Optical and Electrical Properties of Electrochromic Devices Depending on Electrolyte Concentrations and Cell Gaps

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The optical and electrical properties of electrochromic devices (ECDs) have been studied as a function of the electrolyte concentration and the cell gap. During tests, the electrolyte concentration was adjusted from 0.01 to 1 M LiClO₄, and the cell gaps between the positive and negative electrodes were set at 25, 60, and 100 μ m. By varying the electrolyte concentrations and the cell gap, various parameters such as the transmittance, response time, charge consumption, coloration efficiency, and bistability of ECD were comparatively analyzed. Viologen (VO) was used as the reduction electrochromic material, and triarylamine (TAA) was used as the oxidation material.

Keywords: Electrochromic, Transmittance, Response time, Charge consumption, Coloration efficiency, Bistability

Introduction

Electrochromism is a phenomenon in which reversible color changes such as coloration and decoloration occur during electrochemical redox reactions in some materials. Various types of materials are used, including cathodic materials such as viologens (VOs) and WO₃, which display coloration through a reduction process by receiving electrons. There are also anodic materials, such as phenothiazine and NiOx, which work through an oxidation process by losing electrons.^{1,2} Unlike liquid crystal displays (LCDs) or organic light-emitting diodes (OLEDs), which are emissive type of devices, an electrochromic device (ECD) is a nonemissive information display device that provides high visibility even in outdoor settings and has an excellent contrast ratio under strong lighting conditions, such as in sunlight.³ A wide range of benefits of ECDs have been found, such as easy control of light transmittance using a driving voltage, low driving voltage, bistability under open-circuit status, and small dependence on the viewing angle.1-6

ECDs have been the subject of intensive study all around the world.^{1–6} In spite of their long history of research, there are very few commercialized ECD products using any sort of advanced level of this technology. Some products that have been developed are an automotive electrochromic rearview mirror by Gentex,⁷ a crash helmet by Chromogenics,⁸ and a smart window by Sage Glass.⁹ Despite the overall lack of developed products, electrochromic technology can still provide a variety of potential applications, and therefore remains a subject of substantial research. Taking advantage of the nanocrystalline structure of an electrochromic material

when it is mixed in glass, smart window technology development is under way that can enable selective adjustment of the transmittance in the range of visible and infrared light.¹⁰ A sunglass technology is being developed to make available selective adjustment of transmittance in the range of visible light; this material will utilize diverse forms of organic polymers.¹¹ In addition, a reflective information display electrochromic technology is also being developed that can be achieved through stacking up of three colors such as cyan, magenta, and yellow.¹² Furthermore, the following technologies are becoming available: a mirror technology that will enable functions of both transmission and reflection by means of reversible deposition and stripping of Ag⁺ ion on electrodes13; an information display device manufactured with a roll-to-roll process using polymers mixed with an electrochromic material¹⁴; and an electrochromic iris for a camera lens that can control its optical transmission.¹⁵ However, in spite of the variety of applied research, there have been very few analysis results for the basic parameters of ECDs. In this paper, depending on the electrolyte concentration and cell gap, all the following critical features were analyzed: transmittance, colored and decolored response time, electrical charge consumed, coloration efficiency, and bistability.

Experimental

An ECD consists of a three-dimensional (3-D) nanostructured reduction electrochromic layer, an oxidation electrochromic layer, and an electrolyte layer (Figure 1(a)). Figure 2(b) and (c) show the coloration and decoloration images of a viologen-triarylamine (VO–TAA) full cell and



Figure 1. (a) Overall structure of an ECD and the molecular structure of the utilized ECD. (b) Coloration and decoloration images of a VO–TAA full-cell, and (c) the corresponding spectra of coloration at -1.5 V and decoloration at 0.5 V.

the corresponding spectra of coloration at -1.5 V and decoloration at 0.5 V. The coloration image at -1.5 V is blackish, and the measured transmittance has a low value. The reduction and oxidation electrochromic materials were VO and TAA, which were immobilized on 3-D TiO2 nanostructures. LiClO₄ dispersed in propylene carbonate was the electrolyte. An FTO (fluorine-doped SnO₂, sheet resistance of 15 Ω /cm²; TEC-15, Pilkington Co. (Tokyo, Japan)) substrate was used as a conducting substrate, which was washed with methanol, acetone, and water before use. The phosphate-anchored VO (N,N'-4,4'-bis(2-phosphonylethyl)bipyridium dichloride) and TAA (3-[4-(diphenylamino) phenyl]methylphosphonic acid) were synthesized in the laboratory (Figure S1, Supplementary Information).^{1,5,16} The nanostructured reduction and oxidation electrochromic layers were fabricated as follows: High-temperature TiO₂ thin films were formed on FTO glass by the doctor-blade method. High-temperature TiO₂ paste was purchased from ENB Co. (Gumi-si, Korea). The TiO₂ paste was prepared by mixing TiO₂ nanoparticles (with diameter <20 nm), terpineol, lauric acid, and ethyl cellulose. The thin films were placed in a furnace for heat treatment after they were dried at room temperature for 20 min and at 95°C for 30 min. The heat treatment was performed in the furnace for 2 h after the temperature was increased from room temperature to 450°C at a heating rate of 5°C/min (thin-film thickness ~6 μ m).⁵ The substrates were then dipped into 0.5 mM VO and TAA-ethanol solution for 20 h. When the reaction was complete, the substrates were washed with ethanol and then dried with N₂ gas.

The full cell was prepared as follows: The electrodes of the reduction and oxidation electrochromic layers were bonded using a Surlyn film (separation ~25, 60, and 100 μ m, respectively). The devices were 2.0 × 3.0 cm² in size, of which 1.4 × 1.9 cm² was the active area. The two electrodes were joined by subjecting them to heat treatment at 115°C for

~4 min after the Surlyn film was placed between them. Electrolyte was injected into the joined electrodes after evacuating the air from the cells. Solutions of various concentrations (0.01, 0.02, 0.05, 0.1, 0.2, 0.5, and 1 M) of LiClO₄ in propylene carbonate were used as electrolytes. Cyclic voltammetry for the half-cell ECDs was performed using a CHI1030 potentiostat (CH Instruments, Inc., (Austin, TX, USA) USA), and the optical properties of the ECDs were measured using an optical measurement system consisting of a light source (DH-2000-BAL, Ocean Optics, Inc. (Winter Park, FL, USA) USA), optical fibers, and a spectrometer (USB2000 + UVvis, Ocean Optics, Inc., USA). A driving bias was applied using a function generator (Hewlett Packard Co., (Palo Alto, CA, USA) 33120A), a DC power supply (Protek Co., (Tempe, AZ, USA) OPE-303Q), and an isolation board with an operational amplifier.

Results and Discussion

Cyclic Voltammetry. Figure 2(a) shows the cyclic voltammetry (CV) data for a VO-anchored TiO2 half-cell. As the electrolyte concentration increases, the reduction current increases and the reduction potential increases negatively. A CV curve for the TiO₂ half-cell without VO at 0.1 M $LiClO_4$ is shown as a dotted line in Figure 2(a). The TiO₂ layer participated in the oxidation-reduction reaction in the range of negative potentials only. However, the oxidationreduction current of the TiO₂ half-cell without VO was four times lower than that of the VO-anchored TiO₂ half-cell at the same electrolyte concentration of 0.1 M LiClO₄; this was even lower than the oxidation-reduction current at the lowest electrolyte concentration of 0.01 M LiClO₄. Based on these results, it can be concluded that the oxidationreduction current of VO predominates in the overall oxidation-reduction current of the half-cell. Figure 2 (b) shows a reduction coloration image of the VO-anchored



Figure 2. (a) CV spectra (-0.7 to 0.5 V, 5 mV/s) of VO as a function of the electrolyte of concentration of LiClO₄, (b) the corresponding image of coloration at -0.65 V, and (c) the spectra of the VO half-cell at 0.5 V (decoloration), -0.5 V (coloration), and -0.7 V (coloration). (d) CV spectra (0-0.85 V, 5 mV/s) of TAA as a function of the electrolyte concentration of LiClO₄, (e) the corresponding image of coloration at 0.75 V, and (f) the spectra of the TAA half-cell at -0.5 V (decoloration), 0.75 V (coloration), and 0.85 V (coloration). The dotted line in (a) indicates the CV of TiO₂ (0.1 M LiClO₄).

 TiO_2 half-cell at -0.65 V reduction potential. When the half-cell became colored, it turned purple. The spectra of the VO half-cell ECD were taken at 0.5 and -0.7 V for decoloration and coloration during measurement of CV, as shown in Figure 2(c), which shows two transmittance peaks at 550 and 600 nm. The transmittance decreases with the increase in applied voltages.

Figure 2(d) shows the CV curve for the TAA-anchored TiO_2 half-cell. The oxidation potential is observed to be in the range of positive scale; the oxidation current increased with increasing electrolyte concentration, and the oxidation-reduction potential increased positively. Figure 2 (e) shows an oxidation coloration image of the TAA-anchored TiO₂ half-cell when the potential was equal to 0.75 V. The colorized half-cell appeared in moderate golden yellow. The spectra of the TAA half-cell at -0.5 V for decoloration and at 0.75 and 0.85 V for coloration were taken during measurement of the CV, as can be seen in

Figure 2(f), which shows two transmittance peaks at 480 and 690 nm. The transmittance decreases with the increase in the applied voltage.

It was found that the first reduction of VO led to a color change from transparent to purple; the first oxidation led to a color change of TAA from transparent to yellowish. The VO half-cell showed low transmittance in the wavelength region 550–600 nm and high transmittance in the wavelength regions 450 and 750 nm. In contrast, TAA showed high transmittance in the wavelength region 500–600 nm and low transmittance both at 450 and 750 nm. The combination of these two electrochromic materials led to the blackish appearance of the ECD (Figure 1(b)) and resulted in an evenly low transmittance over the entire wavelength region (Figure 1(c)).

Transmittance. Figure 3(a) shows the transmittance spectra in the colored and decolored states measured for a range of electrolyte concentrations of 0.01–1 M LiClO₄ for

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Figure 3. Transmittance spectra as a function of the electrolyte concentration for (a) 25, (b) 60, and (c) 100 μ m cell gaps, 9 s after coloration and decoloration. The coloration and decoloration voltages were -1.5 V (dotted line) and 0.5 V (solid line), respectively.

25 μ m cell gap. All coloration and decoloration voltages were fixed at -1.5 and 0.5 V, respectively. The transmittance in the colored states decreased with increasing electrolyte concentrations, meaning that the coloration at higher electrolyte concentrations was more efficient than at lower concentrations. At a concentration of 0.01 M LiClO₄, the coloration spectrum showed transmittance bands in the wavelength region 550 and ~600 nm. This is similar to the coloration spectrum of the reduced VOs (Figure 2(c)).

TAA did not engage in coloration at 0.01 M LiClO₄. Meanwhile, as the electrolyte concentration increased, a remarkable decrease of the transmittance appeared in the shorter wavelength region of ~480 nm and in the longer wavelength region of ~690 nm. With more than 0.02 M LiClO₄, TAA engaged in coloration, and the decrease of the transmittance became obvious as the electrolyte concentration was increased more and more. With some exceptions for 0.01 M and 1 M LiClO₄, the transmittance in the decolored state remained at almost the same level as in the decoloration transmittance spectra, although a slight difference was observed at the wavelength of ~400 nm. For 0.01 M LiClO₄, the spectrum did not recover to the decolored transmittance level due to the incomplete decoloration of the reduced VOs. Also, for the 1 M LiClO₄, the decoloration spectrum showed a transmittance peak at ~690 nm, which was considered to be due to the incomplete decoloration of the oxidized TAA molecules.

Figure 3(b) and (c) show the transmittance spectra as a function of the electrolyte concentration for 60 and 100 µm cell gaps, respectively. These patterns are similar to those shown in Figure 3(a). The degree of coloration became higher with increase in electrolyte concentration. Compared to the 25 µm cell gap case, a decrease of the transmittance in 0.01 M LiClO₄ for 100 µm cell gap was distinctly observed in the whole wavelength region. Specifically, the decrease of the transmittance turned out to be larger in the shorter (~480 nm) and longer (~690 nm) wavelength regions, meaning that TAA engaged more effectively with the increase of the electrolyte concentration. It appears that, despite the identical electrolyte concentration of 0.01 M LiClO₄, the TAA coloration could be achieved because the number of Li⁺ ions became four times more at 100 µm cell gap (the number of Li⁺ ions: 0.1 μ mol/cm²) than at 25 μ m cell gap (the number of Li⁺ ions: $0.025 \,\mu\text{mol/cm}^2$). For decoloration, the transmittance values all remained similar, except for the 0.01 and 1 M LiClO₄ samples with the gap of 60 µm and for the 1 M LiClO₄ sample with the gap of 100 μ m. The decoloration spectrum in 0.01 M LiClO₄ for the 100 µm cell gap was different from that with 25 µm cell gap. In contrast to the case of the 25 µm cell gap, the decoloration was completed in the 0.01 M LiClO₄ for the 100 µm cell gap. It could be that, although the electrolyte concentration was the same at 0.01 M LiClO₄, the larger cell gap led to an increased number of Li⁺ ions, which in turn caused sufficient oxidation of the reduced VO molecules. As previously reported,¹⁷ the optical density (OD) of VO for 6 μ m TiO₂ layer thickness is ~3.84 at 528 nm (the total number of VO molecules is 0.18 µmol/cm²). From the transmittance spectra shown in Figure 3(a), we can calculate that the optical density of VO molecules is about 0.54 at 0.01 M LiClO₄ concentration, which corresponds to $0.025 \ \mu mol/cm^2$ of VO molecules. This number is very close to the number of Li⁺ ions, namely 0.025 µmol/cm² for 0.01 M LiClO₄ and a 25 µm cell gap; this sample may be incompletely reduced and oxidized.

Incomplete decoloration was observed at the electrolyte concentration of 0.01 and 1 M LiClO₄. Given the implications of the data shown in Figure 2(c) and (f), the incomplete decoloration at 0.01 M was caused by VO and the incomplete decoloration at 1 M was caused by TAA. Other than this, over the range 0.02–0.5 M, decoloration was completely effected. Contrary to the case of decoloration, the coloration transmittance decreased evenly over the entire range 0.01–1 M as the electrolyte concentration increased.

Figure 4(a) shows the transmittance for the coloration and decoloration voltages of -1.5 and 0.5 V in each electrolyte concentration. The transmittance for the coloration and decoloration was not greatly affected by the cell gap, but was rather significantly affected by the electrolyte concentration. The coloration transmittance decreased as the electrolyte concentration increased; that is, the degree of coloration increased effectively as the electrolyte concentration increased. Except for 0.01 and 1 M LiClO₄ electrolyte concentrations, in the region 0.02–0.5 M the decoloration transmittance appeared to have almost the same value; the best transmittance was found in the region 0.02–0.2 M. Figure 4(b) shows how the transmittance changed in response to the variation of the electrolyte concentration during coloration and decoloration for each cell gap. Except for the 1 M LiClO₄ concentration, the higher the electrolyte concentration, the larger was the transmittance change. This appears to be consistent with the notion that the coloration transmittance decreases as the electrolyte concentration is increased for the same coloration voltage (-1.5 V).

Response Time. Figure 5 shows the coloration and decoloration time at the applied voltages of -1.5 and 0.5 V for each of the electrolyte concentrations and for cell gaps of 25, 60, and 100 µm. The coloration time was ~2 to 3 s, which was not significantly affected by the cell gap (Figures S2–S4) as shown in Figure 5(a). The decoloration time did not vary significantly with the cell gap either, but was affected by the electrolyte concentration, as shown in Figure 5(b). Except for the electrolyte concentration of 0.01 M LiClO₄ for the cell gaps of 25 and 60 µm, the decoloration time was less than 1 s for most of the electrolyte concentrations (0.02–1 M LiClO₄) (Figures S2–S4). As the electrolyte concentration was increased, the coloration time decreased, showing that at higher electrolyte



Figure 4. (a) Transmittance in coloration (-1.5 V) and decoloration (0.5 V), and (b) transmittance changes for various cell gaps and electrolyte concentrations at the wavelength 550 nm.



Figure 5. (a) Coloration time at -1.5 V and (b) decoloration time at 0.5 V (within 10–90% transmittance change after coloration or decoloration) at the wavelength 550 nm.



Figure 6. Amount of charge being consumed (9 s after coloration or decoloration) per unit area as a function of the cell gaps and electrolyte concentration at the coloration and decoloration voltage of -1.5 and 0.5 V, respectively.

concentration the coloration became faster. The decoloration time (<1 s) was shorter than the coloration time (2–3 s). The reason for the slower speed of coloration compared to that of decoloration is that there is natural decoloration in the process of coloration, and so the actual saturation of coloration takes longer to offset the natural decoloration. If the electrolyte concentration is very low (0.01 M LiClO₄), the number of ions becomes absolutely insufficient for ion exchange, so that coloration and decoloration work ineffectively and the resulting speed becomes low (the number of VO molecules for 6 μ m TiO₂ thickness: 0.025 μ mol/cm²; the number of Li⁺ ions for 0.01 M LiClO₄ and 25 μ m cell gap: 0.025 μ mol/cm²).

Charge. Figure 6 shows the variation of the consumed charge per unit area versus the electrolyte concentration at the coloration and decoloration voltage of -1.5 and 0.5 V for the cell gaps 25, 60, and 100 µm. The difference of consumed charge was more heavily dependent on the electrolyte concentration than on the cell gap. It should be noted that as the electrolyte concentration was increased, the charge consumption increased very rapidly. Then, saturation of the consumed charge was reached at 0.5 M LiClO₄. It was, however, observed that the charge consumed decreased at a higher concentration of 1 M LiClO₄. The charge consumption was not much affected by the cell gap, but it was significantly affected by the electrolyte concentration. In decoloration, except for the electrolyte concentration of 0.01 M LiClO₄ with cell gaps of 25, 60, and 100 µm, the electrical charge was rapidly consumed in the early stage (within 1 s) for most electrolyte concentrations (0.02-1 M LiClO₄) (Figure S5). In coloration, on the other hand, saturation was not reached even after 9 s for most electrolyte concentrations, and as a result the charge continued to be consumed (Figure S5). This can be compared to the 2-3 s of coloration time measured from the



Figure 7. Coloration efficiency as a function of the electrolyte concentration for (a) 25, (b) 60, and (c) 100 μ m cell gaps for 0.01 M (dark yellow), 0.02 M (magenta), 0.05 M (cyan), 0.1 M (blue), 0.2 M (green), 0.5 M (red), and 1 M (black) LiClO₄ 9 s after coloration. The coloration and decoloration voltage were –1.5 and 0.5 V, respectively. (d) Coloration efficiency 9 s after coloration at the wavelength 550 nm with different cell gaps and electrolyte concentrations.



Figure 8. Tansmittance change (bistability) 60 s after coloration for various cell gaps and electrolyte concentrations, measured after turning power off 9 s after coloration at -1.5 V.

transmittance change, as shown in Figure 5(a). The reason why the saturation of the charge consumed did not reach in 2-3 s might be that there was natural decoloration in the process of coloration, which in turn affected the amount of charge being consumed in coloration. Even though saturation in the coloration transmittance change spectrum was reached, offsetting the natural decoloration, the charge consumed in coloration was continuously included by the charge consumed by the natural decoloration, which was the reason why the charge consumed did not saturate.

In driving the ECD, the consumed charge was not significantly affected by the cell gap, but it was significantly affected by the electrolyte concentration (Figure 6). The lower the electrolyte concentration, the less the charge consumed. This can be compared with the case of the coloration transmittance and the transmittance change, as shown in Figure 4. At the coloration voltage of -1.5 V, the coloration transmittance increased as the electrolyte concentration decreased; then the transmittance change also decreased (Figure 4). In other words, it was found that more charge had to be consumed in order to decrease the coloration transmittance and increase the transmittance change (Figure 6).

Coloration Efficiency. As can be seen in Figure 7(a), the coloration efficiency in 0.01 M LiClO₄ for a cell gap of 25 µm was similar to that with VO alone (Figure S6). For the concentration of 0.01 M LiClO₄, TAA hardly engaged in the coloration. The coloration spectrum of VO typically showed absorption peaks in the wavelength region 550-600 nm.

As the LiClO₄ concentration was increased, the overall coloration efficiency increased, and new absorption peaks were detected at both 518 and 720 nm. This means that TAA engaged more strongly in coloration as the electrolyte concentration increased. TAA coloration proceeded through two stages: the first reduction ended up showing a golden yellow color absorbed at 480 nm, while the second BULLETIN OF THE

(f) and S7). With low electrolyte concentration in the range 0.02-0.1 M, the coloration efficiency peaked at ~518 nm and the golden yellow color of the TAA molecules was dominant, the first reduction; with high electrolyte concentration in the range 0.2-1 M, the coloration efficiency peaked at ~720 nm and the green color of the TAA molecules was dominant (Figures 7 (a)-(c) and S7), the second reduction. As can be seen in Figure 7(b) and (c), the coloration efficiency according to the electrolyte concentration appeared similar to that shown in Figure 7(a). It is understandable that as the electrolyte concentration increased, the coloration efficiency increased. The coloration efficiency $(\eta_{\rm C})$ of an electrochromic device can be expressed as follows: it is proportional to the absorbance, but inversely proportional to the amount of injected charge (with ΔA : absorbance change, $S_{\text{electrode}}$: electrode area, Q: charge).

$\eta_{\rm C} = \Delta A \times S_{\rm electrode}/Q$

Figure 7(d) shows the coloration efficiencies for various cell gaps and electrolyte concentrations at 550 nm. The coloration efficiency showed spectra of a similar pattern regardless of the size of the cell gap, but was strongly affected by the electrolyte concentrations. As the electrolyte concentration of LiClO₄ decreased, the coloration efficiency dropped. It can therefore be concluded that the concentration of LiClO₄ can greatly affect the oxidation-reduction reactions of VO and TAA. It can be seen that, although the transmittance change increases and more charge is consumed as the electrolyte concentration increases, the coloration efficiency increases. The reason for this is that the coloration efficiency is calculated by dividing not the transmittance but the absorbance change by the consumed charge. Also, it should be noted that the higher concentration of Li⁺ ions increases significantly the efficiency of the oxidation-reduction reaction of the electrochromic material. Bistability. Figure 8 shows the bistability versus the electrolyte concentrations for various cell gaps. Power was turned off right after the ECD became colored, which, 60 s later, was followed by measurement of the bistability from the transmittance change ratio. In terms of cell gap, the electrochromic device with a gap of 100 µm showed the best bistability (within 3%). As the cell gap became smaller, the bistability (5-12% for 25 µm) decreased. In terms of electrolyte concentration, the bistability improved as the electrolyte concentration increased. With a low electrolyte concentration, the ion concentration in the solution decreased after coloration, so decoloration proceeded very rapidly, resulting in low bistability. Furthermore, with a narrow cell gap, the bistability appeared low because the number of ions in the solution decreased as the cell gap became smaller. To increase the bistability, it was necessary to enlarge the cell gap and to raise the electrolyte concentration (to a level higher than 0.1 M LiClO₄). It appears that the bistability is related to the number of Li⁺ ions

within the cell and it improves as the number of the electrolyte ions within the cell increases. Therefore, to increase bistability, it is necessary to enlarge the cell gap, and thereby increase the electrolyte concentration.

Conclusion

In this study, overall, it was demonstrated that the optical and electrical properties of ECDs were less affected by the cell gap than by the electrolyte concentration. Coloration turned out to be more effectively achieved by an increase of the electrolyte concentration, while decoloration proceeded in a stable manner with an electrolyte concentration of in the range 0.2-0.5 M. As measured from the transmittance change, the coloration time was 2-3 s while the decoloration time was less than 1 s. As measured from the amount of charge consumed, the decoloration time was less than 1 s, while the coloration time was more than 5 s due to the natural decoloration process that took place. The coloration ratio increased as the electrolyte concentration increased. With a low electrolyte concentration, VO was the main contributor to the spectrum; TAA appeared to make an additional contribution to the spectrum as the electrolyte concentration increased. Bistability was better both when the electrolyte concentration increased and as cell gap increased. Based on all these findings, it was concluded that cell gap and electrolyte concentration have great effects on the performance of ECDs.

Acknowledgment. This work was supported by Institute for Information & Communications Technology Promotion (IITP) grant funded by the Korean government (MSIP) (B0101-16-0133 "The core technology development of light and space adaptable energy-saving I/O platform for future advertising service").

Supporting Information. Additional supporting information is available in the online version of this article.

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