Thermally Tough Electrochromic Devices with Metallo-Supramolecular Polymer: Investigation of Gel Electrolyte Component and Fabrication Process

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We fabricated electrochromic devices (ECDs) with an Fe(II)-based metallo-supramolecular polymer (polyFe) and a gel electrolyte and revealed the influence of the electrolyte components and the fabrication process on thermal stability. Four electrolytes (G1-4) were prepared by mixing of polymer matrix (poly(methyl methacrylate) (PMMA) or poly(ethylene oxide) (PEO)), lithium salt (LiClO₄), and plasticizer (propylene carbonate (PC) or ionic liquid (BMP-TFSI)) (G1: PMMA/PC; G2: PEO/PC; G3: PMMA/BMP-TFSI; G4: PEO/BMP-TFSI). The ECDs with G1,2,4 showed good EC properties upon applying ±3 V. We also found that the electrochromic (EC) properties were improved by thermal annealing of the device at 150 °C. The ECDs with G3 showed the best EC properties with fast response ($t_b = 2.65$ sec, $t_d = 0.15$ sec), high repeating stability ($\Delta T_{100}/\Delta T_i > 99\%$), large color contrast ($\Delta T = 32\%$) and good thermal stability ($T_d > 150$ °C). In addition, when viologen was added in the gel as ion storage material, the repeating stability at high temperature was further improved.

Keywords: Electrochromic devices, Metallo-supramolecular polymer, Thermal stability, Ionic liquid

1. Introduction
Since an electrochromic device is adopted as smart window in a cutting-edge airplane (Boeing 787 Dreamliner) in 2011, electrochromic (EC) materials and devices have received attention again from the viewpoints of memory property and low energy consumption. The electrochromic display is suitable for paper-like rewritable display [1-5] such as an electrical poster, price tag, e-book, signboard and newspaper. In general, electrochromic materials are divided into two types, organic materials such as conjugated polymers [6-8] and viologen [9-11] and inorganic materials such as tungsten oxide [12-14] and Prussian blue [15-17]. Organic electrochromic materials have a lot of color variation and can be easily make a large size film by wet process. However, because usual organic compounds are damaged by air, water, and sunlight, low stability and durability are serious problems for using display. On the other hand, inorganic materials show good durability and stability to these conditions. The color variation was not abundant before, but recent progress including Prussian blue nano-particles [18] and device fabrication utilizing Fabry-Perot nanocavity [19] has achieved the wide color variation. However, development of new electrochromic materials with high durability, low cost, color tunability, and quick response is still required for the display applications. In our group, metallo-supramolecular polymers have been reported as novel electrochromic material [20-23]. The metallo-supramolecular polymers are consist of ditopic ligands and metal ions by complexation and show any interesting property such as a electrochromism [23-28], vapochromism [29], non-volatile memory [30], DNA binding [31,32], emission switching [33,34], due to the electronic interaction between ligand and metal or metal and metal. Electrochromic performance is particularly interesting. The color of these polymers could be
tuned by changing of ligand structure, metal ion [25], counter anion [35], and pH condition [36]. The polymer film in an electrolyte solution shows good electrochromic properties with fast response (<2 sec) and high stability to repeated color changes (>10^5 times), because the color change is caused by the stable redox of metal ions and the fast transfer of electron and anions. For the application as EC windows in vehicles such as cars, high thermal stability is essential to the devices.

In this work, thermal property of our ECDs were investigated and enhanced by the optimization of gel electrolyte. From the viewpoint of a risk of leaking when the device is damaged, a solid electrolyte is the best choice, but we have selected gel electrolyte in this research, because quick color changes are expected by the gel. We investigated ionic liquid (IL) as the plasticizer of the electrolyte. The use of IL is not always favorable in terms of cost and large size device production, but the non-volatility, non-inflammability, wide potential window, and high ionic conductivity are still fascinating as a component of electrolyte layer in the device. An iron(II)-based metallo-supramolecular polymer (Fig. 1a) was used as an electrochromic material because which has a good color change, stable redox property, easy film preparation ability. To make gel electrolyte, PMMA-based gel electrolyte was regarded as a basic gel, matrix polymer and plasticizer were changed to PEO and ionic liquid (IL) in order to increase thermal stability and optimize the ECDs. All the making ECDs were evaluated after/during heating. As a result, thermal annealing process below decomposition temperature of polyFe and gel electrolyte was enhanced EC property of the ECDs. Although the applying voltage under high temperature dramatically damaged to the ECDs, use of PMMA/IL-based gel electrolyte and addition of ion storage material enhanced stability.

2. Experimental
2.1. Materials
All chemicals were reagent grade and used without purification. Poly(methyl methacrylate) (PMMA, M.W. = 350 kg mol⁻¹), and indium tin oxide (ITO)-coated glass substrate (resistivity 8-12 Ω/sq) were obtained from Sigma-Aldrich Co. LLC. Methanol (MeOH), acetonitrile (ACN), acetone, acetic acid, propylene carbonate (PC), poly(ethylene oxide) (PEO, M.W. = 4000 kg mol⁻¹), and 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide (BMP-TFSI) were purchased from Wako Pure Chemical Industries, Ltd. Lithium perchlorate (LiClO₄) was consumed from Kanto Chemical Co., Inc. Synthesis of Fe-based metallo-supramolecular polymer (polyFe) was outsourced to NARD institute, Ltd. who synthesized based on previous our report [18].

2.2. Preparation of gel electrolyte (G1–G4)
A plasticizer and LiClO₄ were dissolved in ACN or acetone followed by addition of matrix polymer under vigorous stirring. The mixture was stirred until the matrix polymer was completely dissolved. The colorless, transparent semi-gel electrolyte was obtained as viscous liquid. The weight ratio of semi-gel electrolytes was listed in Table 1.

2.3. Preparation of viologen containing gel electrolyte (G5)
\(N,N'\)-Dioctyl-4,4’-bipyridinium tetrafluoroborate (V1) was synthesized according to procedures in previous reports [37,38]. A V1 (0.15 mmol) was dissolved in G1 (15 mL) and the resulted mixture was used as a G5.

2.4. Preparation of ECD using polyFe and gel electrolyte
PolyFe was dissolved in MeOH (1 mL of MeOH per 4 mg of polyFe) and filtered by syringe filter (PVDF, 0.45 μm) to remove insoluble residue. The polymer films were coated on ITO glass by spray-coating method using the filtrate and then, smooth and uniform films were obtained (about 4 mL polyFe solution for 2.5×2.5 cm of ITO glass). The semi-gel electrolyte was put on the polyFe coated ITO glass and covered by another ITO glass as a
counter electrode. The resulted devices were placed at room temperature in air for 72 h to evaporate solvent. The device structure was illustrated in Fig. 2.

2.5. Thermal annealing of the ECDs

The ECDs were heated in temperature camber at 50, 100, or 150 °C for 3 hours. After the ECDs cooled down to room temperature, electrochemical properties were investigated by CV and EC measurements.

2.6. Electrochromic changes at high temperature

The ECDs were heated for 30 min in temperature and humidity chamber stored at a temperature of 40, 60, or 80 °C and at a relative humidity of >90%. In the chamber, the ECDs were applied at +3 or −3V by 5 sec for 100 cycles, and the color change of the ECDs were recorded by digital camera. The color change and its contrast of the ECDs before/after 100 cycles of redox in the chamber were compared to evaluate durability.

2.7. Measurements

Optical and electrochromic properties of ECDs were measured by UV-vis absorption spectroscopy (Ocean Optics, DH-2000-BAL UV-vis-NIR light source and USB4000 detector system). Cyclic voltammetry (CV) and amperometric measurements (AM) were performed by electrochemical analyzer (BAS Inc., ALS/CH Instruments Electrochemical Analyzer model 612B). Thermogravimetric analysis (TGA) was conducted by thermogravimetric analyzer (SHII, EXSTAR6000, TG/DTA2000) under nitrogen atmosphere. Before the measurement, all samples were dried at 50 °C for 24 h to remove solvent. Thermal annealing was performed in vacuum oven (EYELA, VOS-201SD). Electrochromic color change at high temperature was observed in a temperature- and humidity-controlled chamber (ESPEC corp., SH-242) and recorded by digital camera (Canon EOS kiss X4).

3. Results and discussion

3.1. Thermal stability of polymer and gel electrolyte

We expect the polymers to be used as EC windows of vehicles such as cars. The required highest temperature will be around 100 °C. Before the device fabrication, we investigated the thermal stability of each component in the device by TGA. The TGA curves and thermal decomposition temperature with 10% loss ($T_{d10}$) were showed in Fig. 2 and Table 1. Before measurement, all the gel electrolyte was kept in Al pan and dried overnight at 50 °C to remove volatile. The polyFe showed good thermal stability due to the aromatic backbone and metal ions under 200 °C. The gradual weight decreases around 150 °C attributed to removal of hydrated water in polyFe. The second weight decrease over 350 °C corresponded to decomposition of acetate ions as a counter anion. These results suggested that a limitation temperature of the ECD was 300 °C.

The PMMA-based gel electrolyte using PC (G1) is very popular for ECD and lithium ion battery. The weight of G1 was gradually decreased for a long range from room temperature to 300 °C, because evaporation of volatile (ACN and PC) was occurred followed by decomposition of PMMA backbone. Because the content of PC greatly affected to ionic and electrical conductivity of gel electrolyte in ECDs, electrochemical property of ECDs using G1 was easily changed by temperature. Therefore, The G1 was not good for the stable ECDs fabrication. The PEO was also used as a matrix polymer for gel electrolyte (G2) to increase thermal stability, however, the composition was also changed even below 100 °C by evaporation of PC and ACN.

| Table 1. Composition of gel electrolyte. |
|------------------------------------------|
| Polymer | Li salt | Plasticizer | wt ratio of ACN vs polymer | Viologen | $T_{d10}$ (°C) |
| G1      | PMMA   | LiClO$_4$   | PC                          |          | 124            |
| G2      | PEO    | LiClO$_4$   | PC                          |          | 118            |
| G3      | PMMA   | LiClO$_4$   | BMP-TFSI                    |          | 249            |
| G4      | PEO    | LiClO$_4$   | BMP-TFSI                    |          | 326            |
| G5      | PMMA   | LiClO$_4$   | PC                          | 10 mM    | -              |

G1 and G5: PMMA / LiClO$_4$ / PC / ACN = 8 / 3 / 27 / 63 (wt ratio). G3: PMMA / LiClO$_4$ / BMP-TFSI / ACN = 7 / 3 / 20 / 210 (wt ratio). The value of 10% weight loss ($T_{d10}$) were collected by TGA curves measured at 10 K/min under N$_2$ (200 mL/min).
3.2. Effect of thermal annealing for ECD using PMMA/LiClO4/PC/ACN (G1)

To resolve the composition change, ionic liquid (IL) was used as a plasticizer in place of volatile PC because IL has good property for safety of the device such as non-volatility, incombustibility. Fig. 2. TGA curves of polyFe and G1-G5 under N2 (flow rate = 200 mL/min). Heating rate: 10 K/min.

PMMA-(G3) and PEO-(G4) based gel electrolyte using 1-butyl-1-methylpyrrolydinium bis(trifluoromethanesulfonyl)imide (BMP-TFSI) were prepared by mixing all components in acetone or ACN. These colorless and transparent gel electrolytes were also evaluated by TGA. Although the weight of G1 was gradually reduced even at room temperature, the weight of G3 and G4 were not reduced almost up to 150 °C. The G3 showed in higher $T_{d10}$ value than PMMA because of electrical interaction between PMMA backbone and IL. The G4 also showed high thermal stability due to stable PEO backbone and IL. These results suggested that IL-used gel electrolytes were suitable for ECDs to use under high temperature condition. Thermal stability of the most basic ECD using G1 was evaluated by thermal annealing in temperature chamber. All the data of electrochemical property were summarized in Table 2. After annealing at 50 °C, appearance and EC property of the ECD was not changed. Figures 3a and 3b showed relationship between transmittance (% $T$) to time after applying voltage. The annealed ECD showed EC property at ±3 V, and fast response time (bleaching time ($t_b$) = 2.39 sec, darkening time ($t_d$) = 0.94 sec) and high color contrast ($\Delta T = 24\%$) were observed. While at the same time, color contrast was gradually decreased by repeated applying voltage. The ratio of color contrast after/before 100 times of redox ($\Delta T_{100}/\Delta T_i$) was 71%. After redox cycles, color of gel electrolyte slightly turned to violet from colorless. It is suggested that polyFe slightly dissolved into the gel electrolyte during redox cycles. In previous work, it is known that the dissolved polyFe was not working as EC materials, therefore, decrease of color contrast was caused by dissolution of polyFe. The reason of dissolution may be due to heat generation by applying voltage or solubility change by Fe$^{2+}$/Fe$^{3+}$ change. These problems were also observed before annealing. It is suggested that thermal annealing at 50 °C does not affect to property of the ECDs.

Next, annealing temperature was increased to 100 °C. The response time was slightly increased from no annealing state ($t_b = 0.91$ sec, $t_d = 0.23$ sec), and repeating stability was also increased ($\Delta T_{100}/\Delta T_i > 90\%$). These results might be caused by changes of gel composition. Because thermal annealing at 100 °C, which is above to boiling temperature of ACN, caused to decrease of the volume of the gel electrolyte due to evaporation of ACN, distance between the two electrodes was decreased, therefore, response time was increased. On the other hand, the gel electrolyte was become hard due to evaporation of solvent. The semi-solid-state gel electrolyte prevented dissolution of polyFe film to the gel. As a result, the repeating stability was enhanced. In case of 150 °C, EC property and repeating stability of the ECD was also increased ($t_b = 2.21$ sec, $t_d = 0.84$ sec, $\Delta T_{100}/\Delta T_i > 99\%$). However, the color contrast was decreased by the thermal annealing. It might be caused by any damage of gel electrolyte by heating process. When the annealing temperature was over 180 °C, the ECD did not show color change. This deactivation was caused by decomposition of gel electrolyte, that is, decomposition of PMMA backbone and evaporation of PC by thermal treatment. These results suggest that a proper thermal annealing at 100-150 °C is very important to improve electrochemical property of the ECDs.

![Graph](image)

Fig. 3. Repeating curves of the ECDs using G1 after annealing at (a) 50 and (b) 150 °C, relative humidity (RH) over 90%.

3.3. Effect of thermal annealing for ECD using PEO/LiClO4/PC/ACN (G2)

In case of PMMA as a matrix polymer for gel
Table 2. EC property of ECDs using G1 after thermal annealing.

| Temp. (°C) | Bleaching time, $t_b$ (s) | Darkening time, $t_d$ (s) | $\Delta T_i$ (%) | $\Delta T_{100}/\Delta T_i$ (%) |
|------------|--------------------------|--------------------------|------------------|-------------------------------|
| 50         | 2.39                     | 0.94                     | 24               | 71                            |
| 100        | 0.91                     | 0.23                     | 10               | >90                           |
| 150        | 2.21                     | 0.84                     | 54               | >99                           |

Table 3. EC property of ECDs using G3 after thermal annealing.

| Temp. (°C) | Bleaching time, $t_b$ (s) | Darkening time, $t_d$ (s) | $\Delta T_i$ (%) | $\Delta T_{100}/\Delta T_i$ (%) |
|------------|--------------------------|--------------------------|------------------|-------------------------------|
| 50         | 2.02                     | 1.88                     | 6.0              | >99                           |
| 100        | 4.70                     | 1.50                     | 26               | >99                           |
| 150        | 1.73                     | 1.18                     | 14               | >99                           |
| 150*       | 2.65                     | 0.15                     | 32               | >99                           |

*Ambient humidity condition (no humidity control).

Table 4. EC property of ECDs using G4 after thermal annealing.

| Temp. (°C) | Bleaching time, $t_b$ (s) | Darkening time, $t_d$ (s) | $\Delta T_i$ (%) | $\Delta T_{100}/\Delta T_i$ (%) |
|------------|--------------------------|--------------------------|------------------|-------------------------------|
| 50         | 4.29                     | 0.54                     | 38               | 86                            |
| 100        | 2.98                     | 0.37                     | 33               | 92                            |
| 150        | 2.67                     | 0.76                     | 40               | >99                           |

3.4. Effect of thermal annealing for ECD using PMMA/LiClO$_4$/BMP-TFSI/ACN (G3)

PC is most famous and usual plasticizer, but it has safety problem because of its flammability and toxicity. Recently, IL has received much attractiveness for electrolyte because of its various good properties such as non-volatility, non-inflammability, wide potential window, and high ionic conductivity. To confirm the effect of IL as a plasticizer in ECDs, G3 was prepared by using BMP-TFSI instead of PC and G3 based ECDs were fabricated. As mentioned above, the colorless G3 showed good thermal stability. The G3 based ECDs were also heated at 50, 100, and 150 °C under >90% RH, respectively. All the results are summarized in Table 3. The response time of the G3 based ECD was slightly increased ($\tau_b = 12.6, \tau_r = 8.42$ sec) after few times of redox cycles at ±3.5V, the ECDs did not work, even if the applying voltage and time increased. This low EC property might be caused by low ionic conductivity of G2.

In general, PEO-based gel electrolytes showed low ionic conductivity because of the strong interaction between oxygen atom of PEO chains and Li salts. Lithium bis(trifluoromethanesulfonil)imide (LiTFSI) is generally used as a Li salt to increase the ionic conductivity, however, it could not be used for our ECDs due to high solubility of polyFe into the LiTFSI-used gel electrolyte. The G2 showed low ionic conductivity due to using LiClO$_4$, therefore, the ECDs needed to high voltage. The high voltage rapidly injured ITO glass and polyFe. These results suggested that G2 gel electrolyte was not suitable for our ECDs.
components were immingled under high temperature. Especially, in case of high temperature and low humidity condition, not only response time but also color contrast was additionally increased (Figs. 4c and 4d). Because the PMMA backbone was hydrophobic, high humidity condition was not so good for the G3 based ECD. Although the color change was also observed after heating at 200 °C, the color contrast was decreased due to remaining of MLCT band (580 nm) of polyFe under applying voltage. This remaining color could not be disappeared by high voltage and longtime applying. These results indicate that the polyFe was damaged by heating over 200 °C because $T_{d10}$ of polyFe was estimated at 193 °C. Therefore, the use of IL as a plasticizer and thermal annealing procedure below 200 °C are quite effective to improve repeating stability and EC property of the device.

3.5. Effect of thermal annealing for ECD using PEO/LiClO$_4$/BMP-TFSI/ACN (G4)

To get a better understanding of the effect of thermal annealing and gel electrolyte using IL, a PEO-based gel electrolyte using BMP-TFSI (G4) was prepared by same procedure as G3, and G4 based ECDs were fabricated. The G4 showed good transparency. EC property after thermal treatment at 50-150 °C are shown in Table 4. In comparison to G3, although appearance of ECDs were not different, EC properties were greatly improved by using G4 (Fig. 5a). A Li salt was also coordinated by PEO chain like a G2, but the IL maybe worked as an ion source like a Li salt, as a result, ionic conductivity of the gel and EC property of the ECDs were increased. Especially, after heating at 150 °C and 100%RH, fast response time ($\tau_b = 2.67$, $\tau_s = 0.76$ sec), stable repeating stability ($\Delta T_{100}/\Delta T_i > 99\%$), and good color contrast ($\Delta T = 40\%$) were obtained (Fig. 5b). Good effect of thermal annealing was also confirmed by these results.

3.6. EC behavior under high temperature

Effects of thermal annealing have been investigated by EC measurement at room temperature after heating in the previous section. In this section, color change behavior of the ECDs under hot environmental condition was measured in order to evaluate device durability. Relatively good gel electrolytes, G1 and G3, were used for the ECDs. The ECDs using G1 were measured in a chamber set at 40, 60, or 80 °C in 35%RH. The color change behavior of the G1 based ECDs at 40 and 60 °C were not different from room temperature. However, after few times of redox cycles at 80 °C, the ECD became dark brown and did not work, despite the G1 based ECDs were stable up to 150 °C in thermal annealing measurement.

Fig. 4. Repeating curves of the ECDs using G3 after annealing. (a) 50 °C, 95%RH, (b) 150 °C, 95%RH, (c) 150 °C, no RH control. (d) First EC curves of (a)-(c).

Fig. 5. Repeating curves of the ECDs using G4 after annealing at (a) 50 and (b) 150 °C, relative humidity over 90%.

To improve a repeating stability of the ECD, we tried to use a sealing reagent, because general organic device is sensitive to oxygen and water in air. Even though a sealing reagent blocked air, repeating stability of the ECD was not increased. After any times of redox cycles at 80 °C, ITO glass which used as a counter electrode, was also turned to dark brown from transparent. These results suggest that these low thermal stabilities of the ECDs were probably caused by damage of ITO glass by electrical charge, not by air or thermal decomposition of gel and polymer. Because there are no ion storage materials in our ECDs, electrical charge accumulated around the ITO glass by oxidation of polyFe. As working at low temperature,
the damage coming from charge accumulation is not so high, but the damage of ITO glass quite increases in high temperature. As a result, the ECDs were rapidly deactivated. In case of using highly stable G3, the ECD partially worked after 100 cycles of redox. This improvement of repeating stability might be caused by the high polar ionic liquid. The high polar ionic liquid in G3 might roll as a buffer storage in the device and decreased to a damage of ITO glass. However, even if G3 is used, counter ITO glass was also damaged by charge accumulation and changed to pale brown, so the color contrast was smaller than that of before redox cycles.

To increase redox stability under high temperature, viologen was used as an ion storage material. The ECDs using a viologen containing gel electrolyte (G5) were prepared and used by same procedure as G1. Due to electrochromism of viologen and viologen-containing gel (G5) from transparent to pale blue by applying +3 V, transparency of the ECDs at +3 V were smaller than that of G1, and color contrast between ground state (0 or -3 V) and oxidation state (+3 V) of the ECDs was also small (Fig. 6). However, the color changes were observed after 100 cycles of redox at 80 °C. Furthermore, the counter ITO glass was not damaged by the redox cycles. These results suggest that thermal stability of gel electrolytes is enough using up to 150 °C, however, suitable ion storage materials are needed in order to stable working of their ECDs under high temperature atmosphere.

4. Conclusion

In summary, we successfully developed thermal tough polyFe-based ECDs by utilizing ionic liquid. Investigations of thermal annealing of ECDs using various gel electrolytes clearly suggest that enhanced EC property and improved repeating stability are obtained by thermal annealing up to 150 °C and the use of gel electrolyte containing IL. The G3 based ECDs achieved comprehensively good property such as fast response time ($t_b = 2.65$ sec, $t_d = 0.15$ sec), excellent repeating stability ($\Delta T_{100}/\Delta T_i > 99\%$), high color contrast ($\Delta T_i = 32\%$) and good thermal stability ($T_d > 150$ °C). Although the G3 based ECDs were stable for redox cycles under high temperature atmosphere, damage of charge accumulation could not be prevented completely. However, when an ion storage material like a viologen was added, we found that repeating stability of the ECDs was improved more than 100 times even if working under high temperature. We believe that this work gives a novel clue for high performance ECDs. In this research we did not use any counter material and focused on thermal stability of the gel electrolyte component in the device and the device fabrication process especially. We selected the suitable electrolyte components on the basis of these research results and reported more thermally stable EC devices by the introduction of a counter material layer very recently [39,40].

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