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Effect of oxygen plasma treatment on the electrochemical properties of Prussian blue electrodes for transparent electrochromic devices

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ABSTRACT

The effect of oxygen plasma on the electrochromic characteristics of electrochromic devices that utilize Prussian blue electrodes is investigated. Prussian blue working electrodes were electrodeposited on fluorine-doped tin oxide films that were grown on glass substrates by electron cyclotron resonance-metal organic chemical vapor deposition. An indium tin oxide coated glass was employed as the counter electrode that served as an ion storage layer. The goal of the oxygen plasma treatment is to increase the oxygen functional groups on the surface of the Prussian blue electrode leading to the enhancement of the oxidation reaction and eventually the increase in coloration efficiency. Improvement of electrochromic properties, such as optical density and response time, was also observed following plasma treatment.

1. Introduction

Electrochromic (EC) materials change color reversibly during the electrochemical process of intercalation and deintercalation [1,2]. The phenomenon, called electrochromism, is the reversible reaction of transmittance and reflectance and is related to electrochemical redox processes [3–5]. Electrochromic device (ECD) using electrochromic materials has excellent potential applicability for smart windows, smart cards, and displays of cellular phones, due to low power consumption, excellent durability, and safety [6,7]. The conventional ECD comprises a glass substrate, transparent electrode layer, counter-electrode layer, electrolyte, EC layer, and transparent electrode layer, which are sequentially formed on a glass substrate [8,9]. Prussian blue (PB) could provide ferrous ions that contribute to the catalytic reaction in EC materials and has attracted much interest by many researchers [10,11]. Also, most PB is inexpensive and can be very easily electrodeposited on conducting and semiconducting substrate. Iron(II,III) hexacyanoferrate(II,III) ($Fe^{III}_4[Fe^{II}(CN)_6]_3$) as a PB material is a metal complex with CN and Fe ion, and in accordance with the difference of atomic value of the Fe ion. Its color changes, so that it is blue in the oxidation state and it is transparent in the reduction state [12].

In the present study, oxygen plasma treatment was carried out on the surface of PB films electrodeposited on fluorine-doped tin oxide (FTO) coated glass. It is important that oxygen plasma treatment increases the oxygen functional group on the surface of the PB electrode, which leads to enhancement of the oxidation reaction, and eventually increases in other performances, such as coloration efficiency, transmittance contrast ratio.

2. Experimental details

FTO films were deposited on glass substrates using the electron cyclotron resonance-metal organic chemical vapor deposition system. The base pressure was maintained below 1.3×10^{-2} Pa and then the chamber was filled with pure argon gas to a working pressure of 12×10^{-1} Pa. Argon was used as a carrier gas for tetramethyltin. Oxygen, sulfur hexafluoride, and hydrogen gas were fed to the chemical vapor deposition reactor to control the properties of films. The distance between organic source and substrate was 90 mm. Depositions were performed with a constant microwave power of 900 W and a magnetic current of 165 A for 30 min at room temperature. PB films were electrodeposited on the pre-grown FTO coated glass at 0.2 mA from a 0.01 M solution of iron(III) chloride ($FeCl_3$), potassium ferricyanide(III) ($K_3[Fe(CN)_6]$), and $LiCl_4$ in deionized water. The counter electrode was a platinum sheet. After the electrodeposition, oxygen plasma treatment was carried out on the PB/FTO thin film in the same chamber. The plasma was generated by applying a microwave power of 600 W, a magnetic current of 165 A for 90 s at room temperature under a working pressure of 33×10^{-1} Pa, and flowing gases of argon of 10 sccm and oxygen of 5 sccm. For preparation of the ECD, the indium tin oxide (ITO) coated glass was placed on the plasma treated PB/FTO film coated glass, and then the two glasses were clamped together with sealant. The electrolyte solution contained 0.01 M $LiClO_4$ dissolved in a solvent mixture of propylene carbonate and ethylene carbonate (1:1 wt.%). In order to solidify the electrolyte, poly(ethylene glycol) dimethacrylate (PEGDMA), and

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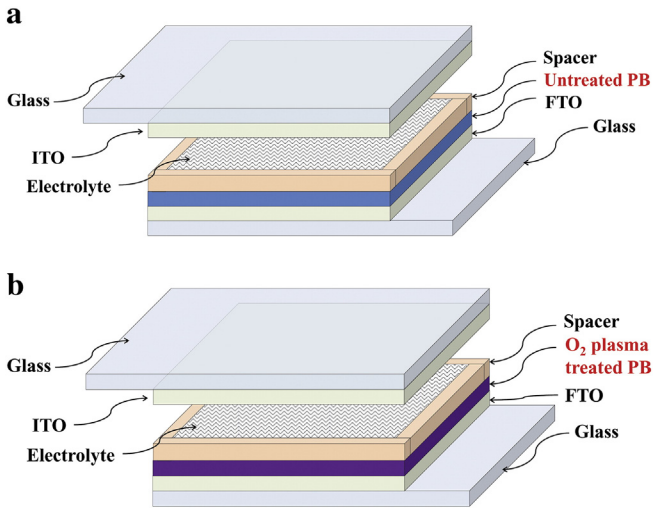

Fig. 1. Schematic of fabrication of an ECD with different EC films of the oxygen plasma (a) untreated and (b) treated PB films.

2,2-dichloroacetophenone were used as a curing agent. UV light was exposed on the sample for 3 min to harden the device. Fig. 1 shows multi-layered structures of oxygen plasma (a) untreated and (b) treated PB/FTO of electrochromic materials as working electrodes for ECD. The component of ECD was similar to those of battery cells and corresponds to an EC layer (positive electrode)/electrolyte (Li^+, H^+)/counter-electrode layer (negative electrode) [13].

In the structural information of the films, the morphology of the films was analyzed by scanning electron microscopy (SEM, NOVA NANO SEM200, FEI Co.) with an accelerating voltage of 10 kV. X-ray photoelectron spectroscopy (XPS, PHI 5000 VersaProbe (UIvac-PHI)) for chemical bond and atomic composition analysis with a background pressure of 6.7×10^{-8} Pa and source of monochromator Al Kα (1486.6 eV) anode (25 W, 15 kV) and calibration of C1s peak (284.6 eV), and the accelerated voltage of 15 kV carried out in the Ar atmosphere [14,15]. To perform elemental components and quantitative analysis, elemental analyzer (EA, Flash EA 1112 series, CE Instruments) measurement was carried out. All electrochemical potential cycling tests were performed using an Autolab PGSTAT 30 Potentiostat/Galvanostat. EC properties were evaluated by switching a pulse potential wave between −3.7 and 3.7 eV, with a duration time of 60 s up to 9 cycles. The transmittance was measured in situ during all experiments using a He–Ne laser (λ = 633 nm). Cyclic voltammetry (CV) was performed in an electrochemical cell between −1.5 and 1.5 V, wherein a PB film deposited on FTO coated glass substrate acted as a working electrode.

3. Results and discussion

Fig. 2 shows the surface morphologies of oxygen plasma untreated and treated PB/FTO electrodes as characterized by SEM. The surface of the oxygen plasma treated PB/FTO film in Fig. 2(c) and (d) was smoother than that of the untreated PB/FTO film in Fig. 2(a) and (b), while the surface grains of all samples become indistinct. The thicknesses of PB and FTO of all films were about 0.1 and 1 μm, respectively.

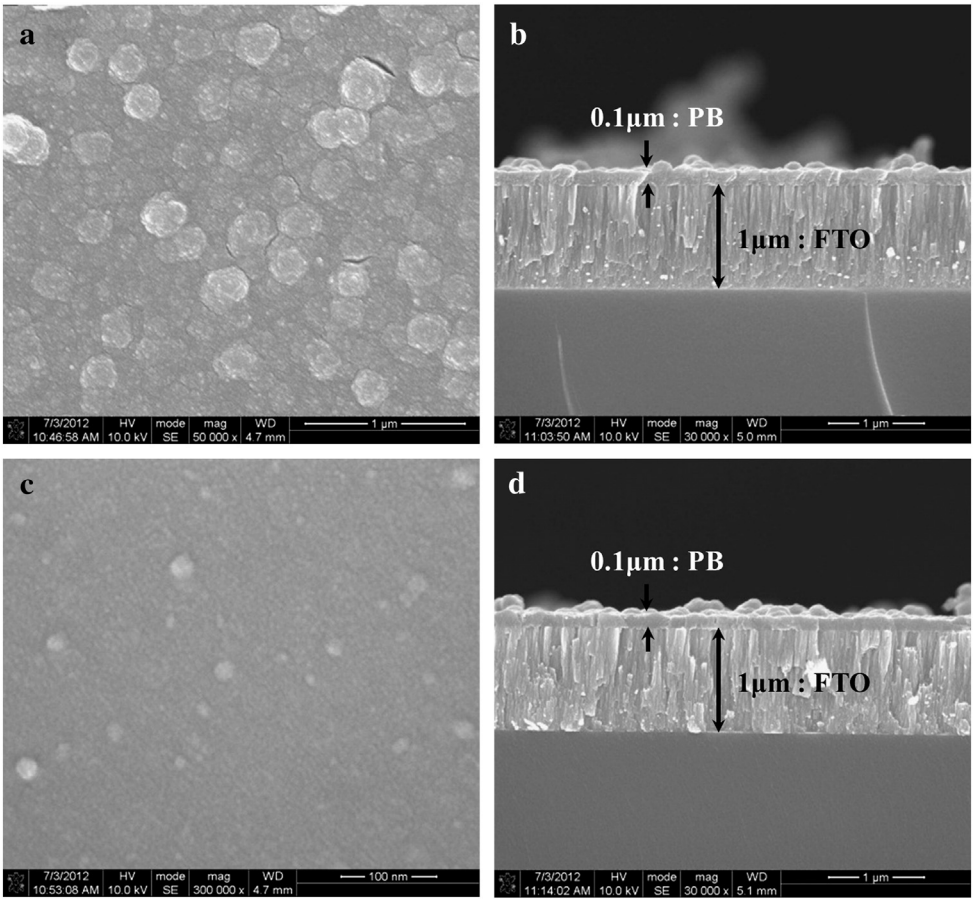

Fig. 2. SEM images of (a) & (c) top views, and (b) & (d) cross sectional views of (above) oxygen plasma untreated and (below) treated PB/FTO coated glass, respectively.

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