

Ultrahigh Cycle Stability in an Electrochromic Device with Fe(II)-Based Metallo-Supramolecular Polymer

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ABSTRACT

Ultrahigh cycle stability more than 100,000 cycles has been achieved in an electrochromic device with an Fe(II)-based metallo-supramolecular polymer layer and a modified counter electrode layer. The reversible color change between bluish-violet and colorless occurred at low applied voltages and the transmittance change reached >60%.

1. INTRODUCTION

Electrochromism (EC) is a reversible switching of optical properties by the applications of external electric stimulus.¹⁻³ Owing to controllable optical properties of EC devices, it can be used in different applications such as windows of cars, airplanes and buildings, anti-glare rearview mirrors, and digital information displays. Representative electrochromic materials are Tungsten oxide, viologens and π -conjugated polymers. We have reported metallo-supramolecular polymers (MSPs) as an efficient electrochromic material with high color contrast, quick response, and high coloration efficiency, easy processability, environmental stability etc.^{4, 5, 6, 7} However, high voltage operation, low optical memory and low cycle stability in device state limited their applications. Therefore, improvement of the device structure is still required to achieve low voltage operation and long-term cycle performance. Incorporation of ion-storage layer is an imperative constituent to improve them. Investigation of redox active layer on counter electrode in such a way that opposing redox reactions occur at the electrodes with respect to working electrode in an ECD.

In this work we report the fabrication of a EC device based with cathodically coloring Fe(II)-based MSP (PolyFe) as electrochromic layer on working electrode, anodically coloring counter electrode layer and a solid LiClO₄-based gel electrolyte in between two ITO-glass as conducting substrate (Fig.1). We have measured optimum operation voltage and cycle performance of fabricated device.

2. EXPERIMENTAL SECTION

Materials: Iron(II) acetate [Fe(OAc)₂], Indium tin oxide (ITO)-coated glass substrates (resistivity 8–12 Ω /cm²), anhydrous lithium perchlorate (LiClO₄) were purchased

from Sigma Aldrich. 1,4-Di[[2,2':6',2''-terpyridin]-4'-yl]benzene (L), poly-(methyl methacrylate) [PMMA, MW 350 kg/mol] were purchased from TCI Chemicals. Propylene carbonate (PC), Ni-hexacyanoferrate (NiHCF), anhydrous acetic acid, spectroscopic grade methanol (MeOH), and acetonitrile (ACN) were supplied by Wako Chemicals.

Preparation of polyFe film: polyFe was synthesized according to our early report.^{8, 9} Typically, 1,4-Di[[2,2':6',2''-terpyridin]-4'-yl]benzene (L) (200 mg, 0.37 mmol) and Fe(OAc)₂ (64 mg, 0.37 mmol) were reflux at N₂-saturated atmosphere in acetic acid (40 mL) medium for 24h. Deep blue solid was collected by evaporating solvent slowly at room temperature. Electrochromic polyFe film on ITO-glass was prepared by spray-coating technique from 4 mg/ml methanol solution of polyFe.

Counter electrode modification: the ion storage layer on counter electrode side was prepared by spin-coating technique from water solution of NiHCF.

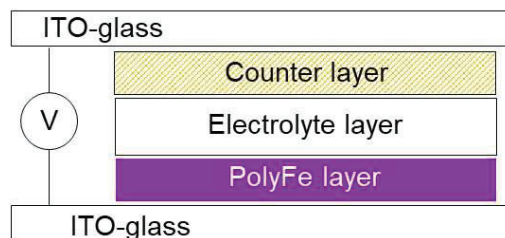


Fig.1: Schematic presentation of electrochromic device structure

Device fabrication: Prior to device fabrication a semi gel electrolyte was prepared by mixing poly(methyl methacrylate) (PMMA), lithium perchlorate (LiClO₄), propylene carbonate (PC) in acetonitrile solvent with 7:3:20:70 weight ratio manner. Prepared semi gel was placed in between two electrodes (polyFe coated working electrode and NiHCF coated counter electrode) by drop casting in sandwich configuration. The structure of fabricated device as: "ITO/polyFe/electrolyte/NiHCF /ITO" shown in Fig.1.

3. RESULTS and DISCUSSION

The EC device shows bright bluish-violet color with maximum absorption (λ_{max} =580 nm), because of the metal-to-ligand charge transfer (MLCT) of the central Fe^{2+} metal ion to terpyridine ligands in quasi-octahedral coordination geometry of polyFe. Fabricated device revealed reversible color change from bluish-violet to colorless and vice versa by the application of a low operation voltage +1.0 and +0.2 respectively (Fig.2a). The chemical structural change during electrochromism is shown in Fig.2b, where Fe^{2+} metal center is oxidized to Fe^{3+} upon application of +1.0V and reduction of Fe^{3+} metal center to Fe^{2+} occurs by the application of +0.2V repeatedly. The corresponding transmittance spectral change during bleaching (oxidation) and coloring (reduction) are shown in Fig.2c. From Fig.2c we have determined optical contrast during electrochromism ~60% monitoring at 580 nm within a very short response time (0.35s for bleaching and 0.32s for coloring).

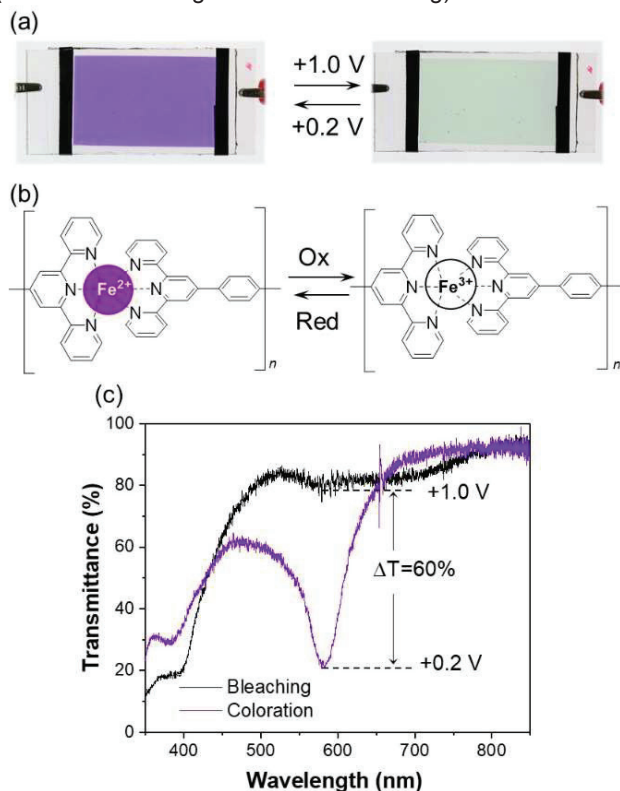


Fig.2: (a) Electrochromic color change of fabricated device; (b) Chemical structural change of polyFe upon oxidation and reduction; (c) Corresponding transmittance spectral change by the application of operating voltage +1.0 and +0.2 V.

During electrochromism a reversible redox reaction happens on polyFe film in working electrode side. At the same time exactly opposite, redox reaction occurs at counter electrode resulted in lowering the operational voltage and fasten the EC response. Very Interestingly, the fabricated device showed extremely high cycle stability

more than 100,000 cycles within operating voltage +0.2/+1.0V at room temperature. Furthermore, introduction of NiHCF layer on counter electrode improve the optical memory of fabricated EC device.

4. CONCLUSIONS

We successfully fabricated ECD based with polyFe as electrochromic layer, polymeric semi-gel as electrolyte layer and NiHCF as an ion storage counter layer. The fabricated device showed ~60% of maximum optical construct (ΔT) between the colored and bleached states over 100,000 cycles at room temperature within +0.2 and +1.0V of the operation voltage

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