid electrolyte, and the distance between the transparent electrode substrate and the LiPON target was 30 cm. The pressure before starting the experiment was 1.0 × 10⁻⁶ Torr, and the sputtering operation was carried out at a pressure of 10 × 10⁻³ Torr at room temperature in a nitrogen atmosphere at a power of 100 W for 30–125 min. The deposition rate of LiPON was 1.6 nm/min and, as shown in Fig. 1, LiPON was deposited to a thickness of about 50–200 nm, so as to form an element consisting of the substrate (glass)/transparent electrode layer (ITO)/electrochromic layer (WO₃)/inorganic solid electrolyte protective film (LiPON). Figure 1 shows a field-emission scanning electron microscopy (FESEM, JEOL 6330F) photograph of the inorganic solid electrolyte protective film (LiPON) deposited by radio-frequency (rf) magnetron sputtering in the present study.

Meanwhile, V₂O₅ was deposited on the transparent electrode (ITO) in an atmosphere consisting of a mixture of argon and oxygen

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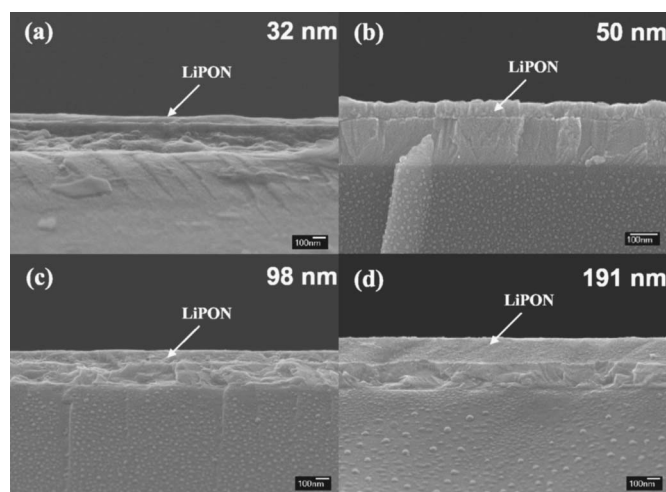


Figure 1. SEM showing the comparison between WO_3 thin films having protective inorganic solid electrolyte layers formed to have various thicknesses.

(5:1) at a power of 300 W for 180 min. The vanadium oxide was deposited at a rate of 0.7 nm/min to a thickness of about 125 nm. LiPON was then deposited on the V_2O_5 layer, so as to form an element consisting of (glass)/(ITO)/(V₂O₅)/(LiPON). Next, a liquid electrolyte (LiClO_4/PC) was injected between the two elements, so as to manufacture an electrochromic device consisting of (glass)/(ITO)/(V₂O₅)/(LiPON)/(LiClO₄/PC)/(LiPON)/(WO₃)/(ITO)/(glass) (see below). Before injecting the liquid electrolyte between the two electrolyte layers, the EC layer was colored by injecting lithium ions, and the counter electrode layer was bleached by releasing the lithium ions. This was performed so as to adjust the charge balance between the two electrodes and to make the driving of the EC device stable. Thus, the EC device is in an initial state wherein the EC layer and the counter electrode layers are colored.

According to the X-ray diffraction (XRD) measurements, the crystallographic structures of the WO_3 , LiPON, and V_2O_5 films were nearly amorphous. The XRD patterns were obtained with a MacScience M18XHF diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda = 0.15418$ nm). All electrochemical potential cycling tests were performed using an Autolab PGSTAT30 Potentiostat/Galvanostat. Pt wire and Ag/AgCl (sat. KCl) were used as the counter and reference electrodes, respectively. 1 M $\text{LiClO}_4/\text{propylene carbonate}$ (PC) was used as an electrolyte.

The EC properties were evaluated by switching a pulse potential wave between -2.5 and 1.5 V (vs anodic coloring material) with a duration of 30 s. This procedure is referred to as switched pulse potential cycling. The EC response time was measured by applying a pulse potential wave with a duration of 30 s. The transmittance was simultaneously measured in situ during all of the experiments using a He-Ne laser (633 nm). The in situ transmittance measurement technique represents the optical behavior as a function of time during the coloring/bleaching process of the EC active film and provides a better understanding of the differences in optical performance between the samples. The transmittance of the (glass)/(ITO) with the electrolyte and cell window was assumed to be 100%.

The ac impedance measurement was made with a three-electrode configuration in 1 M LiClO_4/PC . The used frequency range was 10^5 Hz–5 mHz with an ac amplitude of 10 mV (Zahner IM6). Software of ZPlot/ZView (Scribner Associates, Inc.) was used for the numerical calculation.

Results and Discussion

The parameters listed in Fig. 1 were kept constant, except for the rf power and deposition time. In this way, various devices were

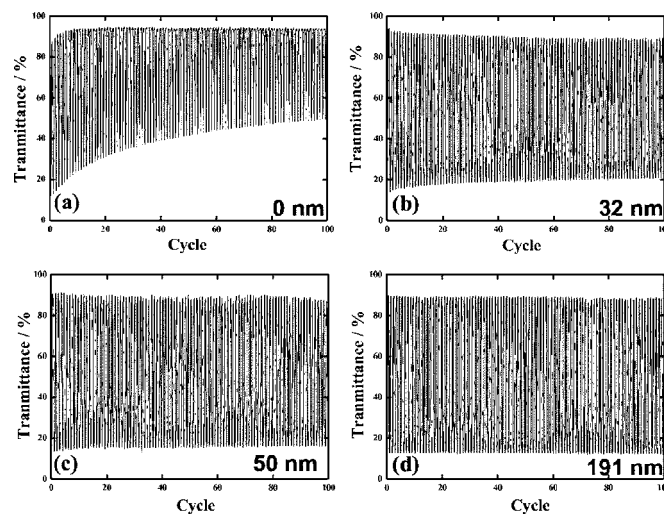


Figure 2. In situ transmittance curves obtained during switched pulse potential 100 cycling tests of WO_3 thin films with various thicknesses of a LiPON protective layer.

fabricated, each consisting of (glass)/(ITO)/(WO₃)/(LiPON), in which the thicknesses of the inorganic solid electrolyte films were 10, 32, 50, 98, and 199 nm, respectively. The thickness of each of the inorganic solid electrolyte films increased with increasing deposition time, and the scanning electron microscope photographs of the EC layer (WO_3) and protective inorganic solid electrolyte film (LiPON) for each of the devices are shown in Fig. 1.

The changes in the optical transmittance of each of the devices were monitored using the in situ transmittance measurement technique, and the results are shown in Fig. 2. Also, the reduction rates of optical transmittance after one cycle and 100 cycles for each of the devices are shown in Fig. 3. As shown in Fig. 2 and 3, the tungsten oxide thin film having no protective inorganic solid electrolyte film showed a greater reduction in optical transmittance (reduction rate of optical transmittance: 36%) with increasing number of cycles. On the other hand, the tungsten oxide thin film including the protective inorganic solid electrolyte film showed little or no change in its optical transmittance, indicating that the electrochemical properties of the device remained highly stable during cycling. Particularly in the case where the thickness of the protective inorganic solid electrolyte film was 30 nm or more, the reduction rate of optical transmittance was less than 7%, indicating a significant improvement in the electrochemical stability.

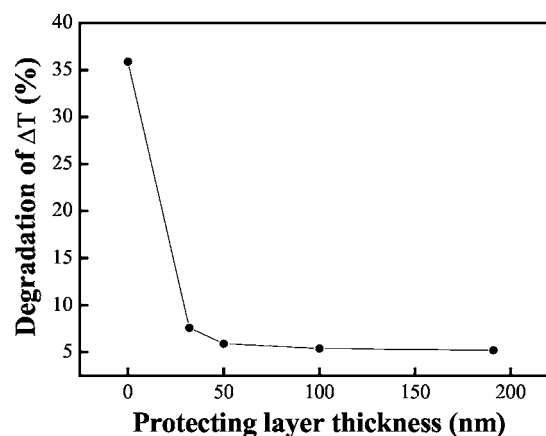


Figure 3. Change in the transmittance of WO_3 thin films according to pulse voltage with changing thickness of a LiPON protective layer.

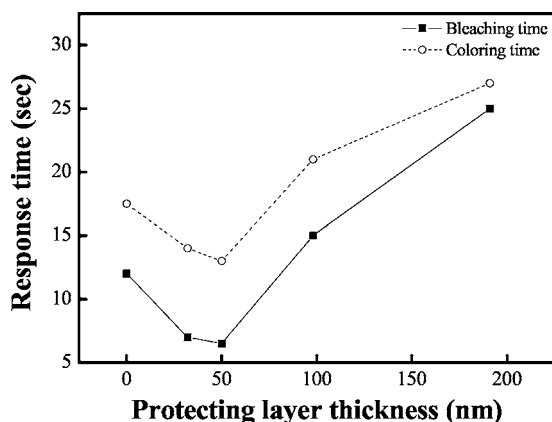


Figure 4. Change in the bleaching response time and coloring response time of WO_3 thin films with changing thickness of a LiPON protective layer.

Furthermore, the bleaching response time and coloring response time of each of the devices were measured, and the results are shown in Fig. 4. As shown in Fig. 4, the thickness of the protective inorganic solid electrolyte film had a significant effect on the bleaching response time and coloring response time of the devices. Namely, in the case where the thickness of the protective inorganic solid electrolyte film was over 100 nm, the durability of the device was improved, whereas its bleaching response time and coloring response time were significantly increased compared to those of the tungsten oxide thin film having no protective inorganic solid electrolyte film, suggesting that the properties of the device were reduced.

The bleaching response and coloring response times of electrochromism are very important characteristics in EC devices, particularly when they are used for such applications as display devices. In these devices, although the electrochromic stability is important, the thickness of the protective inorganic solid electrolyte film needs to be optimized to allow the various device characteristics, such as the bleaching response time and coloring response time, to be optimized together with the stability. This is because the reductions in the response rates of EC bleaching and coloration caused by the protective inorganic solid electrolyte film can be disadvantageous to EC devices.

In the device comprising the protective inorganic solid electrolyte film, the EC layer was not degraded or cracked by the electrolyte, thus causing it to have higher durability, unlike in the case of the device without the inorganic solid electrolyte film. Particularly, by optimizing the thickness of the protective inorganic solid electrolyte film, it is possible to increase the bleaching and coloring response rates of the electrochromic device, so as to maximize its efficiency. The electrochromic device developed in this study comprises the inorganic solid electrolyte as a protective film, and thus has excellent durability, fast bleaching and coloring response rates. Particularly, the protective inorganic solid electrolyte film can reduce the interfacial resistance between the electrolyte and the electrodes and protect the working electrode from external physical or chemical invasion, thus making it useful as a protective film for working electrodes not only in EC devices, but also in thin film battery cells, thin film fuel cells, and dye-sensitized solar cells.

To identify the interface at which degradation occurs during cycling, we employed electrochemical impedance spectroscopy (EIS). Figure 5 shows the Nyquist plots of the (glass)/(ITO)/(WO_3) and the (glass)/(ITO)/(WO_3)/(LiPON:32–191 nm) measured at -1 V after the potential 1000 cycling tests and fitting results using an equivalent circuit model. We varied between 10 kHz and 5 mHz as a function of the applied frequency. These impedance spectra were analyzed on the basis of the complex nonlinear least-squares (CNLS) fitting using an appropriate equivalent circuit model in-

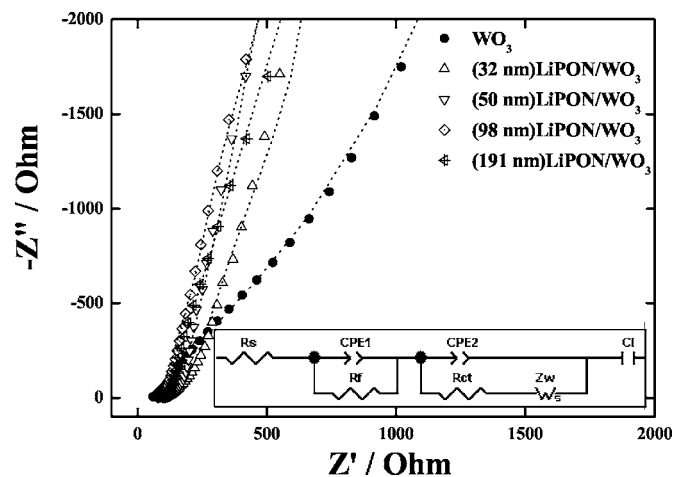


Figure 5. Nyquist plots of impedance spectra obtained from WO_3 thin films and WO_3 thin films with changing thickness of a (32–191 nm) LiPON protective layer after 1000 cycles and their equivalent circuit and fitting results (dot line) using the equivalent circuit model.

serted in Fig. 5. In these circuits R_s denotes the electrolyte resistance, R_f is the ionic resistance of the LiPON layer, R_{ct} is the charge transfer resistance associated with the ion injection from the electrolyte into the electrochromic electrode, Z_w is the Warburg a diffusion impedance of finite-length type, and C_l is the limiting capacitance. The CPE1 is a constant phase element describing the distributed capacitance of the electrochemical double layer between the electrolyte and the WO_3 film and the CPE2 is a constant phase element describing the distributed capacitance of the plate capacitor formed by electrolyte, LiPON layer, and conductive intercalation host (Li^+).²¹ For the two layers, the impedance measured between electrolyte, LiPON layer and WO_3 film is significantly different for various LiPON thicknesses. There was observed the existence of two time constants that were modeled by the electrical equivalent circuit. The impedance spectra presented in Fig. 5 are results fitted by the equivalent circuit model. The R_s was found to be 30–33 Ω for all samples, due to the similarity of the electrolyte and cell components. Figure 6 shows the charge transfer resistance for Li ion interaction into a WO_3 thin film with no LiPON coating and WO_3 thin films with changing thickness of a LiPON protective layer. The charge transfer resistance of WO_3 thin films without a protective layer increases significantly up to ~ 2000 Ω after 1000 cycle and

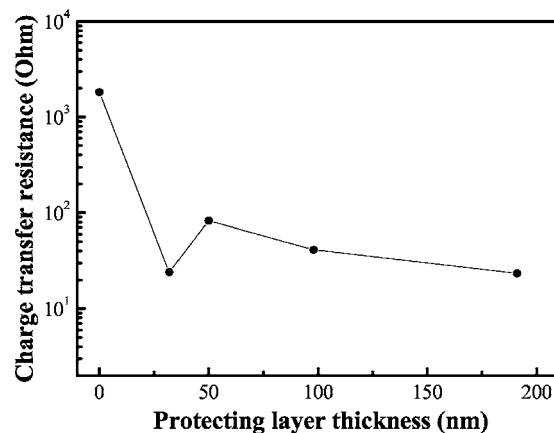


Figure 6. Charge transfer resistance for Li ion interaction into a WO_3 thin film with no LiPON coating and WO_3 thin films with changing thickness of a LiPON protective layer. Data are obtained by electrochemical impedance spectroscopy from fits of type shown in the Fig. 5.

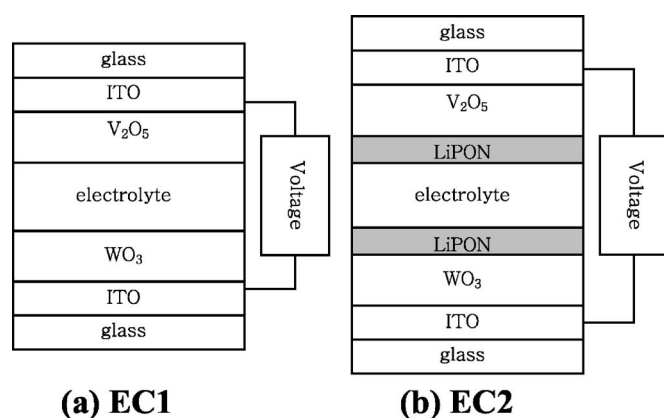


Figure 7. Schematic diagrams of EC devices (a) without and (b) with a LiPON protective layer on top of WO_3 and V_2O_5 .

that of WO_3 thin films with a LiPON protective layer have increased slightly, ranged from 20 to 80 Ω . On the other hand, as is obvious from the displayed spectra, the charge transfer resistance is much larger for WO_3 thin films without a protective layer than for WO_3 thin films with a LiPON protective layer after 1000 cycle. This phenomenon is associated with the barrier the Li ions have to pass to enter the WO_3 thin film and the increased ohmic polarization of the WO_3 thin film during intercalating and deintercalating of the Li ions. The increased charge transfer resistance of the samples is probably caused by the degradation of the EC device performance. However, the transfer of the Li ions can be limited by several different aspects of the electrochromic devices, including the type of ions (H^+ , Li^+ , etc.), the resistance of the transparent conducting electrode, the conductivity of the electrolyte, charge transfer resistance, and the rate of diffusion of the ions in each electrode material.²² Particularly, the parameters such as response time (coloring/bleaching time) and reversibility of ions related with reliability of the electrochromic devices are dependent on a good understanding of the diffusion processes and charge transfer process in the electrochromic electrode. Therefore, further discussion is needed to investigate the relationship between the thickness, the conductivity (resistance), the capacity, and the reliability of ECDs.

To investigate the effect of the interfacial property of the protective layer, the optical transmittance and electrochemical properties of EC 1 consisting of (glass)/(ITO)/(V_2O_5)/(LiClO₄/PC)/(WO_3)/(ITO)/(glass), as shown in Fig. 7a, and EC 2 consisting of (glass)/(ITO)/(V_2O_5)/(LiPON)/(LiClO₄/PC)/(LiPON)/(WO_3)/(ITO)/(glass), as shown in Fig. 7b, were compared.

As shown in Fig. 8, the changes in the optical transmittance of EC 1 and EC 2 were measured after 1000 cycles by pulse voltammetry. As shown in Fig. 8a, the EC device made from EC 1 showed a decrease in transmittance as the bleaching and coloring processes progressed. This is because the intercalation and deintercalation reactions of the electrolyte ions to both of the electrodes occur irreversibly with increasing number of cycles.^{23,24} Such irreversible intercalation and deintercalation reactions are believed to be caused by the conversion of the small amount of water in the tungsten oxide thin film into hydroxyl radicals, which react with the lithium ions to form lithium oxide (Li_2O) which, in turn, is accumulated in the tungsten oxide.¹² Thus, these irreversible reactions result in the deterioration in the electrochromic properties and a reduction in the durability of the electrochromic device. On the other hand, as shown in Fig. 8b, the EC device showed a constant change in transmittance (18–78%) during the bleaching and coloring processes and had excellent durability.

The measured coloration efficiencies of EC 1 and EC 2 were 31 and 89 cm^2/C , respectively. Also, the bleaching response time and coloring response time of EC 1 were 3.5 and 6 s, respectively, and

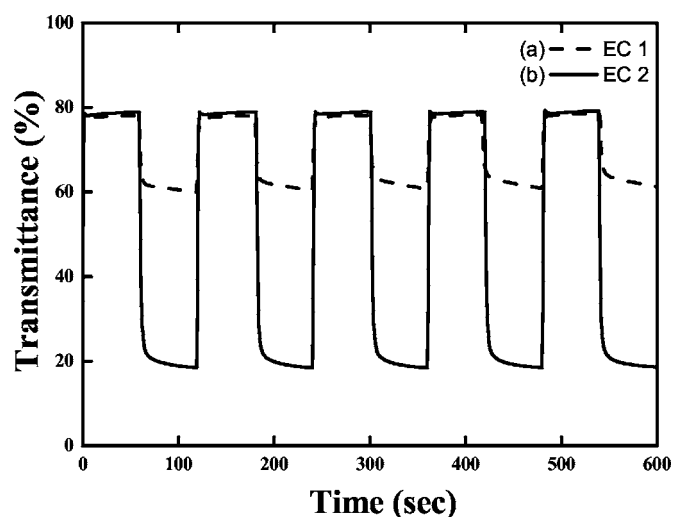


Figure 8. In situ transmittance curves obtained during switched pulse potential cycling tests conducted after 1000 cycles for (a) EC 1 (dashed line) and (b) EC 2 (solid line).

the bleaching response time and coloring response time of EC 2 were 2.5 and 4 seconds, respectively, indicating that the bleaching and coloring response rates of EC 2 are significantly faster than those of EC 1.

Conclusions

WO_3 only, LiPON/ WO_3 , and two types of EC devices were prepared by rf magnetron sputtering and their electrochromic properties were compared in Li ion-conducting electrolytes by performing in situ transmittance measurements. The electrochemical properties of the devices incorporating the tungsten oxide thin film including the protective inorganic solid electrolyte film were examined as a function of the thickness of the protective film. By using an optimized thickness (50–100 nm) of the protective inorganic solid electrolyte film, it was possible to increase the bleaching and coloring response rates of the electrochromic device, so as to maximize its efficiency. ac impedance analyses reveal that the charge transfer resistance for WO_3 thin films with no LiPON coating increased significantly during 1000 cycle while WO_3 thin films with a LiPON layer increased slightly. Two types of EC devices were fabricated—(glass)/(ITO)/(V_2O_5)/(LiClO₄/PC)/(WO_3)/(ITO)/(glass) and (glass)/(ITO)/(V_2O_5)/(LiPON)/(LiClO₄/PC)/(LiPON)/(WO_3)/(ITO)/(glass). The EC properties of the two ECD types, including their response times, CE, and optical transmittance, were compared. In comparison to EC 1, EC 2 provided good transmittance modulation and durability, and a high CE. It could be considered that the electrochromic durability was reduced by the trapping of the charges due to the irreversible chemical reactions between the EC matrix and the inserted Li ions, and by the cracking and degradation of the EC matrix under the stresses imposed by the intercalation of the inserted Li ions. The LiPON film plays an important role in protecting the EC matrix in the Li ion-conducting electrolytes. Although more detailed studies are required, we confidently predict that LiPON films will play a useful role in the fabrication of practical EC devices.

Acknowledgments

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