

Fullerene coated indium tin oxide counter electrode of Prussian blue electrode for enhanced electrochromic properties

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ARTICLE INFO

Article history:

Received 19 August 2014

Received in revised form

2 March 2015

Accepted 9 March 2015

Available online 30 March 2015

Keywords:

Electrochromic device

Fullerene

Thermal evaporation

Ion storage layer

Prussian blue

ABSTRACT

Fullerene coated ITO electrodes were prepared by a vacuum thermal evaporation system where fullerene (C_{60}) powders were used as a deposition source. The fullerene coated electrodes act as an ion storage layer for electrochromic devices (ECDs). The ECDs are comprised of Prussian blue (PB) electrodes as the EC electrode, fullerene coated ITO electrodes as the counter electrode, and an electrolyte containing $LiClO_4$ salt. By employing fullerene coated ITO electrodes, the lower transmittance in the colored state (T_c) was achieved because of the lower transmittance of fullerene coated ITO. It led to an increase in the change in optical density (ΔOD) according to the increase in the thickness of the fullerene films. Also, the charge density per electrode area (Q_d) of the ECDs increased with the increase in the thickness of the fullerene films. This result indicates that the amounts of lithium ions and PB molecules, which are used for the EC phenomenon, were increased. As a result, EC properties such as the ΔOD and response time were enhanced by employing fullerene coated ITO electrodes because fullerene films provided the ion storage layer as the counter electrode of the PB electrode.

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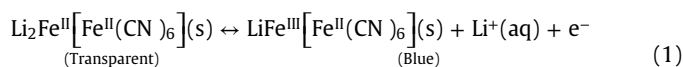
1. Introduction

The smart window is an attractive technological device for reducing energy consumption and increasing energy efficiency in office buildings [1]. Those benefits are possible by controlling the transmission of energy through the smart window by changing its color. This remarkable phenomenon is called electrochromism [2]. It is caused by electrochemical redox reactions on electrochromic (EC) materials [3]. That is, electrochromism is based on the electrochemical intercalation and extraction of cations, such as H^+ and Li^+ , in EC materials, in a manner similar to the reaction mechanism of conventional lithium secondary batteries when charging and discharging [3]. Given this characteristic, electrochromism can be applied to a smart window by fabricating an electrode that includes EC materials into a battery-like device, called an electrochromic device (ECD) [4,5]. Due to its unique optical switching properties, ECDs can also be applied to other applications such as rear-view mirrors in cars [4,6], sunglasses [7], and electrochromic displays [4,8].

The ECD consists of an EC electrode, an ion storage electrode (which can be another EC electrode), and an electrolyte containing cations [4,9]. To apply the ECD to a transparent window, the EC and

ion storage materials should be formed on transparent conducting substrates such as indium tin oxide (ITO)/glass substrates or ITO/plastic substrates [4]. By applying a voltage to the transparent conducting layer in the EC and ion storage electrodes, cations are transferred between both electrodes through the electrolyte, and the EC phenomenon occurs [3].

Various EC materials have been investigated over the years. Specifically, EC materials can be classified into two types depending on whether their coloration mechanism is cathodic or anodic [6,10,11]. For example, $Fe_4[Fe(CN)_6]_3$ (Prussian blue, PB) [4,8,12] and nickel oxide (NiO_x) [13–15] become colored when oxidized, while tungsten oxide (WO_3) [1,4–6,9–11,16], poly(3,4-ethylenedioxythiophene) (PEDOT) [4,17], and polyaniline (PANI) [11,18] become colored when reduced. In particular, PB is bleached and colored as shown in Eq. (1) [4].



PB has a zeolite-like structure, and therefore it shows high electrochemical stability [19]. In addition, PB electrodes can be easily fabricated by typical electroplating methods [8,12].

The ECD can also include an additional EC electrode as the counter electrode to the first EC electrode [4,9–11]. This counter electrode acts not only as an EC electrode but also provides an ion storage layer in the ECD. The ECD with the ion storage layer exhibits

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better EC properties since cations can be placed more stably in both electrodes.

In this work, fullerene (C_{60}) coated ITO electrodes were fabricated by a vacuum thermal evaporation process and employed as the counter electrode of a PB electrode in ECDs. According to previous research, alkali ions such as lithium ions can be accommodated in the fullerene lattice under an applied electric field [20,21]. Moreover, the color of fullerene films can be converted to dark brown when alkali ions intercalate into the films [20–24]. Therefore, fullerene films can act as an additional EC electrode as well as the ion storage layer. The color of fullerene films is altered according to the following equation [23,24]:



In this study, fullerene films were employed as an ion storage layer and their effect on EC properties was investigated by switching the color of ECDs between bleached and colored states. To be specific, the thickness dependence of fullerene films was studied in detail. The thickness of the fullerene films was limited to under 34 nm, since such fullerene films in their bleached state are light brown-tinted [23,24]. As mentioned above, the bleached color of the ECD has to be as transparent as possible to be practical in applications to transparent windows [25]. Therefore, thicker fullerene films are inappropriate for the ECD.

2. Experimental methods

2.1. Fabrication of electrochromic devices

Prussian blue (PB) electrochromic (EC) electrodes were fabricated by a conventional electroplating method as follows [8,12]. Firstly, a plating solution of PB was prepared, consisting of 0.01 M lithium chloride ($LiCl(aq)$), 0.01 M iron (III) chloride ($FeCl_3(aq)$), and 0.01 M potassium ferricyanide (III) ($K_3[Fe(CN)_6](aq)$). After stirring the solution for 30 min, the solution was left unmolested for 12 h. In order to exclude impurities in the solution, the supernatant solution was only used for the electroplating of PB. ITO glass substrates and a Pt plate were used as the working electrode and the counter electrode, respectively. The electroplating was carried out galvanostatically for 5 min at room temperature by applying a cathodic current density of $15 \mu A/cm^2$. During the electroplating, the voltage between the two electrodes was approximately 0.4 V.

Fullerene (C_{60}) films were deposited by a vacuum thermal evaporation process on 180 nm thick indium tin oxide (ITO)-coated glass substrates ($5 \Omega/sq$) as follows [26,27]: ITO glass substrates were cleaned by acetone, ethanol, and deionized water, in sequence, and then put into the vacuum chamber. 0.1 g of commercialized fullerene (C_{60}) powders (99.9%, Sigma-Aldrich, Co.) were put on a tungsten boat in the vacuum chamber. The distance between the substrate and the exhaust nozzle of the boat was fixed at 5 cm. Base pressure was under 1×10^{-4} Torr, and then Argon gas of 30 sccm was fed into the chamber. During the deposition, the pressure in the chamber was fixed at 2.5×10^{-2} Torr, and a constant current of 20 mA was applied to the boat. The deposition was carried out for 30–90 s to coat fullerene films of varying thickness onto the substrates. In order to eliminate moisture, both fullerene coated ITO electrodes and PB electrodes were dried in a vacuum oven at $80^\circ C$ for 4 h.

ECDs were assembled in a dry room with PB electrodes as working electrodes, fullerene coated ITO electrodes as counter electrodes, and an electrolyte [12]. The electrolyte was propylene carbonate (PC)/ethylene carbonate (EC) (1:1 wt%) solution containing 0.01 M $LiClO_4$. For the curing of the electrolyte, poly(ethylene glycol) dimethacrylate (PEGDMA), and 2,2-dichloroacetophenone were added into the electrolyte as hardening agents. Double-sided

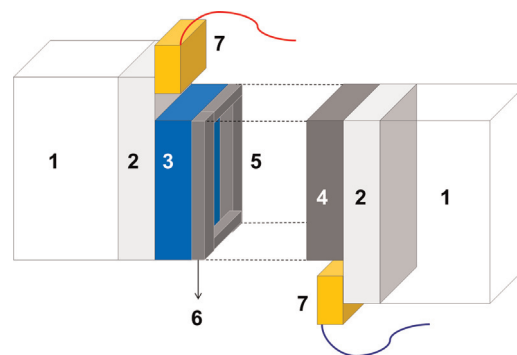


Fig. 1. Fabrication schemes of electrochromic devices employing a fullerene coated ITO electrode. (1: glass substrate, 2: ITO layer, 3: Prussian blue films, 4: fullerene films, 5: PC:EC (1:1 wt%) electrolyte containing 0.01 M $LiClO_4$, 6: spacer, and 7: Cu tape.)

tape with high adhesion (3 M) was used as a spacer between the two electrodes. The assembled ECDs were cured by ultraviolet light for 3 min with UV power of 24 W and UV range of 355–420 nm. Fig. 1 shows the fabrication schemes of the ECDs in this work.

2.2. Characterization and evaluation of electrochromic properties

The microstructure and thickness of the fullerene films were examined by scanning electron microscopy (SEM, NOVA NANO SEM200, FEI Co.) with an accelerating voltage of 10 kV. The surface morphology of each electrode was studied by atomic force microscopy (AFM, XE-100, Park Systems Co.) scans in non-contact mode. In addition, the chemical characteristics of the fullerene films were examined by Raman spectroscopy (Nicolet Almega with 514 nm Ar Laser) and X-ray photoelectron spectroscopy (XPS–VG Scientific). The transmittance of fullerene coated ITO electrodes was analyzed over a wide-range of wavelengths (200–800 nm) by UV/vis/NIR Spectrophotometer (Varian Model Cary 5000).

EC properties of the ECDs were examined by Autolab PGSTAT30 Potentiostat/Galvanostat [12,14]. Electrochemical potential cycling tests were performed with PB electrodes as working electrodes, and fullerene coated ITO electrodes as counter electrodes. These tests were carried out with an auto current of 1 mA by switching a pulse potential wave between 3.7 V and -3.7 V with a duration time of 60 s up to 5 cycles. Simultaneously, the in-situ transmittance of the ECDs was measured by He–Ne laser ($\lambda=633$ nm), and the charge density per electrode area (Q_d) was estimated. Furthermore, in order to investigate the difference in interfacial properties of fullerene coated ITO electrodes, electrochemical impedance spectroscopy (EIS) measurements were performed on BioLogic VMP3 Multi Potentiostat/Galvanostat with EIS by applying a 5 mV ac signal over the frequency range of $0.01-5 \times 10^5$ Hz [28,29]. The pristine ITO electrode and fullerene coated ITO electrodes were used as a working electrode, and lithium plates were employed as counter and reference electrodes for the measurements. Also, PC/EC/dimethyl carbonate (DMC) (1:1:1 vol%) solution containing 1 M $LiClO_4$ salt (purchased from PANAX ETEC Co., Ltd.) was used for an electrolyte.

3. Results and discussion

3.1. Characterization of fullerene coated ITO electrodes

Plan-view and cross-sectional SEM images of the pristine ITO electrode and fullerene coated ITO electrodes are shown in Fig. 2. As shown in Fig. 2, the ITO substrates were fully covered by the deposited fullerene powders, and the shape of the fullerene grains

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