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Enhanced lithium electrochromic performance of flexible tungsten oxide films by tantalum addition with an atmospheric pressure plasma jet

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ABSTRACT

Enhanced lithium electrochromic performance of flexible tungsten oxide films by the addition of tantalum with an atmospheric pressure plasma jet in a rapid synthesis onto flexible 40 Ω/□ polyethylene terephthalate/indium tin oxide substrates was investigated. The flexible organic–inorganic hybrid composites WO_yC_z, $WTa_xO_yC_z$ and TaO_yC_z films were synthesized by injecting the precursors tungsten carbonyl [$W(CO)_6$] and/or tantalum ethoxide [$Ta(OC_2H_5)$] into an air plasma jet under an atmospheric pressure and the ambient temperature (~23 °C). The addition of tantalum into tungsten oxide films improves the optical modulation (ΔT) from 62.3% to 74.8% (at a wavelength of 800 nm, even after 200 cycles of reversible Li^+ ion intercalation/de-intercalation in a 1 M $LiClO_4$-propylene carbonate electrolyte), reduces the coloration time from 13 s to 8 s, and increases the diffusion coefficient of the lithium ion from 0.4×10^{-10} cm^2/s to 1.2×10^{-10} cm^2/s.

1. Introduction

Electrochromic (EC) materials have been reported in numerous organic and inorganic materials (mainly transition metal oxides) for numerous applications in EC related devices such as photovoltaic-powered EC-smart windows, photo-EC devices, gas sensors, EC displays, EC sunroofs and EC mirrors [1]. Regarding inorganic EC materials, tungsten oxide (WO_x) is the most widely studied transition metal oxide [2]. EC WO_x film is reversed 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 according to the intercalation/de-intercalation reaction (1):

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

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

Nevertheless, EC tungsten oxide films have poor chemical stability in an acidic electrolyte solution (i.e., a protonic H^+ ion-containing electrolyte) during electrochemical cycling due to the film's dissolution in the H_2SO_4 electrolyte solution [3]. Therefore, the non-protonic lithium-containing electrolytes are generally used to assure the reversible Li^+ intercalation into and deintercalation out from tungsten oxide films. To enhance the lithium electrochromic properties of WO_x, several dopants such as Au crystals [4], TiO_x [5], MoO_x [6], FeO_x [7] and carbon nanotubes [8] have been added into WO_x films. Tantalum oxide (TaO_x) thin films have received attention as suitable proton and Li ion conductors due to their high conductivity [9]. Mixed tungsten/tantalum oxide (WTa_xO_y) films have previously been deposited onto rigid glass/indium tin oxide (ITO) substrates by means of co-sputtering [10] or pulsed laser [11] for enhancing proton intercalation reversibility. This study attempts to enhance the tungsten oxide films' lithium electrochromic properties by doping with tantalum under an atmospheric pressure plasma jet (APPJ).

Cracks sometimes occur in inorganic (WTa_xO_y) thin films during flex tests owing to the films' poor adhesion with the flexible polyethylene terephthalate (PET)/ITO substrates or their own fragile in nature. In this study, a rapid deposition of flexible organic–inorganic hybrid composites, WO_yC_z, $WTa_xO_yC_z$, and TaO_yC_z films onto flexible PET/ITO substrate by a low temperature plasma-enhanced chemical vapor deposition (PECVD) method, under atmospheric pressure, via injecting the precursors of tungsten carbonyl [$W(CO)_6$] and/or tantalum ethoxide [$Ta(OC_2H_5)_5$] into an air plasma jet at a short exposure duration of 33 s was studied. This study investigated how the Ta precursor concentrations affect the film properties, the electrochromic performance, and the uniformity in light modulation of APPJ-synthesized WO_yC_z, $WTa_xO_yC_z$ and TaO_yC_z films. The electrochemical and transmittance measurements were used to analyze the electrochromic performance of the flexible films. Field emission scanning electron microscopy (FESEM) was utilized to measure the surface

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morphology and the thicknesses of the WO_yC_z, $WTa_xO_yC_z$ and TaO_yC_z films. Raman spectroscopy, X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS) were used to gain insight into how the films' properties influence their lithium electrochromic performance.

2. Experimental details

2.1. Synthesis of WO_yC_z, $WTa_xO_yC_z$, and TaO_yC_z films

The schematics of the APPJ set-up for the deposition of WO_yC_z, $WTa_xO_yC_z$ and TaO_yC_z films onto flexible PET/ITO substrates (40 Ω/square, 125 μm thick, 3 cm × 3 cm) in ambient air are shown in Fig. 1. An atmospheric-pressure non-equilibrium glow discharge for the air plasma jet of the APPJ was generated by a power supply at an audio frequency of 20 kHz and a power of 300 W. The precursors of tungsten carbonyl [$W(CO)_6$] and tantalum ethoxide [$Ta(OC_2H_5)_5$] powders were individually put in sublimators and heated to 115 °C. Next, 0.8 sccm of Ar gas (99.9% pure) was separately fed into the tanks to carry the 0–5.4 sccm of $W(CO)_6$ vapor and 0–5.4 sccm of $Ta(OC_2H_5)_5$ vapor (the gas line was heated at 125 °C) to be injected into the air plasma jet at an angle of 30° (with respect to the nozzle). The flow rates of $W(CO)_6$ or $Ta(OC_2H_5)_5$ vapors were respectively calculated by substracting the Ar gas flow rates from the total flow rates of the mixed gases of $W(CO)_6$ or $Ta(OC_2H_5)_5$ vapors with Ar gases fed into the vacuum chamber. The PET/ITO substrates were mounted 2.0 cm below the nozzle of the air plasma jet. To deposit the WO_yC_z, $WTa_xO_yC_z$ and TaO_yC_z films, the film-formable reactive species in the plasma jet were sprayed onto the surface of the PET/ITO substrate at a substrate moving speed of 15 cm/s with a reciprocating motion. The diameter of the air plasma torch for PET/ITO substrate exposure is typical at 0.4 cm, which is an exposed duration of about 0.027 s for one pass under a substrate moving speed of 15 cm/s. The PET/ITO substrates are exposed directly to the air plasma torch for 1220 passes at a substrate moving speed of 15 cm/s; i.e., the cumulated exposure duration for the reactive species sprayed onto the substrate is about 33 s (calculated based on 0.027 s/pass × 1220 passes). The detailed settings are shown in Table 1. To reduce the differences in experimental measurements causing by the water absorbed into the APPJ-synthesized WO_yC_z, $WTa_xO_yC_z$ and TaO_yC_z films from the air, the measurements on the specimens were completed within 30 min under a temperature of ~23 ± 1 °C and a relative moisture of ~40 ± 5%. The experiment variations between the five different samples prepared with the same conditions were controlled to less than 10%.

2.2. Thin film analysis

FESEM images of the top surfaces and cross sections of the WO_yC_z, $WTa_xO_yC_z$ and TaO_yC_z films were used to determine their surface morphology and thickness. The surface morphology of the films was interpreted by the grain boundary fractions (%) on the films' surfaces. The grain boundary fraction (%) on the surface of each sample was calculated by dividing the area of grain boundary by the total area of the FESEM images with 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 prepared with the same conditions was found to be less than 5%.

Table 1
Settings for deposition of WO_yC_z, $WTa_xO_yC_z$ and TaO_yC_z films onto PET/ITO substrates by APPJ.

Parameters	Settings				
Power (watts)	300				
Frequency (kHz)	20				
Precursor injection angle θ (deg)	30				
Substrate moving speed (cm/s)	15				
Substrate distance (cm)	2				
Exposed duration (s)	33				
Ar flow rate (sccm)	1.6				
O_2 flow rate (sccm)	0.5				
Ta gas flow ratio: R_{Ta} (%)$=\left(\frac{f_{Ta}}{f_{Ta}+f_W}\right)\times 100\%$	0	5.6	18.5	50	100
Ta flow rate f_{Ta} (sccm)	0	0.3	1.0	2.7	5.4
W flow rate f_w (sccm)	5.4	5.1	4.4	2.7	0

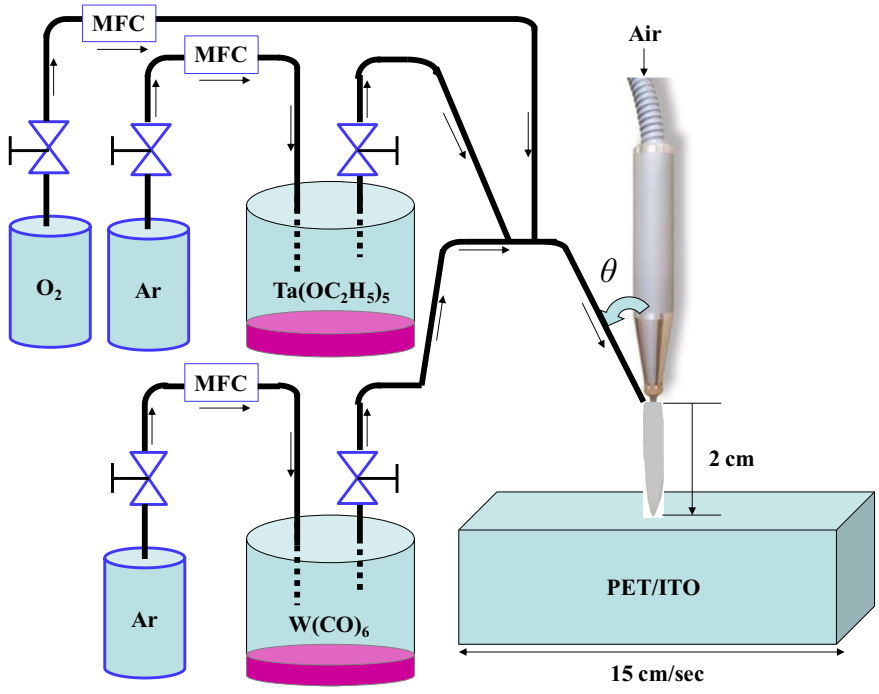

Fig. 1. Schematics of the APPJ set-up for deposition of WO_yC_z, $WTa_xO_yC_z$ and TaO_yC_z films onto PET/ITO substrates.