The Effect of Temperature on Electrodeposition Behavior of Ag Deposition-based Electrochromic Device

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ABSTRACT

We have reported Ag deposition-based electrochromic (EC) device which showed reversible color change from transparent to magenta, cyan, yellow, green, black and silver-mirror in a single device. In this study, effect of temperature on electrodeposition behavior of Ag nanoparticles was investigated in the multi-color EC device. As a result, we confirmed that morphologies of deposited Ag nanoparticles and the reflection behavior were affected by temperatures of the electrolyte solutions.

1 INTRODUCTION

Electrochromism is a phenomenon of reversible color change induced by electrochemical redox reactions of functional materials. Simple structure, large viewing angle, and low power consumption are some of the advantages of electrochromic (EC) devices for optical modulation systems in comparison with the conventional systems such as liquid-crystal display systems with backlight or organic light-emitting diodes. Electronic papers, digital signages and smart windows are examples of potential applications of the EC system.^{1,2} Recently, we have reported multicolor EC device using LSPR of silver metal. This device achieved six optical states-transparent, silver mirror, black, cyan, magenta and yellow-in a single device on the basis of an electrochemical Ag deposition mechanism.3-5 The Ag deposition-based EC device for reversible electrodeposition systems are basically composed of a pair of transparent electrodes with a gel electrolyte containing Ag⁺ between them. The application of a negative voltage causes the Ag metal deposition on the electrode substrate to prepare metal nanoparticles or thin film that alters the optical properties of the surface. Optical states-mirror, black and three primary colors of cyan, magenta, yellow-can be changed controlling the shape and size of Ag deposition.

In order to control the shape and size of deposited Ag nanoparticles, it is important to manipulate crystal growth process of Ag nanoparticles. The crystal growth process of metal nanoparticles during electrodeposition are greatly affected by reaction rate which depends on diffusion rate of Ag⁺. In addition, the viscosity of the electrolyte solution decreases with increasing its temperature, and the diffusion rate of Ag⁺ increases.^{6,7} Therefore, the electrodeposition behavior of the Ag nanoparticles, i.e.

electrochemical reactivity, deposition rate, morphology of the deposited Ag nanoparticles and their optical properties, would be influenced by the temperatures of the electrolyte solutions. In order to control the optical properties of this EC device, it is of importance in clarifying the influence of temperature.

In this paper, we investigated the effect of temperature on electrodeposition behavior of Ag nanoparticles in Ag deposition-based electrochromic device.

2 EXPERIMENT

2.1 Materials

Silver nitrate (AgNO₃, Kanto Chemical Co. Inc.) was used as received. Dimethyl sulfoxide (DMSO, Sigma Aldrich Japan) was used as solvent as received. Lithium Bromide (LiBr, Kanto Chemical Co. Inc.) was used as supporting electrolyte without further purification. Poly (vinyl butyral) (PVB, Sekisui Chemical Co. Ltd.) was used as a host polymer for electrolyte gelation. The ITO electrode (Matema, 10 Ω/\Box) was used after adequate washing.

2.2 Sample preparation

The electrolyte for the electrochromic device was prepared as follows: 50 mM of AgNO₃ as electrochromic material, 250 mM of LiBr as supporting electrolyte were dissolved in DMSO.

2.3 Fabrication of electrochromic device

The three-electrode cells for measurements of electrochemical properties were constructed with a flat ITO electrode (apparent reaction area of the electrode was 1 cm²) as the working electrode, a Pt wire as the counter electrode, a Ag/Ag⁺ electrode as the reference electrode, and DMSO-based electrolyte solution.

2.4 Apparatus

Electrochemical measurements were carried out using a potentiostat/galvanostat (ALS, 660A, CH Instruments Inc., USA) equipped with a computer. Absorption spectra were recorded by on a diode array detection system (USB2000, Ocean Optics, USA). The surface morphologies of electrodes were analyzed using scanning electron microscope (SEM, JEOL JSM-6510A).



Fig. 1 Cyclic voltammograms of the 3electrode cell at various temperatures; 26, 35, 45, 60 °C.

3 RESULTS AND DISCUSSION

First, in order to investigate effect of temperature on electrochemical reactivity, we carried out 3-electrode cyclic voltammetry measurements. Fig.1 shows the cyclic voltammograms at various temperatures; 26, 35, 45, 60 °C. As the potential swept in the negative direction, the cathodic current was observed from ca. -1.4 V. This reduction current was due to the electrodeposition of Ag nanoparticles on the working electrode. As the potential swept in the positive direction, the anodic current appeared from -0.9 V, reflecting the oxidative dissolution of the Ag nanoparticles. These currents for electrochemical reaction of Ag⁺ increased at higher temperatures (45 °C and 60 °C) of the electrolyte solution.

The reflection spectra of the 3-electrode EC cell at various temperatures were also measured (Fig. 2). The Ag nanoparticles were electrodeposited on the working electrode by applying constant potential of -2.5 V until reaction charge reached to 25 mC. As deposition of Ag, reflectance increased at the whole wavelength of visible region and the working electrode were turned to mirror states. As shown in Fig. 2, higher temperature affected to increase the overall reflectance of the deposited Ag in 10~20 %

Then, in order to discuss the difference of the optical properties, morphologies of the deposited Ag were investigated by using SEM. Fig. 3 shows the SEM images and photographs of the Ag nanoparticles at mirror states deposited at each temperature. At higher temperature, deposited Ag nanoparticles densely connected each other and formed film-like planar structure. Also, density of deposited Ag nanoparticle seemed to be increased.

The changes of the morphologies of deposited Ag were discussed in terms of electrodeposition rate of Ag nanoparticles on the working electrode. Fig. 4 shows the chronoamperometric curves for Ag deposition in the EC cell during the application of constant potential -2.5 V until reaction charge reached to 25 mC. Transient current increased with temperature increase, especially at 60 °C.



Fig. 2 Reflection spectra after application constant potential –2.5 V until reaction charge reached to 25 mC at various temperatures; 26, 35, 45, 60 °C.



Fig. 3 SEM images and photographs of working electrode of the EC device after application constant potential -2.5 V until reaction charge reached to 25 mC at various temperatures; 26, 35, 45, 60 °C.

The increase of transient currents suggested the flux of Ag⁺ from the electrolyte solution to surface of working electrode increased with temperature.

This increase of flux of Ag⁺ can be explained by diffusion coefficients of the Ag⁺ ions. To calculate the diffusion coefficients, Cottrell plots were drawn from the chronoamperometry. Table 1 shows the diffusion coefficient at various temperatures. The diffusion coefficients increased with temperature of the electrolyte solution (from 4.62×10^{-6} cm² s⁻¹ for 25 °C to 3.59×10^{-5} cm² s⁻¹ for 60 °C). The increase of the diffusion coefficients would be due to decrease of viscosities of the electrolyte solutions with temperature.

During the electrochemical deposition of Ag nanoparticles, because the Ag⁺ are consumed by the electrochemical reaction, the concentration of the Ag⁺ on surface of the working electrode become guite low. In



application of constant potential (-2.5 V) until reaction charge reached to 25 mC at various temperatures; 26, 35, 45, 60 °C.

this situation, the flux of Ag^+ to the electrode surface should be considerably affected by the diffusion coefficients. The increased diffusion coefficients at higher temperature would increase flux of Ag^+ , leading to promote electrochemical deposition of Ag nanoparticle as shown in Fig. 4.

From these results, we suggested that the rapid formation of Ag nanoparticles at higher temperature induced higher density of deposited Ag nanoparticles. And following rapid growth of the Ag nanoparticles would promote formation of film-like planar structure because of 3D diffusion process of Ag⁺ due to large amount of Ag⁺ flux from solution to surface of the electrode. By formation of the planar structure, the reflectance of the deposited Ag increased with temperature.

4 CONCLUSION

We confirmed the effect of temperature on electrodeposition behavior of Ag nanoparticles in Ag deposition-based electrochromic device. With temperature, the diffusion coefficient and flux of Ag+ increased. We also investigated morphology of the deposited Ag nanoparticles. At high temperature of 60 °C, the density of the Ag nanoparticle increased and planar structure was formed. The reflectance of the deposited Aq also increased with temperature, i.e. formation of planar structure. Results of this research suggested that the optical properties of the EC device, such as reflectance, transmittance and their colors should finely control by adjusting the device temperature adequately.

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Table 1 Values of diffusion coefficients of Ag^+ at various temperatures; 26, 35, 45, 60 °C

Temperature (°C)	26	35	45	60
Diffusion Coefficient <i>(D)</i> (10 ⁻⁶ cm ² s ⁻¹)	4.62	21.8	29.4	35.9

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