



Investigation of dry-deposited ion storage layers using various oxide particles to enhance electrochromic performance



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ABSTRACT

Various ion storage layers were fabricated on ITO-glass substrates by a dry deposition process to study their effects in electrochromic devices. Dense nickel oxide (NiO) film was formed using micro-sized NiO particles, a porous film was formed using nano-sized NiO particles, and a porous antimony tin oxide (ATO) film was formed using nano-sized ATO particles. Electrochemical analyses revealed that the nano-porous NiO layer had a high charge capacity with a low charge transfer resistance. Moreover, an electrochromic device using a NiO film with nano-sized pores had an optical transmittance difference of 42% and a stable cyclic transmittance for 1 h at a wavelength of 630 nm. We assessed the effects of the different ion storage layers by evaluating the electrochromic device in terms of the following important properties: 1) high charge capacity, 2) low charge transfer resistance at the interface between film and electrolyte, and 3) high diffusion rate from film to electrolyte. Based on these criteria, we found that the ion storage layer formed with nano-sized NiO particles best satisfied these conditions. Finally, we confirmed that stable and high electrochromic performance can be achieved through improving these properties in ion storage layers.

1. Introduction

Electrochromic materials can change in terms of optical transmittance, reflectance, and adsorption properties upon application of an external voltage or current within the device. One such electrochromic device is a ‘smart window,’ which changes its properties via electrochromism [1–3]. In the 1980s, researchers developed another type of smart window, called ‘energy-efficient fenestration’ [4,5]. These concepts have also been applied to develop rear-view mirrors [6–8]. Additionally, eyewear, such as sunglasses and helmet visors, have used electrochromic functions instead of photochromic functions [9]. As a result, problems associated with photochromic devices, such as difficulty of use indoors and long switching times at low temperatures, have been solved.

An electrochromic device consists of an electrochromic film, an electrolyte, and an ion storage layer or a counter electrode between two transparent conductive electrodes (TCE) [10–12]. The electrolyte is an ionic conductor that is placed between the two electrodes, such as an electrochromic film and an ion storage layer. Ions in the electrolyte are moved by generating an electrical field between two electrodes, and

become inserted or extracted into the electrochromic film and ion storage layer as a matrix in which the electrochromism phenomenon can occur. Electrochromic films typically have two different types of electrochromic oxide materials. When an ion is inserted, cathodic electrochromic materials become colored, and anodic electrochromic materials become colored when extracted. Tungsten oxide [13–16] is the most widely used electrochromic material, along with molybdenum oxide [17], niobium oxide [18], and titanium oxide [19].

In addition to metal oxides, researchers have studied electrochromic devices using conductive polymers and organic electrochromic materials, such as polyaniline [20] and Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) [21]. Organic electrochromic materials generally have a high switching time with high transmittance under low-voltage conditions, but polymer-based electrochromic films typically have poor adhesion on the substrate. To improve adhesion, a metal oxide support may be formed with the polymer as a hybrid electrochromic film, such as WO₃-PEDOT:PSS [22], Prussian blue-PEDOT:PSS [23], TiO₂-PEDOT [24], and TiO₂-PEDOT:PSS [25]. Among those hybrid composite film, TiO₂-PEDOT:PSS has shown very stable performance for 500 cycles [25]. Based on this finding, we have used

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TiO₂-PEDOT:PSS hybrid composite film as the electrochromic layer in this study.

As electrons transfer from the TCE to the electrochromic film, small cations in the electrolyte become inserted into this film because of the attractive force of the electrons. At this time, anions in the electrolyte are inserted into the ion storage layer, which is located on the opposite side. This phenomenon is referred to as the ion charge balance, and the color of the electrochromic film changes concurrently [26]. Generally, the ion storage layer that is located on the counter electrode is used as a charge storage film and this film is in a reduced (oxidized) state as the electrochromic film is oxidized (reduced). Thus, the ion storage layer is important for three reasons: 1) when the ion storage layer has the same cathodic or anodic coloration as the electrochromic film, minimal color change will be seen, 2) it should have a high charge capacity, and 3) the charge transfer resistance of the film should be as low as possible to improve the switching speed of the electrochromic device.

Many researchers have fabricated and evaluated the characteristic of electrochromic devices using bare ITO-glass as a counter electrode with no ion storage layer. Bare ITO-glass with no ion storage material film usually has a relatively high transmittance, but it does not aid the performance of the electrochromic device because of its poor charge storage properties [27]. Therefore, the ion storage layer is an important component to achieve improved electrochromic performance.

Generally, the ion storage layer is fabricated using stable metal oxides, such as CeO₂ [28], V₂O₅ [29,30], nickel oxide [31], and antimony-doped tin oxide (ATO) [32]. Among these materials, nickel oxide is generally inexpensive and widely used, and has a high capacity of 781 mAh/g [33,34]. It has been used in solar cells [35], supercapacitors [36], lithium-ion batteries (LIBs) [34], and in electrochromic materials because of its high energy density. ATO in the form of thin film, is a conductive material with high optical transparency, and ATO thin films have been studied as an energy storage material, such as in LIBs, due to its stable and inexpensive nature [37,38].

In this study, ion storage layers were fabricated by a dry deposition method. In particular, various sized nickel oxide (NiO) powders and ATO powder were used to control the microstructure of ion storage layers. Additionally, electrochromic devices using various ion storage layers were evaluated by observing optical properties with cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) with a three-electrode system.

In summary, a TiO₂/PEDOT:PSS hybrid composite as a working electrode in the electrochromic device was used as a driver under low-voltage conditions. The microstructure of the ion storage layer was controlled by a dry deposition method using micro-/nano-sized nickel oxide powders. Additionally, a thin ion storage film was fabricated using nano-sized ATO powder. Three types of ion storage layer, along with bare ITO-glass, were compared through electrochemical analyses so that different particle size of the same powder as well as different materials in similar particle size, can be evaluated to choose the optimum ion storage layer for the fabricated electrochromic device. Therefore, electrochromic devices using each ion storage layer were evaluated to explore how the microstructure of the ion storage layer influenced electrochromic performance.

2. Experimental details

2.1. Fabrication of electrochromic film

Commercially available FTO-glass (Pilkington) with an area of 2.0 × 2.5 cm² was cleaned ultrasonically in 99.9% ethanol (Daejung) for 15 min. Next, the FTO-glass substrate was dipped in 50 mL deionized (DI) water with 0.22 mL TiCl₄ solution (titanium (IV) chloride, Junsei) and placed in an oven for 30 min at 70 °C. Then, the sample was rinsed twice in ethanol solution and DI water.

TiO₂ (Nanoamor Co.) particles with an average diameter of 15 nm were deposited on the treated substrate using a dry deposition method known as the nano particle deposition system (NPDS), which is an aerosol dry deposition technique [39–42]. TiO₂ powder was deposited at a scanning speed of 700 μm/s onto the FTO glass through a nozzle with its size of 10 × 3 mm². The stand-off distance (SoD), the distance between the substrate and the end of the nozzle, was fixed at 3 mm, while the bed flow rate was 27.5 L/min at 3 bar. Finally, a TiO₂ thin film with an area of 10 × 10 mm² was obtained by removing residual particles using blown air. A PEDOT:PSS dispersion (Sigma Aldrich) with a TiO₂ film for TiO₂/PEDOT:PSS fabrication was prepared by adsorbing PEDOT:PSS solution onto the pre-deposited TiO₂ film for 30 min. Residual PEDOT:PSS dispersion was removed from the nano-porous film by spin coating the PEDOT:PSS adsorbed TiO₂ film (1500 rpm, 60 s). After the composite film was fabricated, it was annealed at 130 °C for 3 h in an argon atmosphere to increase adhesion to the substrate and to dry any residual solvent.

2.2. Fabrication of ion storage layers

Three kinds of ion storage layer, micro-sized NiO (1–2 μm, TASC0), nano-sized NiO (20 nm, Alfa Aesar), and nano-sized ATO (30 nm, Nanoshell) particles, were deposited onto ITO-glass using NPDS. Previous studies have shown that the deposited microstructure changes with varying size of particles on the substrate due to the deposition mechanism [39–42]. Thus, the microstructure was controlled using micro-/nano-sized NiO particle in the NPDS process. Micro- and nano-sized NiO powders were deposited at a scanning speed of 40–60 μm/s. Moreover, nano-sized ATO powder was deposited to compare the electrochemical differences between ATO and NiO. The powder was deposited through a nozzle at a scanning speed of 800 μm/s (size: 10 × 3 mm², aerosol flow rate: 27.5 L/min, injection pressure: 3 bar, SoD: 3–4 mm). Finally, the three ion storage layers were successfully deposited onto cleaned ITO-glass while keeping the thickness at ~ 400 nm with an area of 10 × 10 mm².

2.3. Evaluation of the thin films in electrochromic devices

The surface morphology and cross-sectional microstructure of the nanoporous TiO₂ film, composite film composed of PEDOT:PSS and TiO₂, and the various ion storage layers were characterized using field-emission scanning electron microscopy (FE-SEM; SU70, Hitachi, Tokyo, Japan). Electrochemical analyses, including cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS), were performed in a three-electrode system using Pt as the counter electrode, Ag/AgCl as the reference electrode, and various ion storage layers on ITO-glass with an area of 2.0 × 6.0 cm² as the working electrode using 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMIM-TFSI, Sigma Aldrich) as the ionic liquid electrolyte. The external potential was controlled using a potentiostat (Versa STAT4, Princeton, NJ, USA).

All ion storage layers evaluated in terms of electrochemical properties via CV were scanned at a rate of 10 mV/s from –1.5 V to +1.5 V for one cycle. EIS results of all films at DC potential of 1.0 V, with an amplitude of 10 mV, were measured in the range of frequencies between 100 kHz and 10 Hz. Finally, Surlyn (thickness: 300 μm), a thermal polymer adhesive, was used between the hybrid composite electrode and the various ion storage layers. EMIM-TFSI, the electrolyte, was injected into the electrochromic device through drilled holes, and the device was completed by sealing the holes. The optical transmittance spectra of all electrochromic devices were recorded over the range of –1.5 V to +1.5 V using a V-650 ultraviolet-visible (UV-vis) spectrophotometer (Jasco, Tokyo, Japan) with the potentiostat upon application of a voltage.

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