（課程博士用）
(for Degree earned by Completing Doctoral Program)

（別記様式－博７）

千葉大学審査学位論文（要約）（Summary）

先進理科学 専攻 物質科学 コース
Division Department

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論文題名（外国語の場合は、その和訳を併記） Thesis Title（foreign language title must be accompanied by Japanese translation）
英題：Small Organic Molecules Based Multicolor Electrochromic Device Having Hybrid Capacitor Architecture 和題：有機低分子系材料を用いたハイブリッドキャパシタ型マルチカラーエレクトロクロミックデバイス

Chapter 1 Introduction

Optoelectronics is an exciting and rapidly evolving technology field, and has produced applications and innovations that significantly improve our daily lives. Electrochromic (EC) technology is a key branch of optoelectronic technology. Its history can be traced back to 1969, when S.K. Deb reported the reversible change of color to colorless state of tungsten oxide effected due to the application of an external electrical bias. This device can be considered the first EC device (ECD). Since then, EC research has proliferated, including the development of EC materials, the structure and components of ECDs, and associated manufacturing technologies. Multiple practical applications have been developed, such as smart windows, smart glasses, displays, and wearable electronic devices, some of which have been successfully commercialized.

Since significant improvement has been made in optimizing the ECDs, the current challenge is to develop ECDs that exhibit multicolor functionality. Multicolor functionality can significantly expand the market opportunities of ECDs, because it enables the manipulation of light and color over time through the application of different voltages. Small organic EC molecules exhibit superior color purity and easily transition from colorless to colored states. In recent years, in efforts to improve the functionality of ECDs, many studies have investigated multicolor ECDs. However, in order for an ECD to display multiple colors, it requires a patterned electrode or multi-electrode structure that is typically very complex. In practice, a device that performs multicolor switching and has a simple structure is desired. However, in a device consisting of two transparent conducting oxide electrodes sandwiched an electrolyte containing anodic and cathodic EC molecules, an EC reaction occurs at the working electrode while a redox reaction occurs at the opposite electrode to compensate for the amount of charge consumed. Consequently, only a color mixture of the two molecules is obtained. In order to display different colors independently, mechanisms other than electrochemical redox reactions must be used to compensate for the amount of charge consumed by the EC reactions.

This thesis reports the introduction of an electrical double layer capacitor (EDLC) with a non-Faraday reaction process into an ECD; that is, an ECD featuring a hybrid capacitor architecture is developed and fabricated that employs an EDLC electrode as the counter electrode and combines both anodic and cathodic EC molecules in a simple structure. In this ECD, the charge accumulated by the electrical double layer (EDL) that forms on counter electrode is expected to compensate for the charge consumed by the EC reactions, the anodic and cathodic redox reactions will occur independently, allowing the display of multiple individual colors using a simple device structure.

Chapter 2 Organic, Multicolor ECD featuring a Particle-modified ITO Electrode

In this chapter, two small EC molecules of phenothiazine (PTZ) and 2,5-bis(N-benzyl pyridinium)-1-phenylpyrrole (D-1) are employed. The EC properties of the PTZ and D-1 molecules are investigated. As an anodic molecular material, PTZ produces a color change when an oxidation reaction occurred. The absorption spectrum of the colored state shows two absorption peaks at approximately 450 nm and 650 nm, producing a blue-green color. On the contrary, D-1 molecule exhibits the characteristics of reduction reaction discoloration. The absorption spectrum of the colored state shows an absorption peak at around 540 nm, producing a magenta color.

Next, an EDLC electrode with transparent characteristics is introduced, that is, a particle-modified ITO electrode. Compared with the flat ITO electrode, the particle-modified ITO electrode has a porous morphology and a large surface area. Owing to the porous surface morphology of a particle-modified ITO electrode, the cyclic voltammogram of a cell featuring a particle-modified ITO electrode shows a typical current–voltage curve, due to the formation of an EDL. And, the capacitance of the flat ITO electrode of 0.026 mF (0.013 mF/cm^2) is significantly less than that of the particle-modified ITO electrode: 2.92 mF (1.46 mF/cm^2) via calculation. When these two types of electrodes are employed as the counter electrodes in ECD containing PTZ molecules, they exhibit different electrochemical characteristics. In the ECD in which both the working electrode and the counter electrode are flat ITO electrodes, no current or absorbance changes associated with the oxidation of PTZ are observed until +1.2 V. On the other hand, the CV curve and corresponding absorbance profile of the ECD featuring a particle-modified ITO electrode as the counter electrode, respectively, reflect changes in current and absorbance associated with the oxidation of PTZ. When the potential is swept in the positive direction, the oxidation current increases from around +0.5 V, and concomitantly, a significant increase in absorbance at 630 nm is observed due to the oxidation of PTZ. This reaction occurs because the amount of charge consumed by the oxidation of PTZ on the working electrode is compensated for by the formation of an EDL on the particle-modified ITO electrode.

In view of the particle-modified ITO electrode as the counter electrode accumulated charge in an EDL to compensate for the charge required for the EC reaction on the working electrode, the multicolor ECD containing PTZ and D-1 molecules featuring a flat ITO electrode (working electrode) and a particle-modified ITO electrode (EDLC counter electrode) is fabricated. For comparison, the ECD with a flat ITO electrode as the counter electrode is also fabricated. In the case of the ECD featuring the flat ITO electrode as the counter electrode, the achievement of multicolor is failed. The application of a voltage of +1.3 V or −1.3 V to the device for 10 s, induced the appearance of strong and weak absorption signals at 540 nm and 650 nm, respectively, in its absorption spectra, and the display of a deep red color. This result can be considered that the redox reactions of PTZ and D-1 molecules occurred in pairs. On the other hand, the ECD with the particle-modified ITO electrode exhibits completely different EC properties. The application of positive voltages of 0.9 to 1.1 V to the working electrode induces the appearance of absorption bands at approximately 650 nm in the corresponding absorption spectra because only PTZ reacted (is electrochemically oxidized) on the working electrode. Accordingly, the color of the ECD changes from light yellow to green. In this voltage range, the electrical charge consumed by the oxidation of PTZ is compensated for by the formation of an EDL on the particle-modified ITO electrode (with its large surface area). The application of negative voltages to the working electrode, induces the appearance of absorption bands in the corresponding absorption spectra associated with the reduction D-1. The magenta color of D-1 is obtained at –1.1 V.

Evidently, the novel ECD is able to change its color between pale yellow, green and magenta through the application of an appropriate voltage. The results suggest that the charge compensation property of the particle-modified ITO electrode is appropriate for the selected EC materials that undergo electrochemical redox reactions on the working electrode. Due to the charge compensation associated with the formation of an EDL on the particle-modified ITO electrode, selective EC reactions can be induced on the flat ITO electrode to achieving multicolor functionality.

Chapter 3 Improvement of the Color Performance of an ECD featuring a Hybrid Capacitor Architecture

In practical EC applications, the color performances of EC materials are very important. For example, the density of a color directly affects its perceived vividness. However, in the multicolor which be fabricated in Chapter 2, although several colors have been achieved in a single device, the absorbance of different color states varied a lot form the absorption spectra. This is mainly because the color efficiency of the two materials is quite different. One way to solve this problem is to optimize the concentration of various materials. More importantly, at the ECD featuring the hybrid capacitor architecture, EDLC electrode effectively compensates for the equivalent amount of charge consumed by the EC reaction. Increasing the capacitance of the EDLC electrode will accumulate more charges and produce more color species due to the EC reaction. This chapter focuses on the method of increasing the electrostatic capacitance of the particle-modified ITO electrode and the effect on the color performance of the ECD featuring a hybrid capacitor architecture.

Increasing the specific surface area of the electrode can improve its electrostatic capacitance. In this section, the specific surface area of the electrode is changed by adapting its ITO-nanoparticle coating, that is, by changing the film thickness of the electrode, to improve its electrostatic capacitance. Five particle-modified ITO electrodes are prepared, and their film thicknesses are 1.3 μm, 3.3 μm, 4.7 μm, 6.6 μm and 8.8 μm, respectively. The capacitance of the particle-modified ITO electrodes with different film thicknesses are determined. The particle-modified ITO electrode with a film thickness of 1.3 μm has a capacitance of 1.4 mF/cm^2. While the particle-modified ITO electrode with a film thickness of 8.8 μm has a capacitance of 8.5 mF/cm^2. Evidently, the capacitance of the particle-modified ITO electrode increases with increasing film thickness.

Next, The EC properties of two-electrode PTZ molecule based ECDs featuring a flat ITO electrode or the particle-modified ITO electrodes with different film thickness as the counter electrodes are investigated. When a flat ITO electrode is used as the counter electrode, the ECD exhibits high transparency, but the application of voltage does not induce a color change. This indicates that the absence of a charge-compensation mechanism at the counter electrode prevents the oxidation of PTZ at the working electrode. However, the application of a particle-modified ITO electrode as the counter electrode significantly limits the transmittance of radiation with wavelengths of ~450 nm and ~650 nm. This phenomenon suggests that the charge accumulated by the formation of an EDL successfully compensates for the charge consumed by the oxidation of PTZ. The colored states realized through the application of the particle-modified ITO electrodes as counter electrodes, decrease the transmittance (of radiation with a wavelength of 650 nm) of the respective ECDs by 15% (1.3 μm), 19% (3.3 μm), and 23% (4.7 μm). However, as the film thickness of the particle-modified ITO electrode increases, the transparency of the ECD decreases. The colorless state of the ECD featuring a particle-modified ITO electrode with a film thickness of 4.7 μm is significantly less transparent than that of the ECD featuring a flat ITO electrode as the counter electrode. Although a high film thickness limits device transparency, it indeed promotes a more intense color change.

These results indicate that the film thickness of the particle-modified ITO electrode as the counter electrode indeed affects the color performance of an ECD based on a PTZ molecule. As the thickness of the ITO nanoparticle coating of the electrode increases, its capacitance increases to accommodate the accumulation of a higher amount of electrical charge. The higher the amount of charge that the counter electrode can accommodate, the higher the amount of PTZ that is oxidized on the working electrode. As a result, the color performance of the device improves, i.e., its transmittance decreases.

Chapter 4 ECD featuring a Hybrid Capacitor Architecture that Displays White, Yellow, Purple-red, and Blue-green by Employing a Graphite Electrode

Several EC small organic molecules, which undergo multiple redox reactions and have uncomplicated synthesis procedures, can be used to realize an ECD that displays multiple colors. 4,4'-biphenyl dicarboxylic acid diethyl ester (PCE), producing two color changes (yellow and purple-red) is one of them. To achieve greater color variation, multicolor EC materials, such as a PCE molecule, can be introduced into an ECD featuring a hybrid capacitor architecture. However, the ECD contained PTZ and PCE with the particle-modified ITO counter electrode, under a negative voltage, neither the yellow color of the first reduced state of PCE nor the purple-red color of its second reduced state is obtained. Instead, once electrochemical reactions occur (−2.4 V and −2.7 V), the absorption band of oxidized PTZ (640 nm) is observed together with the absorption bands of reduced PCE. These results suggest that the EDL on the particle-modified ITO electrode is unable to compensate for the charge consumed during the electrochemical reduction of PCE on the working electrode. As a result, the electrochemical oxidation of PTZ is induced on the particle-modified ITO electrode.

To overcome this issue, an alternative EDLC electrode with greater capacitance is required as the counter electrode. A graphite electrode has a larger specific surface area and a higher capacitance than the particle-modified ITO electrode, and is widely used in electrochemical capacitors. In this chapter, the fabrication of an ECD featuring a hybrid capacitor architecture, i.e., a graphite electrode as the counter electrode, is reported.

Both of the same thickness (3.3 μm) of the ITO particle film and the graphite electrode are fabricated. The capacitance of the particle-modified ITO electrode is calculated to be 3 mF (1.5 mF cm^{-2}). In contrast, the capacitance of the graphite electrode of 82 mF (41 mF cm^{-2}) is nearly 30 times higher than that of the particle-modified ITO electrode.

Then, the two-electrode ECD is fabricated by sandwiching a white gel electrolyte between a flat ITO electrode (working electrode) and a graphite electrode (counter electrode). When a positive voltage of +1.1 V is applied to the ECD, the reflectance at ~450 nm and ~640 nm is low due to oxidization of PTZ, resulting in a vivid blue-green color. This is because only the PTZ molecule undergoes an electrochemical reaction at the working electrode. When a negative voltage, −2.2 V, is applied to the ECD, the reflectance at 400–500 nm is low due to the first reduction of PCE, producing a clear yellow color. Finally, when a voltage of −2.6 V is applied to the ECD, because of the second reduction of PCE, its reflectance spectrum shows a minimum at 570 nm, corresponding with the appearance of a purple-red color. These results indicate that the charge compensation associated with the formation of an EDL on the graphite electrode enables the targeted reaction of EC molecules on the working electrode.

The EC response times are investigated. For the blue-green color, the coloring response time and bleaching response time are 6 s and 14 s, respectively. For the yellow color, the coloring response time and bleaching response time are 2 s and 12 s, respectively. Due to the poor stability of the second reduced species of PCE, the purple-red color characteristics are not evaluated. The open-circuit memory properties of the blue-green and yellow colors are also investigated. In the case of the blue-green color, after applying a voltage of +1.1 V for 10 s, it takes the ECD ~2.5 min to recover its initial reflectance. In the case of the yellow color, after applying a voltage of −2.2 V for 10 s, it takes the ECD ~3.2 min to recover its initial reflectance. The stability of the multicolor ECD was measured by cycling each color 100 times. The device provides a stable and reproducible yellow color. On the other hand, in the case of the blue-green color, the reflectance shows unstable changes. This might be ascribed to the serious diffusion of the PTZ molecule into the electrolyte and its adhesion to TiO_2. However, the current change remains stable, indicating that PTZ molecule had not been resolved yet. If the PTZ molecule is modified on the ITO electrode, this problem can be solved.

Chapter 5 Conclusions

This thesis presents a collection of studies that aim to contribute to this field by promoting the development of simple, ECDs with multicolor functionality. The culmination of the research conducted during these studies is the development and fabrication of an ECD that features an electrical double layer capacitor electrode and combines both anodic and cathodic EC molecules in a simple structure. When the transparent, particle-modified ITO electrode is used as the counter electrode of an ECD, the colored states of anodic PTZ molecule and cathodic D-1 molecule can be displayed in the same device. When a graphite electrode is introduced as the counter electrode, due to its large electrostatic capacity, a large amount of charge is successfully accumulated, which compensates for the charge consumed by the EC multiple reactions. As a result, the ECD displays four well-defined colors (white, blue-green, yellow, and purple-red) by employing PTZ and PCE.

To the best of our knowledge, a multicolor ECD featuring an EDLC as a counter electrode has not been reported. I hope that this novel, easily-fabricated, multicolor display system represents a significant breakthrough that will inform the development of color devices and expand the potential of EC technology.