Solar Energy Materials & Solar Cells 163 (2017) 200–203

Contents lists available at ScienceDirect

Solar Energy Materials & Solar Cells

journal homepage: www.elsevier.com/locate/solmat

In situ measurements of electrode potentials of anode and cathode in organic electrochromic devices

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ARTICLE INFO

Keywords:
Electrode potential measurement
Electrochromism
Electrochemical cell
Electronic paper

ABSTRACT

The *in situ* electrode potentials of anodes and cathodes in electrochromic (EC) devices were investigated. The solution-based 2-electrode EC device was fabricated with electrolyte solutions containing anodic and cathodic EC molecules. The electrochemical reaction in a 2-electrode EC device was controlled by the electrode reaction when electroactive molecules in smaller concentrations were used. In addition, the electrode showing less electrochemical activity in the EC device was subjected to larger overpotential under the application of a driving voltage, leading to the promotion of the redox reaction at the electrode. The results showed that the electrode potentials of the device were spontaneously regulated to facilitate both electrode reactions. It is very important to know the potential at each electrode in order to understand the reaction in detail in the 2-electrode EC device.

1. Introduction

Electrochromism is a phenomenon of reversible change of color based on electrochemical reactions that can occur in an electrolyte regardless of the phase (e.g., solution, gel, solid, and liquid crystal) [1–3]. Electrochromic (EC) reactions have attracted much attention as a strong candidate for manufacturing optical-modulated windows (smart windows), anti-glare mirrors and novel display devices [4–9]. Their use in photoelectrochromic systems of dye-sensitized solar cells is also of great importance. The photoelectrochromic-based EC device, which consisted of an EC layer (e.g., tungsten trioxide) and a photoactive layer (e.g., dye-covered titanium dioxide), has been recently gaining a lot of interest by many researchers because no external voltage source is necessary for coloration of such devices [10–12]. Additionally, some researchers have recently reported that this EC device shows the long-term stability by the introduction of a polymer electrolyte.

In the early 2000s, many researchers extensively studied viologen [13–16] and conductive polymers such as poly(3,4-ethylenedioxythiophene) (PEDOT) [17–19] as typical organic EC materials for EC devices. Recently, many of these materials were used to make flexible EC devices [20–23]. Among these EC materials, we have focused on the electrochemical properties of phthalate derivatives [24]. These phthalate derivatives show the color change from colorless clear to the three primary colors (cyan, magenta, and yellow) by electrochemical reduction. We have also demonstrated multicolor representation [25], flexible EC devices with gel electrolytes [26], and the solvent effect for phthalate derivatives [27], which are useful for the development of full-color electronic paper devices. Moreover, the introduction of counter-reaction materials such as a NiO film in a phthalate-based EC device resulted in good coloration properties such as optimal response time and cycle stabilities [28]. However, the detailed reaction behaviors of the EC materials and counter materials during electrochemical reactions in 2-electrode EC devices have not been identified. Even though various researchers have carefully studied the properties of the EC devices, such as coloration characteristics and switching stability for application of display devices, to date, an in-depth analysis of the electrode potentials of the anode and cathode in an EC device have not yet been reported.

In general, an EC device comprises two facing electrodes. The simplest 2-electrode EC device is fabricated by sandwiching an electrolyte solution containing an oxidizable material and a reducible material between two electrodes. In the 2-electrode EC device, electrochemical reduction of the reducible material occurs on the cathode, accompanied by electrochemical oxidation of the oxidizable material on the anode. These electrochemical oxidation and reduction reactions occur in tandem, and consume the same amount of charge. Therefore, the onset driving voltage (V_{onset}) of the EC device is theoretically determined by the difference between the onset oxidation potential

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http://dx.doi.org/10.1016/j.solmat.2017.01.035
Received 13 December 2016; Received in revised form 19 January 2017; Accepted 22 January 2017
Available online 30 January 2017

(E^{ox}_{onset}) of the oxidizable material and the onset reduction potential (E^{red}_{onset}) of the reducible material of the device. These indicate that the reductive and oxidative reactions in the EC device strongly influence the EC properties such as coloration characteristics and switching stability. However, a measurement technique for estimating the electrode potentials of the anode and cathode, other than V_{onset}, during the application of driving voltage has not yet been established for the EC system as far as we know. In the past, driving voltages of EC devices have been determined based on the voltage that generates a sufficient color change and avoids the degradation during the coloration-bleaching switching cycles. To improve the coloration characteristics and switching stability of the EC device, it is necessary to measure the mean electrode potentials of the anode and cathode during the use of the device. In this study, the electrode potential of the anode and cathode were measured while applying a specified voltage to the EC device and transient changes in the electrode potential were reported and discussed.

2. Experimental

Dimethyl terephthalate (DMT; Tokyo Chemical Industry Co. Ltd., Japan) as the EC material (reductive material) and ferrocene (Fc; Tokyo Chemical) (oxidative material) as a counter material were used as received. Tetra-*N*-butylammonium perchlorate (TBAP; Kanto Chemical Co. Inc., Japan) as a supporting electrolyte was used without further purification. Dimethyl sulfoxide (DMSO; Sigma-Aldrich Co., USA) was used as a solvent after removing water with molecular sieves.

The liquid electrolyte was prepared by dissolving 50 mM TBAP in DMSO. The EC solutions for the 2-electrode cyclic voltammogram (CV) and electrode potential measurements were prepared by dissolving DMT and Fc in the liquid electrolyte in combinations of [DMT:Fc] =[25 mM:25 mM], [25 mM:5 mM] and [5 mM:25 mM]. The CV and electrode potentials were recorded on a potentiostat/galvanostat (ALS440A, ALS660A and ALS2323, CH Instruments, Inc., USA) equipped with a DOS/V computer. The scan rate was 50 mV/s. Absorption spectra were recorded in situ by using a diode array detection system (USB2000, Ocean Optics Co., USA) during the potential sweep. The 3-electrode cell was equipped with two Pt wires as a working electrode and a counter electrode and a Ag/Ag^+ electrode as a reference electrode. All measurements were conducted at the ambient laboratory temperature (20–25 °C). The electrode potential measurement was performed by combining three potentiostats (Fig. 1). This measurement requires a voltage source for applying a voltage between the working electrode and the counter electrode as the 2-electrode device, and a potentiometer for measuring the potential of the anode or cathode versus the reference electrode. In this study, the potentiostat/galvanostat (ALS440A) was used as the voltage source, and two potentiostats/galvanostats (ALS2323 and ALS660A) were used as the potentiometer. The working electrode terminal of ALS440A was connected to the ITO working electrode, and the counter and reference electrode terminals were connected to the ITO counter electrode for applying the voltage in the 2-electrode device. This device is considered as a 2-electrode EC device with a long inter-electrode distance of 10 mm. The working electrode terminal of ALS660A (CH Instruments) was connected to the ITO anode, and the reference electrode terminal was connected to the Ag/Ag^+ reference electrode for measuring the electrode potential of the ITO anode. The working electrode terminal of ALS2323 was also connected to the ITO cathode, and the reference electrode terminal was connected to the Ag/Ag^+ reference electrode for measuring the electrode potential of the ITO cathode. The electrode potentials of the anode and the cathode could be obtained by measuring the electrode potentials of each electrode versus Ag/Ag^+ reference electrode while applying a specified voltage to the anode and cathode as 2-electrode device. The absorption change and CV and electrode potential change of the anode and the cathode could be acquired simultaneously.

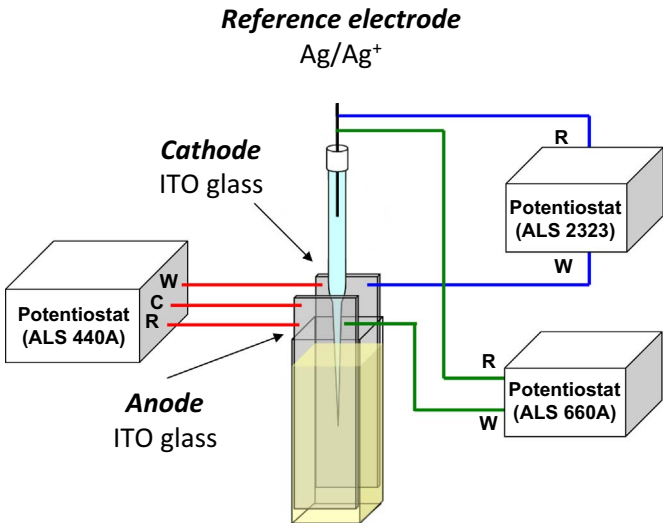

Fig. 1. Diagram of the experimental setup for electrode potential measurement in 2-electrode EC device.

3. Results and discussion

The CV of the [DMT:Fc]=[25:25] solution measured in the 3-electrode cell is shown in Fig. 2. The E^{red}_{onset} of DMT and the E^{ox}_{onset} of Fc were −1.95 V and −0.10 V (vs. Ag/Ag^+), respectively. Therefore, the V_{onset} of the DMT-Fc device is estimated to be 1.85 V.

Fig. 3 shows the absorption changes at 530 nm (a) and current responses of the DMT-Fc 2-electrode devices (b) with different concentrations of DMT and Fc. When a driving voltage is applied to the EC devices, current responses and absorbance of the devices increased with increasing redox current. As a result, the color of the 2-electrode EC device changed to magenta, as reported in our previous works [29]. As expected, V_{onset} of the DMT-Fc device was found to be almost the same as 1.85 V. In the case of the [DMT:Fc]=[25:5] and [25:25] solutions, although the amount of DMT was the same, the current response and absorption change of the [25:5] solution (red-dashed line) were smaller than those of the [25:25] solution (black solid line). The experiment with the [5:25] solution, which contained a smaller amount of DMT, had almost the same amount of current flow as with the [25:5] solution. From the result of 3-electrode cell, it was difficult to explain the electrochemical behavior of the 2-electrode EC device shown in Fig. 3(a) and (b). Therefore, the reactions occurring in the 2-electrode EC device were observed *in situ* by measuring the electrode potential of the anode and the cathode (Fig. 3(c)). The changes in the

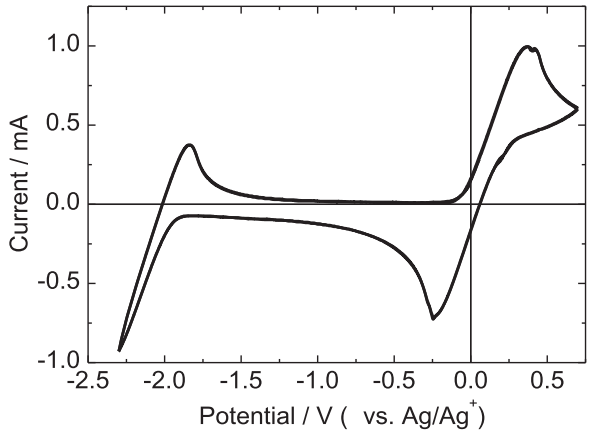

Fig. 2. Cyclic voltammogram of DMT (left) and Fc (right) in DMSO electrolyte. (Scan rate=50 mV/s).