

Highly Durable and Nonvolatile Electrochromic Devices with Metallosupramolecular Polymers for Smart Window Application

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Abstract

Electrochromic devices (ECDs) with metallosupramolecular polymers (MSPs) have been developed. The suitable choice of MSP, electrolyte, and counter material resulted in showing high stability and long memory properties in the ECDs. The fabricated ECDs have been installed as smart window on windows of the Ibaraki Prefectural Office building.

Author Keywords

Metallosupramolecular polymer; electrochromic device; smart window; durability; nonvolatile property.

1. Introduction

Electrochromic devices (ECDs) have received much attention as smart window application. The device performance greatly depends on the electrochromic (EC) materials. Tungsten oxide, viologens, and π -conjugated polymers are representative EC materials. On the other hand, we have developed metallosupramolecular polymers (MSPs) as new EC materials. As an example, EC changes of an Fe(II)-based MSP (polyFeL1) film is shown in Figure 1. The EC changes are driven by electrochemical redox of Fe(II) ions in the polymer. The color of the polymer changes from blue to colorless by the electrochemical oxidation of Fe(II) to Fe(III). The blue color is based on the metal-to-ligand charge transfer (MLCT) absorption from Fe(II) to the bisterpyridine ligand, but the color disappears in the Fe(III) state, because the d electron that causes the MLCT is removed electrochemically. On the contrary, the colorless film becomes blue again by the electrochemical reduction of Fe(III) to Fe(II).

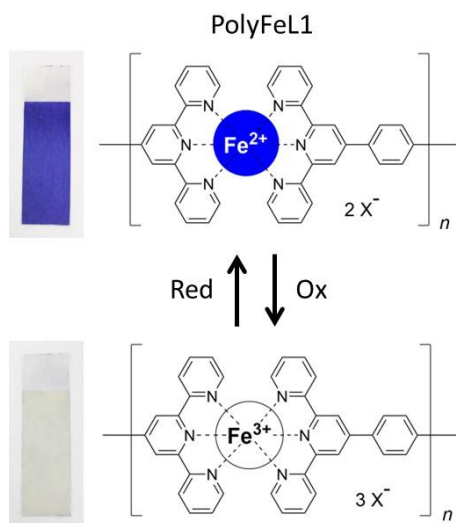


Figure 1. Electrochromic properties of Fe(II)-based metallosupramolecular polymer (polyFeL1).

Compared with the other EC materials, MSPs have several advantages including wide color variation, coloration efficiency

higher than $250 \text{ cm}^2/\text{C}$, spray-coating under ambient conditions. This presentation reports ECDs with an MSP layer. It was found that the device performance such as durability and nonvolatile property was significantly improved by optimization of the device components.

2. Results and Discussion

An ECD structure with an MSP layer: An ECD with an MSP layer is composed of a pair of ITO glass, an MSP layer, an electrolyte layer, and a counter material layer (Figure 2). Previously, we did not use the counter material layer, but the device showed reversible color changes by applying 3 V or -3 V, probably because the counter ITO layer worked as capacitor.¹ However, the device stability to the repeated color changes was not so high and the irreversible coloring of the counter ITO glass caused by the degradation was observed with increasing the number of the EC changes.

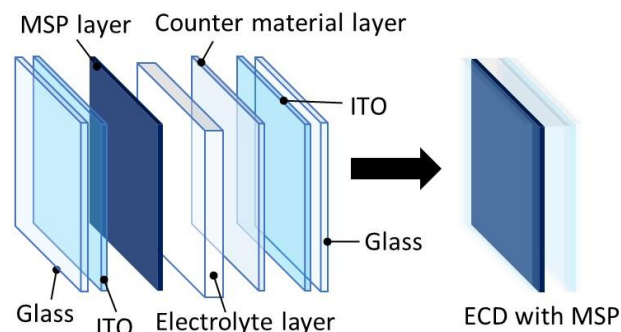


Figure 2. An ECD structure with an MSP layer.

Selection of the counter material: To prevent the degradation of the counter ITO layer, various redox-active materials were investigated as the counter material of the ECD. Among them, it was found that Nickel hexacyanoferrate (NiHCF) was a good candidate as the counter material, because NiHCF showed EC changes between yellow and colorless and the oxidized state (Fe(III) state) had the yellow color. The anodically tinted material is suitable as the counter material of an Fe(II)-based MSP (polyFeL1), because it shows opposite color changes with polyFeL1, which is a cathodically colored EC material.

In addition, NiHCF has an advantage as the counter material of an ECD with an MSP from the viewpoint of ion transfer process inside the device, too. According to the redox between Fe(II) and Fe(III) in a polyFeL1 layer, anion transfer happens between the polyFeL1 layer and an electrolyte layer, as shown in Figure 3. On the other hand, the redox between Fe(II) and Fe(III) in NiHCF accompanies cation transfer. Therefore, both anion and cation species of the electrolyte could contribute to the ion transfer in the ECD with polyFeL1 and NiHCF (Figure 3).²

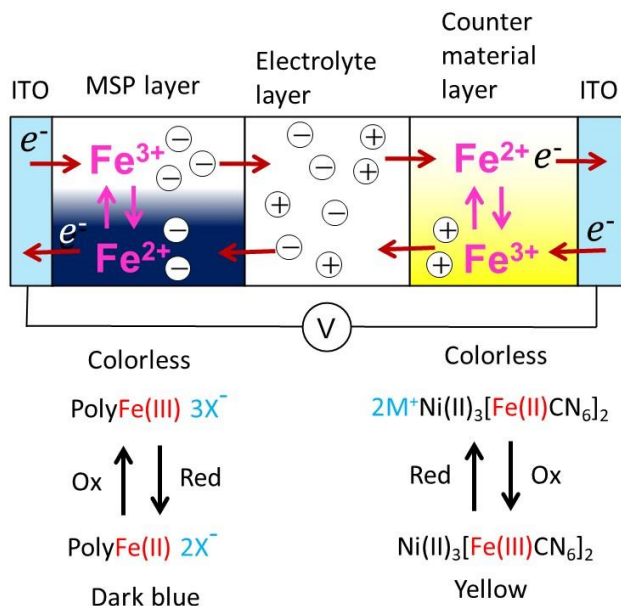


Figure 3. An ECD structure with polyFeL1 and NiHCF and a scheme of the electron and ion transfer processes during the EC changes.

Selection of the electrolyte: After selecting NiHCF as the counter material, the suitable electrolyte was looked for. In our previous study it has been found that perchlorate anion (ClO₄⁻) is the best anion to enable quick and reversible redox between Fe(II) and Fe(III) in a polyFeL1 film.³ So, we focused on the cation species of an electrolyte in this ECD and investigated Na⁺ and Li⁺. In the cyclic voltammograms of the devices it was revealed that the device with Na⁺ showed the EC changes at the voltage about 0.1 V lower than that with Li⁺, probably because Na⁺ is preferable than Li⁺ as the counter cation of NiHCF.

Durability for repeated EC changes more than 100000 cycles: With gel electrolyte composed of LiClO₄, propylene carbonate (PC), and polymethylmethacrylate (PMMA), we fabricated an ECD with polyFeL1 and NiHCF. By optimizing the film thickness and the operation voltages (+1.0 V and +0.2 V for bleaching and coloring, respectively), the ECD achieved high durability for the repeated color changes more than 100000 cycles.⁴

Selection of the MSP: Moreover, it was revealed that the different ligands of MSPs dramatically reduced the operation voltage of the ECD. When an MSP with a tetrakis(*N*-methylbenzimidazolyl)bipyridine ligand was used instead of an MSP with a bis(terpyridyl)benzene (L1) ligand, the driving voltage (0.8 V) of the ECD became further small down to 0.6 V and the memory time enhanced more than 10 hours.⁵

Smart window application: The optimized ECDs were installed as smart window on windows of Ibaraki Prefectural office building (Figure 4).

3. Conclusion

An ECD structure with a polyFeL1 layer was optimized by selecting the suitable counter material and the electrolyte. The ECD showed high durability for repeated EC changes more than

100000 cycles, owing of the low driving voltage (0.8 V). In addition, an ECD with an MSP, which showed lower redox potential than polyFeL1, was driven at 0.6 V and it exhibited long memory properties more than 10 hour. The fabricated ECDs were installed as smart window on window of the Ibaraki Prefectural office building.

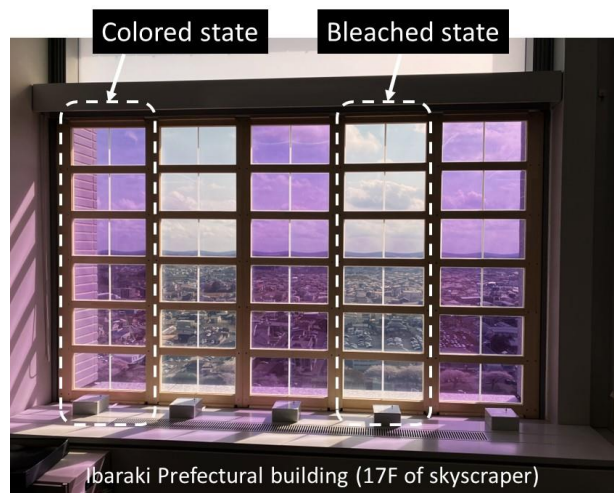


Figure 4. The ECDs installed as smart window.

4. Acknowledgements

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5. References

- Higuchi M, Akasaka Y, Ikeda T, Hayashi A, Kurth DG. Electrochromic Solid-State Devices Using Organic-Metallic Hybrid Polymers, *J. Inorg. Organomet. Polym. Mater.*, **2009**, 19, 74–78.
- Lu H-C, Hsiao L-Y, Kao S-Y, Seino Y, Santra DC, Ho K-C, Higuchi M. Durable Electrochromic Devices Driven at 0.8 V by Complementary Chromic Combination of Metallo-Supramolecular Polymer and Prussian Blue Analogues for Smart Windows with Low-Energy Consumption, *ACS Appl. Electron. Mater.*, **2021**, 3, 2123–2135.
- Zhang J, Hsu C-Y, Higuchi M. Anion Effects to Electrochromic Properties of Ru-based Metallo-Supramolecular Polymers, *J. Photopolym. Sci. Technol.*, **2014**, 27, 297–300.
- Mondal S, Roy S, Fujii Y, Higuchi M. Highly Durable Electrochromic Devices for More than 100,000 Cycles with Fe(II)-Based Metallo-Supramolecular Polymer by Optimization of the Device Conditions, *ACS Appl. Electron. Mater.*, **2023**, 5, 6677–6685.
- Santra DC, Mondal S, Yoshida T, Ninomiya Y, Higuchi M. Ru(II)-Based Metallo-Supramolecular Polymer with Tetrakis(*N*-methylbenzimidazolyl)bipyridine for a Durable, Nonvolatile, and Electrochromic Device Driven at 0.6 V, *ACS Appl. Mater. Interfaces*, **2021**, 13, 31153–31162.