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Coloration Properties of the Electrochromic Device with Hybrid Capacitor Architecture Effected by Electrolyte Composition

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ABSTRACT

We have already reported a novel multicolor electrochromic (EC) device by introducing a porous counter electrode having high capacitance. In this paper, we investigated the effect of electrolyte species on electric double layer capacitance and coloration properties of the EC device.

1 Introduction

Electrochromism is defined as reversible color change induced by an electrochemical redox reaction. In the past few decades, electrochromic devices (ECDs) have extensively been investigated because of their potential field of application, such as displays or smart windows.[1]

Despite the significant improvements have been achieved with the regard to the EC properties, a further challenge was to find ECDs that exhibit multicolor EC behavior. In our previous work, we fabricated hybrid capacitor-type ECD by introducing a porous capacitive electrode as counter electrode.[2] The hybrid capacitor ECD is different from typical ECDs using some complementary redox species as the counter-reaction material, a porous ITO particle-electrode was introduced as the counter electrode. In this novel and simple ECD, the amount of charge accumulated by the formation of the electric double layer on the counter electrode compensated the charge consumptions on the working electrode. As a result, individual color-switching on working electrode has been successfully achieved, even two EC molecules with different polarities mixed in the same ECD. We also found that increasing the capacitance of the counter electrode improves the coloration performance.[3] As the thickness of the ITO nanoparticle coating increases, larger amount of charge accumulated, resulting in a deeply colored state. However, the transparency of the ECD is greatly reduced by increasing the thickness of the ITO nanoparticle coating, so other methods to improve charge accumulation should be considered.

In this paper, ECDs having hybrid capacitor architecture were fabricated using various kind of electrolytes with different cations or anions. Firstly, the effect of electrolyte species on the capacitance of the ITO particle modified electrode is discussed, and then the coloration properties of ECDs due to capacitance changes are investigated.

2 Experiment

2.1 Materials

10-phenylphenotiazine (PPT), 1,1'-diheptyl-4,4'-bipyridinium (HV^{2+}) dibromide, tetraethylammonium tetrafluoroborate ($TEABF_4$), tetrabutylammonium tetrafluoroborate ($TBABF_4$), and tetraethylammonium trifluoromethansulfonate ($TEACF_3SO_3$) were purchased from Tokyo Chemical Industry Co., Ltd. Tetrahexylammonium tetrafluoroborate ($THABF_4$), tetraethylammonium hexafluorophosphate ($TEAPF_6$), and the ITO dispersion were purchased from Sigma-Aldrich Co. LLC. Propylene carbonate (PC) was obtained from Kanto Chemical Co., Inc. 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 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 200 °C for 1 h. Then repeat the above operation 2 times.

2.3 Preparation of the electrolytes solutions

The PC solutions containing 500 mM $TEABF_4$ or $TBABF_4$ or $THABF_4$ or $TEAPF_6$ or $TEACF_3SO_3$ were prepared for measuring electrochemical properties of the ITO particle-modified electrode. EC electrolyte solution was prepared by dissolving PPT (30 mM) and each electrolyte ($TEABF_4$, $TBABF_4$, $THABF_4$) of 500 mM in PC or HV^{2+} and each electrolyte ($TEABF_4$, $TEAPF_6$, $TEACF_3SO_3$) of 500 mM in PC.

2.4 Fabrication of electrochemical devices

The three-electrode cells for measurements of capacitor properties were fabricated with ITO particle-modified electrode (working), Pt sheets (counter) electrode, and Ag/Ag^+ electrode (reference).

The two-electrode ECDs were fabricated by sandwiching the EC solution between ITO electrodes (working) and ITO particle-modified electrodes (counter). The inter-electrode distances were 350 μm and the effective electrode area of the ECD was 1.0 × 1.0 cm^2.

3 Results and Discussion

3.1 Electrochemical properties of ITO particle-modified electrodes

The capacitances of ITO particle-modified electrodes with different electrolytes were investigated by galvano-static charge-discharge measurements at a constant current of 0.02 mA (Fig. 1). In all electrolytes, both charging and discharging processed showed almost linear changes. This indicates that these processes were caused by formation of an electrical double layer without electrochemical redox reactions. The capacitance (*C*) can be calculated from $C=Q/V$ (*Q*: the accumulated charge, and *V*: the potential change of the electrode). The capacitances with electrolytes containing different cations were 13.9 ($TEABF_4$), 9.7 ($TBABF_4$), and 9.2 ($THABF_4$) mF/cm^3. The effect of anions on the capacitances were also investigated: 7.8 ($TEABF_4$), 7.6 ($TEAPF_6$), 6.3 ($TEACF_3SO_3$) mF/cm^3. The ionic size of the cations of the electrolytes were $THA^+ > TBA^+ > TEA^+$, and the ionic size of the anions were $CF_3SO_3^- > PF_6^- > BF_4^-$, indicating that the electric double-layer capacitance increases with the smaller size of the adsorbed ions.

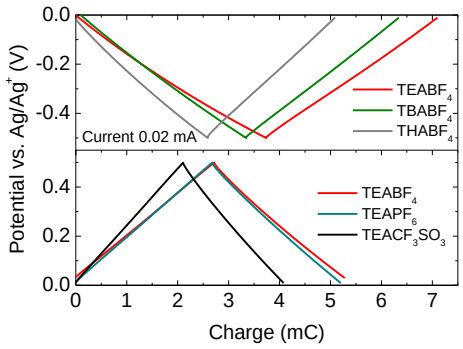

Fig. 1 Charge-discharge curves of ITO particle-modified electrode in different electrolyte; $TEABF_4$, $TBABF_4$, $THABF_4$, $TEAPF_6$, and $TEACF_3SO_3$.

3.2 EC properties of hybrid capacitor two electrode ECDs

Then we investigated the EC properties of a two-electrode ECDs containing anodic EC molecule of PPT and electrolytes with a different cations. Fig. 2(a) shows the change in absorption spectra of the ECDs under application of positive voltage of 1.2 V for 20 s. In the all ECDs, the absorbance at 520 nm increased and color of ECDs changed from transparent to pink. This was because PPT molecule received electrochemical oxidation reaction on working electrode. The change of absorbance was highest in the ECD with $TEABF_4$, followed by $TBABF_4$ and $THABF_4$. The amount of charge consumed by the ECDs calculated from integrating the current with respect to time, was also greatest in the ECD with $TEABF_4$.These results are consistent with the order of the capacitance measurement results.

Similar results were obtained for electrolytes with different anion species, containing the cathodic EC molecule HV^{2+} (Fig. 2(b)).

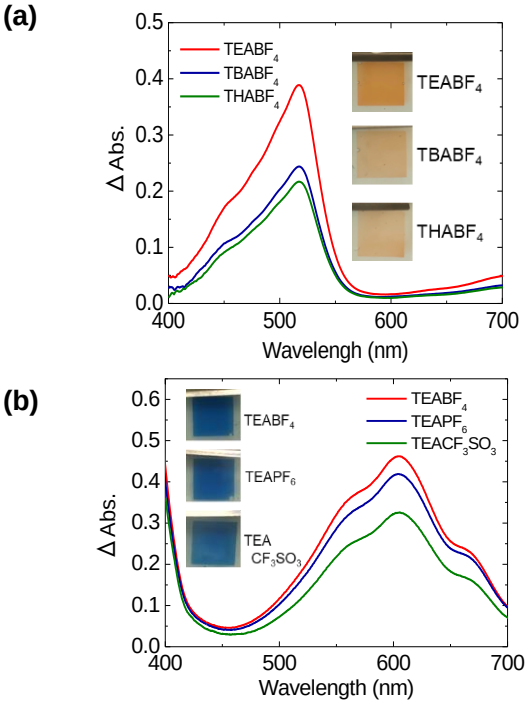

Fig. 2 (a) Change in absorption spectra of the EC device containing PPT under applied +1.2 V / 20 s and (b) containing HV^{2+} under applied -1.5 V / 20 s.

4 Conclusions

In this work, we discussed the effects of electrolyte species on the electric double-layer capacitance and the coloration performance of ECDs having hybrid capacitor architecture. The electric double-layer capacitance of the counter electrode varied with the electrolyte species and improved the coloring properties of the ECD. Through this study, fabricating a hybrid capacitor architecture by employing suitable electrolyte, which provided great possibilities for the multicolor ECD with excellent initial transparency and brightly colored states.

References

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