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Enhanced electrochromic performance of flexible $WFe_xO_yC_z$ films by O_2 gas addition using low temperature plasma polymerization

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ABSTRACT

An investigation was conducted into the prominent lithium electrochromic performance of flexible organo-tungsten-iron oxide ($WFe_xO_yC_z$) films deposited onto flexible (60 Ω/□ polyethylene terephthalate/indium tin oxide) substrates. The simple one-step low temperature (~23 °C) plasma polymerization method was used to inject the precursors tungsten hexacarbonyl [$W(CO)_6$] and biscyclopentadienyl iron [$Fe(C_5H_5)_2$] into the plasma chamber, whilst being mixed with O_2 gases at various gas flow rates. The plasma-polymerized $WFe_xO_yC_z$ films at a certain addition of oxygen gases achieved outstanding lithium electrochemical reversibility of Li^+ ion intercalation and de-intercalation proven by a potential sweep switching between −1 V and 1 V at a scan rate of 50 mV/s in a 1 M $LiClO_4$-propylene carbonate electrolyte. High values for optical transmittance modulation (ΔT) of up to 83.2%, optical density (ΔOD) of up to 1.08 and color efficiency (η) of up to 62.3 cm^2/C at a wavelength of 854.9 nm were obtained for the amorphous $WFe_xO_yC_z$ films synthesized by the addition of oxygen gases at a flow rate of 17 sccm. The results verified that the proper addition of oxygen gas provides a suitable routine to enhance the electrochromic properties of plasma-polymerized $WFe_xO_yC_z$ films.

1. Introduction

The climate conditions become more and more harshly towards hotter summers and colder winters, initiates the increases in energy consumption of air conditioning and peak energy needs [1]. The 20–40% of total energies in developed countries is consumed by both residential and commercial buildings [2]. Therefore, energy savings in buildings are crucial. Electrochromic (EC) glazings, so-called smart windows or switchable windows decrease 71% of energy consumption in buildings with switchable optical transmittances allow the thermal energy savings by reducing the thermal heat through the buildings windows [1]. The oxides of transition materials are the main materials with EC properties, used in EC smart windows. Tungsten oxide (WO_x) is the most widely reported transition metal oxide, utilized in EC smart windows and in other numerous applications, such as gas sensors, EC displays, EC sunroofs and EC mirrors [3]. EC WO_x film was altered from a bleached state (colorless) to a colored state (dark-blue) to produce tungsten bronze ($M_\alpha WO_x$) by intercalating both ions and electrons, in conjunction with the intercalation/de-intercalation reaction (1), and vice versa:

$$WO_x + \alpha M^+ + \alpha e^- \leftrightarrow M_\alpha WO_x \quad (1)$$

where M^+ denotes H^+, Li^+, Na^+ or K^+ ions.

The nanocomposites of the polymer matrix [polyaniline, poly(di *p*-phenyamino phenyl-naphthalalene tetracarboxylic diimide and poly(*p*-phenylenebenzodisthiazole)] and the nanoparticles ($MgFe_2O_4$, $ZnWO_4$, WO_3, graphite oxides) have been demonstrated to offer durability of EC performance in acidic electrolyte solutions [4–9]. However, EC tungsten oxide films in an acidic electrolyte solution (i.e., a protonic H^+ ion-containing electrolyte) possess poor chemical stability during electrochemical cycling due to the film's dissolution in the H_2SO_4 electrolyte solution [10]. WO_x thin films demonstrate cycling durability for Li^+ intercalation (coloration)/deintercalation (bleaching) in Li^+ ion-containing electrolyte [1 M $LiClO_4$-propylene carbonate (PC) solution] [11]. Some additives, such as Au crystals [12], TiO_x [13], MoO_x [14], TaO_x [15] thin films and carbon nanotubes [16], were added in WO_x films to enhance Li^+ EC performance. Iron oxides (FeO_x) have comparable properties to

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WO_x as their valence states can be easily changed with potential cycling by low electrical potentials [17]. This study attempted to co-synthesize the FeO_yC_z into tungsten oxide (WO_yC_z) films using a low temperature plasma polymerization method by injecting the precursors of tungsten carbonyl [$W(CO)_6$] and ferrocene [$Ta(C_5H_5)_2$] into the plasma chamber whilst mixing with O_2 gases at various flow rates to improve the Li^+ EC performance of the mixed tungsten/iron oxide ($WFe_xO_yC_z$) films. This study inspected how the O_2 gas flow rates affected the film properties and the EC performance of low temperature plasma-polymerized $WFe_xO_yC_z$ films.

Flexible EC devices produced on polymer substrates allowing EC technologies affordable and commercially capable on EC smart windows by reducing the costs whist fabricated by roll-to-roll processes [18], attached to existing windows as a layer and alternated for full replacement [19]. The advantages of PECVD over sputtering have been demonstrated by decreasing a cost in a factor of 3 lower for deposition of EC tungsten oxide films due to the potentially higher deposition rates [20]. The study investigates the deposition of $WFe_xO_yC_z$ films onto flexible PET/ITO substrates by a plasma polymerization method, i.e., a particular PECVD method. The EC performance of the flexible $WFe_xO_yC_z$ films is characterized by both the electrochemical and transmittance measurements. Field Emission Scanning Electron Microscopy (FESEM) was used to analyze the surface morphology and the thicknesses of the $WFe_xO_yC_z$ films. Raman Spectroscopy, X-ray Diffraction (XRD), and X-ray Photoelectron Spectroscopy (XPS) were utilized to evaluate how the films' properties influenced their Li^+ EC performance.

2. Experimental details

2.1. Synthesis of $WFe_xO_yC_z$ films

Fig. 1 shows the schematics of the low temperature plasma polymerization system using parallel plates type electrodes for deposition of $WFe_xO_yC_z$ films onto flexible PET/ITO substrates (60 Ω/square, 125 μm thick, 3 cm × 3 cm, Sheldahl) as the substrates are placed onto electrically grounded cathode electrode plate with a 30 cm diameter. The precursors, such as tungsten carbonyl [$W(CO)_6$, 99%, purchased from Acros Organics] and ferrocene [$Fe(C_5H_5)_2$, 99%, obtained from Acros Organics] powders, were individually set in sublimators, heated to 115 °C and 140 °C, respectively. 1 sccm of Ar gas (99.9% pure) was separately supplied to the tanks using a gas mass controller to carry the 3.2 sccm of $W(CO)_6$ vapor and 0.8 sccm of $Fe(C_5H_5)_2$ vapor (the gas line was heated to 140 °C) and precision metering needle valves, respectively, to the plasma chamber through the precursor injection tube. The flow rates of the vapors of the precursor $W(CO)_6$ and $[Fe(C_5H_5)_2$ were calibrated by feeding the precursor vapors into the plasma chamber carried by Ar gases and controlled by precision metering needle valves. The detailed settings are shown in Table 1. The experiment variations between the five different samples prepared under the same conditions were controlled to less than 10%.

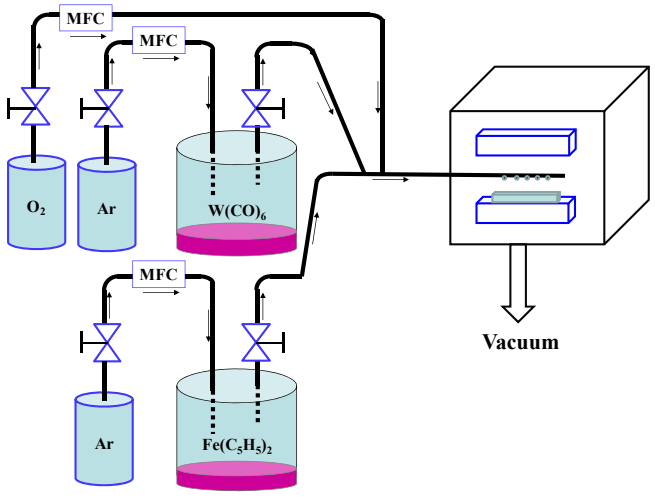

Fig. 1. Diagram of the plasma polymerization set-up for deposition of $WFe_xO_yC_z$ films onto PET/ITO substrates.

2.2. Thin film analysis

The FESEM images of the top surfaces and cross sections of the films were used to monitor the surface morphology and thickness of the $WFe_xO_yC_z$ films. The surface morphology of the films was determined by the grain boundary fractions (%) between the grains on the films' surfaces. The grain boundary fraction (%) of the sample was estimated by dividing the area of the grain boundary between the grains by the total area of the FESEM images using Image-Pro Plus-Version 4.5.0.29 software (purchased from Media Cybermetics, Inc). The variation in grain boundary fraction (%) between the five different samples produced with the same conditions was controlled to less than 5%.

The deposition rates of the plasma-polymerized $WFe_xO_yC_z$ films were determined by dividing the films' thicknesses (from the FESEM image of the cross section) by the deposition duration. A HITACHI S-4800, with an electron gun emitting a cold field, an electrical voltage of 1 kV, and an electrical current of 5 μA, was used to gather the FESEM images. The data over a scan area of 500 × 500 nm^2 with 1024 × 840 pixels were recorded. The variations in thickness and deposition rate between the samples were less than 5%.

A Renishaw 1,000B Raman spectrometer with a × 50 magnitude microscope and an InGaN semiconductor type laser at a wavelength of 532 nm was used to collect the Raman spectra of the specimen. Data were taken using a laser beam at a focused spot of 5 × 5 μm^2. To prevent any localized heating of the specimen, a low power of 14 mV was chosen. Raman shifts were examined at the wave numbers of 250–2000 cm^{-1}.

The X-ray diffraction patterns of the specimen were detected by a Bruker/D8 Discover diffractometer with monochromated Cu Kα radiation. A wavelength of 0.154 nm, a voltage of 40 kV, a current of 35 mA, a scan rate of 1°/min, and the 2θ ranging from 10° to 80° were used to analyze the samples.

The compositions of the specimen were detected by a JEOL JAMP-9500F Probe and an XPS system with the settings of an Al Kα X-ray source at 2000 eV, a pass energy at 58.7 eV, and a charge compensation at 0.4 mA. Prior to analysis, the samples were pre-sputtered the top layer of a 5 nm thick film to remove the surface carbon contaminants. XPS data of the samples were characterized

Table 1
Settings for deposition of $WFe_xO_yC_z$ films onto PET/ITO substrates by plasma polymerization at various O_2 flow rates.

Parameters	Settings				
Power (watts)	200				
Frequency (MHz)	13.56				
Precursor injection angle θ (degree)	45				
Substrate distance (cm)	1.5				
Chamber pressure (mtorr)	120				
Ar flow rate (sccm)	2				
Fe flow rate f_{Fe} (sccm)	0.8				
W flow rate f_w (sccm)	3.2				
O_2 flow rate f_{O_2} (sccm)	8	11	14	17	20
Exposed duration (min)	9	9	9	10	10