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Low Driven Voltage Electrochromic Devices Using Conducting Polymer LB Films

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Electrochromic (EC) devices which can be operated at just low driven voltage of 0.2 V have been investigated. The EC devices consist of emeraldine salt (ES) form of polyanilne (PANI) LB films on the both of display and counter electrodes. Since ES can be oxidized or reduced to produce pernigraniline (PS) or leucoemeraldine salt (LES), respectively, each reaction takes place at the both electrodes and such a low driven voltage has been achieved. The color of the display electrode shows green at no bias and is turned to dark blue at the bias. The EC properties, which are contrast, response time, lifetime and memory effect was characterized.

Keywords: conducting polymer; electrochromic device; polyaniline

INTRODUCTION

Conducting polymers have some attractive features, such as conductivity, electric charge, semiconducting behavior and electrochromic phenomenon to expect application to organic electronic and photonic devices. The electrochromic behavior takes place for the color change corresponding to the redox state of conducting polymers [1]. The conducting polymers are generally modified on the display electrodes and the electrochemical oxidation and reduction of the conducting polymers causes the color change. However, the opposite reaction is needed on the counter electrode to lead to electrochromic behavior reversibly. We assume that polyaniline (PANI) is suitable for this requirement because PANI has three redox states, which are fully

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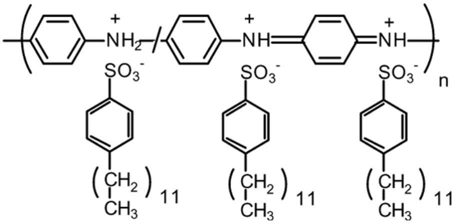

FIGURE 1 Chemical structure of PANI/DBSA.

reduced leucoemeraldine salt (LES), partially oxidized emeraldine salt (ES) and fully oxidized pernigeraniline (PS) [2]. Moreover, the three redox states of PANI are known to show different color, which are yellow green, green and dark blue at LES, ES and PS, respectively. Therefore, when ES state of polyaniline is employed as the both display and counter electrodes, the operational voltage becomes low to compare with a bare counter electrode. PANI is one of the most frequently investigated conducting polymers because of ease of chemical and electrochemical polymerization, chemical stability and inexpensiveness. However, PANI has less processability for infusible and insoluble into common organic solvents except a few solvents, such as *N*-methyl-2-pyrrolidone (NMP) [3] and formic acid [4]. Attempts to make PANI soluble into organic or aqueous solvents have been carried out by many researchers. Recently, we have reported that PANI/dodecylbenzenesulfric acid (DBSA) polyion complex is soluble into chloroform and forms LB film (Fig. 1) [5]. In this study, we fabricated EC devices composed of the same PANI/DBSA LB films at the both of display and counter electrodes. The PANI/DBSA LB film EC device was characterized by spectroelectrochemistry.

EXPERIMENTALS

Organic solvent-soluble PANI was prepared by modifying colloid solution method reported by Madathil *et al.* [6]. After the chemical oxidative polymerization, the PANI/DBSA ion complex colloids in water were extracted into chloroform solution. The extracted PANI/DBSA in chloroform was dehydrated using anhydrous Na_2SO_4 for overnight. Surface pressure-area isotherm was measured in LB trough (USI) in the subphase of the deionized water or 30 mM HCl solution at 20°C. The monolayer was transferred onto an ITO electrode at the deposition pressure of 25 mN/m. UV-vis absorption spectra and electrochemical spectroscopy were measured with Hitachi U-2800 spectrometer. Cyclic voltammetry was carried out by three electrode cell which was composed of the PANI/DBSA monolayer LB film on an ITO electrode as a working electrode, saturated calomel electrode (SCE) as a reference electrode and Pt wire as a counter electrode in the potentiostat (Hokuto Denko) in 0.1 M Na_2SO_4 solution with 50 mM H_2SO_4. Current-voltage curve was carried out by two electrode cell which was composed of two PANI/DBSA monolayer LB films on ITO electrodes as a display electrode and as a counter electrode in the source meter (Keithley 2400) in 0.1 M Na_2SO_4 solution with 50 mM H_2SO_4.

RESULTS AND DISCUSSION

PANI LB films on ITO electrodes were prepared by deposition of monolayer for PANI/DBSA ion complex on a water surface [5]. Cyclic voltammogram (CV) for PANI LB films on the ITO electrode shows two redox couples at 0.7 and −0.2 V vs. SCE, assigned to ES/PS and LES/ES couples, respectively, with the open-circuit potential of 0.5 V vs. SCE [5]. In order to fabricate the low driven voltage EC device, the open-circuit potential is shifted to be 0.58 V vs. SCE, where the polyaniline is still ES state and is easily oxidized to PS. The EC device composed of PANI LB films with 60 layers on the both of display and counter electrodes is found to be operated at such a low voltage of 0.2 V as shown in Figure 2. The Current-voltage curves show charging and

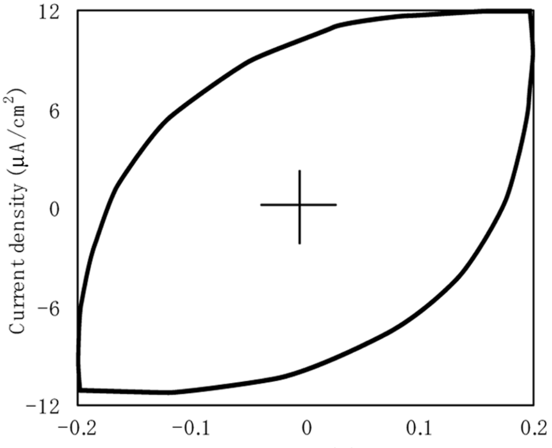

FIGURE 2 Current-voltage curves for EC device at the scan rate of 0.1 V/s.

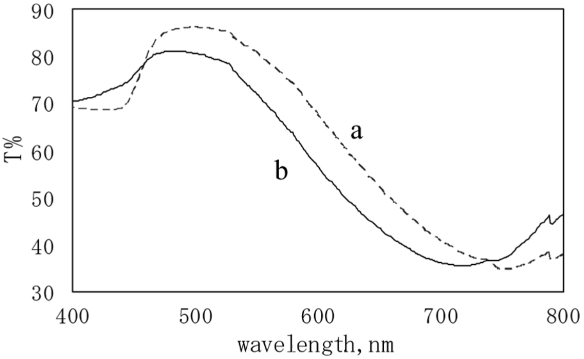

FIGURE 3 Transmittance spectra of EC device at 0.0 V (a) and 0.2 V (b).

discharging behavior like a capacitor with stable repeating cycles. Meanwhile, at the EC device using bare ITO as the counter electrode, the operating voltage is needed to be 1.8 V. This large difference in the operational voltage between PANI LB film on ITO electrode and bare one as a counter electrode is due to whether the opposite reaction is compensated at the counter electrode. The opposite reaction that is reducing reaction from ES to LES occurs at small overpotential at the PANI LB film, whereas a large overpotential is needed to take place the reducing reaction which might be reduction of water solvent or cathodic deposition of indium oxide at the bare ITO electrode. The transmittance spectra of the PANI LB film on ITO electrode as a display electrode of the EC device applied at the voltage bias of 0 V and 0.2 V is shown in Figure 3. The spectrum of the EC device at the zero bias indicates two typical absorption bands at 430 and 760 nm, which are assigned to π-π^* transition and polaron transition, respectively, indicating that the state of PANI is emeraldine salt [2]. The absorption peak at 760 nm is blue-shifted to 710 nm and the absorbance at 430 nm decreases when the EC device is applied at the voltage bias of 0.2 V. The spectrum obtained at the voltage bias of 0.2 V is not fully oxidized polyaniline but more oxidized state than emeraldine salt. The visible color change takes place from green at 0 V to dark blue at 0.2 V. In order to investigate the electrochromic switching characteristic, the wavelength of 630 nm where the difference in the transmittance is the largest value of 11.2% is selected. The electrochromic switching is measured by monitoring the transmittance at 630 nm at the EC device applied at the step voltage between 0 V and 0.2 V during the interval of 10 sec (Fig. 4). The shape of transmittance response is almost corresponding to that of the step voltage. This switching is

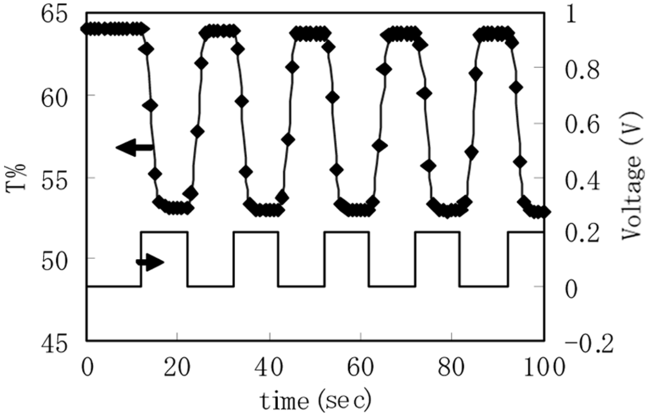

FIGURE 4 Electrochromic switching between 0 V and 0.2 V.

especially stable with little change in the transmittance during several step voltage cycles. The response time for 90% full transmittance changes is 3 sec, which is quite fast. The lifetime of the EC device is also measured as shown in Figure 5. The transmittance change almost disappears above the cycle number of 500. The result shows that the voltage bias of 0.2 V is too small to oxidize emeraldine salt of PANI LB films on the display electrodes because the transmittance does not decrease with increasing cycle number. This is because the open circuit potential might be shifted to cathodic potential with increasing cycle number. The lifetime, which is defined as the cycle number for 90% full transmittance changes, is observed to be 365 cycles.

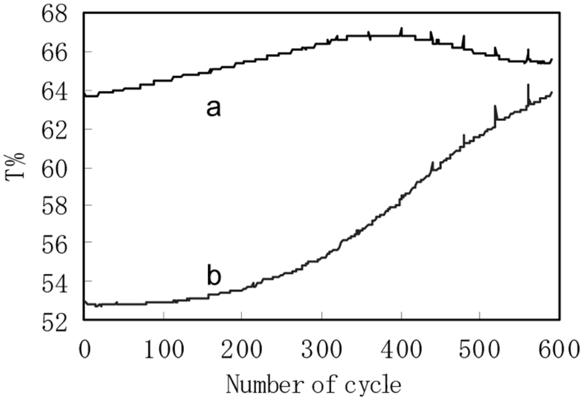

FIGURE 5 Dependence of transmittance on cycle number between 0 V (a) and 0.2 V (b).

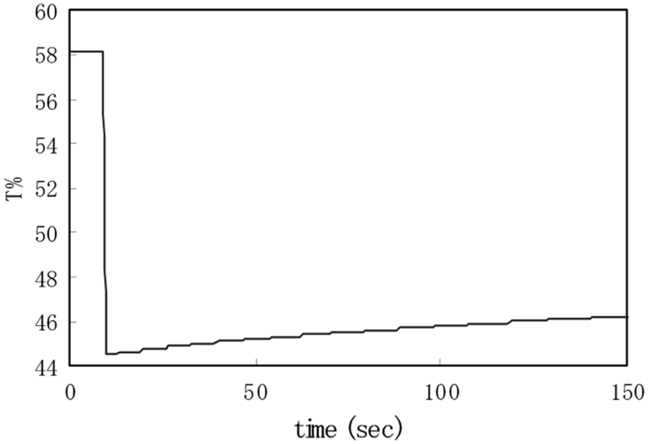

FIGURE 6 Transmittance response of EC device applied at 0.2 V for first 10 sec and then at the open circuit potential.

The memory effect is also investigated by the transmittance response of EC device applied at 0.2 V for first 10 sec and then at the open circuit potential as shown in Figure 6. The 58% transmittance decreases immediately to 45% at the voltage bias of 0.2 V but it recovers gradually at the open circuit potential. The memory time, which is defined as the time when 90% full transmittance change is recovered, is observed to be 90 sec. Since the emeraldine salt of PANI LB film oxidized at the voltage bias of 0.2 V is not fully oxidized according to the UV-vis spectra data, the transmittance change at the open circuit might takes place sensitively.

CONCLUSIONS

We demonstrate that the EC devices using PANI LB films on the both of display and the counter electrodes show lower driven voltage of 0.2 V and reversibility. The electrochromic proterties are obtained to be the transmittance change of 11.2%, the switching time of 3 sec, the lifetime of 365 cycles, and the memory time of 1.5 min. The operational voltage of 0.2 V has been the lowest voltage in EC devices so far.

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