Relationship of Thickness of ITO Particle-modified Counter Electrode into Electrochromic Properties of 10-methylphenothiazine

Zhuang Liang, Kazuki Nakamura, Norihisa Kobayashi

Graduate School of Engineering, Chiba University,
1-33 Yayoi-cho, Inage-ku, Chiba, 263-8522, Japan
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ABSTRACT

We have already reported a novel multicolor electrochromism in a single device by introducing a porous counter electrode having high capacitance. In this paper, we investigated effect of capacitance properties of counter electrode into coloration properties of 10-methylphenothiazine molecule.

1 INTRODUCTION

Electrochromic (EC) materials, including some inorganic metal oxides, organic molecules such as viologens, and conducting polymers, can change their color reversibly, by electrocheomical redox reactions. Electrochromic devices (ECDs) have extensively been investigated because of their potential fields of application, such as displays,[1] rearview mirrors,[2] or smart windows[3] for automotive and building industries.

To expand the potential of the electrochromic technology, researchers have conducted a large amount of inquiry in recent years on generating full-color devices and diversifying the colors of the EC materials.[4,5] In our group previous work, We fabricated hybrid capacitor type ECD by introducing a porous capacitive electrode as counter electrode.[6] The hybrid capacitor ECD is different from typical ECDs using some complementary redox species as the counter-reaction material, a porous ITO particle-modified electrode as the counter side was introducted in this device. With this novel and simple device structure, the amount of charge accumulated by the formation of the electrical double layer on the counter electrode compensated the charge comsumption on the working electrode. As a result, individual color-switching on working electrode has been successfully achieved, even though containing two kinds of both anodic and cathodic EC materials. We also found that the capacitance also has a greater impact on the various kind of colors.[7] By using a porous carbon electrode with a large capacitance as the counter electrode, we successfully obtained four color changes in a single ECD. However, the effect of the increasing capacitance on the color performance of the device has not been studied.

In this paper, we fabricated several ECDs having hybrid capacitor structure with flat ITO electrode as working side and ITO particle-modified electrodes which having different thickness as counter side. As the EC molecule, we employed EC molecule of 10-methylphenothiazine. We also discussed the effect of electrical double layer capacitance on coloration performance in the hybrid capacitor ECD.

2 EXPERIMENT

2.1 Materials

10-methylphenothiazine (MPT) was purchased from Tokyo Kasei Industries Ltd. Propylene carbonate (PC) was purchased from Kanto Chemical Co., INC. Tetra-n-butylammonium perchlorate (TBAP) was obtained from Wako Pure Chemical Industries Ltd. ITO nanoparticle dispersion liquid (< 100 nm particle size (DLS), 30 wt % in isopropanol) was purchased from Sigma Aldrich. All chemicals were reagent grades and were used as received without further purification. The Ag/Ag^+ reference electrode was purchased from ALS Co., Ltd. Indium tin oxide (ITO) glass substrates (R_{sh} 10 Ω sq^{-1}) were supplied by GEOMATEC Co., Ltd., and cleaned with deionized water, warm acetone and UV-ozone treatment prior to use.

2.2 Preparation of the electrolytes

All the experiments were conducted at the ambient laboratory temperature (20–25 °C). The EC electrolyte solution was prepared by dissolving MPT (10 mM) and TBAP (200 mM) in PC. The EC solutions were used for electrochemical measurements of the EC properties in three-electrode cells and the two-electrode ECDs.

The electrolyte solution for capacitor measurements was prepared by dissolving TBAP (200 mM) in PC. It was used for electrochemical measurement of properties of ITO particle-modified electrodes in three-electrode cells.

2.3 Preparation of ITO particle-modified electrodes

ITO nanoparticle dispersion was dropped onto a planar ITO substrate and spin coated at 500 rpm for 15 s followed by 1500 rpm for 15 s. After spin coating, ITO-nanoparticle film on ITO substrate was heated to 210 °C for 1 h on a hot plate. Then repeat the above operation 2-5 times.

2.4 Fabrication of electrochemical devices

Three-electrode electrochromic cells were fabricated with ITO electrode as a working electrode and Pt wire as a counter electrode, and an Ag/Ag^+ electrode as a reference electrode.

Three-electrode electrochemical cells for measurements of capacitor properties were fabricated with ITO particle-modified electrodes as working electrode side and Pt sheet as counter electrode side, and an Ag/Ag^+ electrode as a reference electrode.

The two-electrode ECDs were fabricated by sandwiching the EC solution between ITO electrode (working) and ITO particle-modified electrodes (counter) which having different thickness, keeping inter-electrode distance of 350 μm by silicon spacers. The effective electrode area of the ECD was 1.0 × 1.0 cm^2.

2.5 Electrochemical measurements

Cyclic voltammograms (CVs) were measured by ALS model 660A potentiostat/galvanostat equipped with a computer. The scan rate was 50 mV/s. Absorption spectra and reflectance spectra were recorded in situ by using Ocean Optics USB2000 diode array detection system.

3 RESULTS

3.1 EC properties of the MPT solutions in three-electrode

To characterize the electrochemical behavior of EC materials, CV measurement is usually used in combination with the spectrometric method. We used anodic EC molecule MPT. The CV curves measured by three-electrode cell is shown in Fig. 1 for discussing the EC characteristics of the molecules. The potential was swept from 0 V to the positive direction. From +0.4 V, the absorbance at 510 nm increased as a result of the oxidation of MPT on the ITO electrode, resulting in a pink color. Because the colored MPT molecule diffused into the electrolyte solution as the reaction proceeded, the absorbance of the colored PT molecule still kept in a higher value at around 0.4 after scanning for positive potentials.

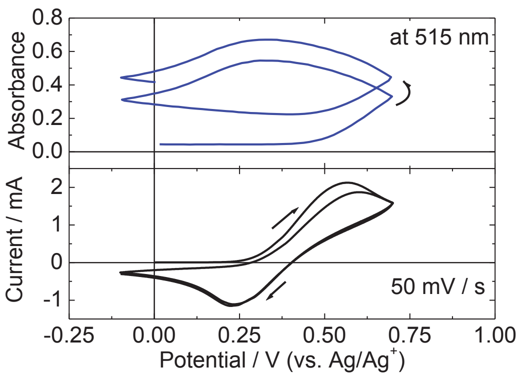

Fig. 1 Changes in absorbance (top) and CV curves (bottom) of MPT (scan rate=50 mV/s)

3.2 Electrochemical properties of ITO particle-modified electrodes

We measured the capacitance of the ITO particle-modified electrodes having different thickness. Among the measurement methods for evaluating the capacitance of the electrochemical capacitor, the chronoamperometric measurement was chosen. In the chronoamperometric measurement, a constant current is passed through the cell, and the capacitance can be evaluated from a change in the potential by the Coulomb's law, $C = Q/V$ (C: capacitance; Q: the accumulated charge by the formation of the electrical double layer; V: the potential change of the capacitor electrode). Fig. 2 shows the relationship between electrostatic capacitance and thickness of ITO particle-modified electrodes. From the result, we can clearly know that with the increase of thickness, the capacitance showed an increasing trend.

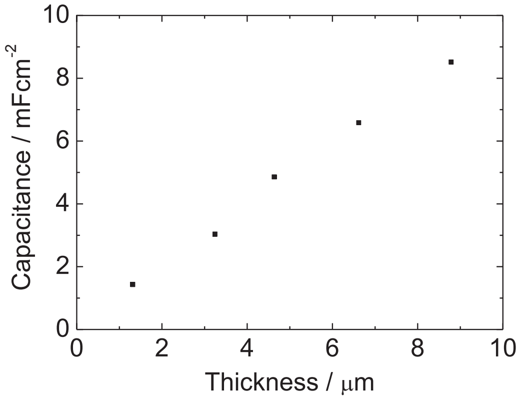

Fig. 2 Relationship between capacitance and thicknesse of the ITO particle-modified electrode.

3.3 EC properties of hybrid capacitor two-electrode ECD

Then, we investigated EC properties of the two-electrode ECDs containing anodic EC molecule of MPT with flat ITO electrode as working side, ITO particle-modified electrodes which having different thickness as counter side.

Fig.3 shows the the current change of esch hybrid capacitor ECD under application of +1 V for 10 s. The insert table shows the relationship between the thickness of the ITO particle-modified counter electrode and the charge consumption by EC reaction. The total amount of charge consumed by the ECD can be calculated by integrating the current with respect to time. Via calculation, with the increase of the thickness of the ITO particle-modified electrodes, the amount of charge consumed were also significantly increased.

Fig. 4 shows the transmission spectra of the ECDs under application of positive voltage of 1 V for 10 s. At any ECD, the characteristic of transmittance decrease due to oxidized MPT molecule appeared at around 515

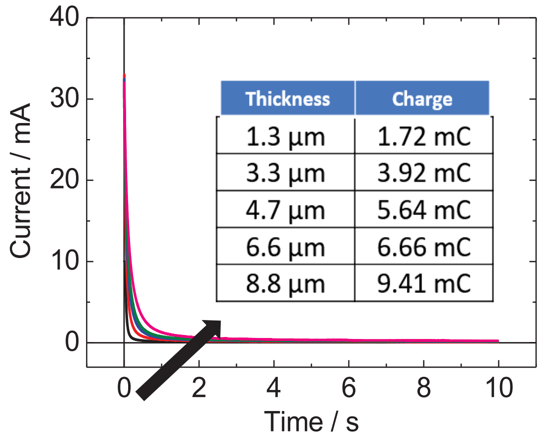

Fig. 3 Changes in time dependence of currents of the ECDs having ITO particle-modified electrodes with different thickness (as counter side) under applied voltage of +1 V for 10 s.

nm. This was because MPT molecule received electrochemical oxidation reaction on working electrode. As the result, color of ECDs changed from transparment to pink. With the increase of the thickness of the ITO particle-modified electrodes, the density of pink deeply increased. Fig. 5 shows the photographs of the ECDs with the ITO particle-modified counter electrodes (thickness: 1.3 μm, 4.7μm and 8.8μm).

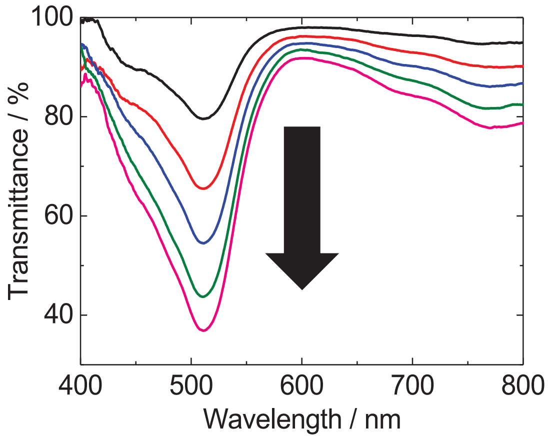

Fig. 4 Transmission spectra of the hybrid capacitor ECDs having flat ITO electrode (as working side) and ITO particle-modified electrodes with different thickness (as counter side) under applied voltage of +1 V for 10 s.

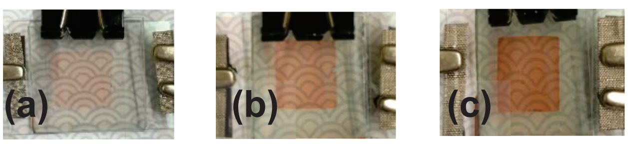

Fig. 5 Photographs of the ECDs with the ITO particle-modified counter electrodes (thickness: (a) 1.3 μm, (b) 4.7μm and (c) 8.8μm).

4 CONCLUSIONS

In this work, we fabricated several hybrid capacitor ECDs with ITO particle-modified electrodes which having different thickness as counter side. With the thickness of counter electrode, larger amount of charge has been successfully accumulated, which satisfies the more reaction charge consumed by the ECD, resulting in deeply colored atate. The results reasonably explain the effect of electrostatic capacity on the color variation of ECD. We believe that this hybrid capacitor architecture will surely contribute field of electronic paper, digital signage, and smart windows.

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