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A substoichiometric tungsten oxide catalyst provides a sustainable and efficient counter electrode for dye-sensitized solar cells

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Abstract

Development of Pt-free catalyst materials for the counter electrode (CE) in dye-sensitized solar cells (DSSCs) has been regarded as one of the crucial steps to improving energy conversion efficiency and cost effectiveness of DSSCs. In this work, low cost tungsten oxide (WO_{3-x}) counter electrodes, prepared by annealing tungsten metal sheets under an Ar and low O₂ atmosphere, exhibited high catalytic activity and energy conversion efficiency. The highest efficiency achieved here for DSSCs with WO_{3-x} counter electrodes, was 5.25%, obtained from a 500 °C annealed tungsten sheet. TEM and XPS analysis suggested the formation of sub-stoichiometric tungsten oxide layer (~ $\text{WO}_{2.6}$) with the presence of W⁶⁺, W⁵⁺ and W⁴⁺ oxidation states at the tungsten metal surface after the 500 °C annealing. Only W⁶⁺ and W⁵⁺ oxidation states were detected after a 600 °C annealing indicating the formation of a more stoichiometric tungsten oxide layer (~ $\text{WO}_{2.8}$) and resulting

in a drop in efficiency of the DSSC. We suggest that mixed valence tungsten states account for the excellent catalytic activity and good electrical conductivity as evidenced by the highest cyclic voltammetry response of 0.76 mA/cm^2 and the lowest impedance value of 44.33Ω , respectively.

Keywords : substoichiometric tungsten oxide, counter electrode, dye-sensitized solar cell

1. Introduction

The counter electrode (CE) is regarded as one of the most important components of dye-sensitized solar cells (DSSCs) since it acts as the electron collector from the external circuit and facilitates the reduction reaction of tri-iodide ions (I_3^-) [1]. In addition, high catalytic activity and high electrical conductivity are required for a good catalyst for DSSCs. Pt is a catalyst typically used in DSSCs. However, it is costly, rare and is readily corroded by an iodide electrolyte [2]. Identifying and developing alternative materials to substitute for Pt in the CE of DSSCs is a crucial challenge and success could reduce production costs sufficiently to increase the use of DSSCs. Candidate materials already proposed as replacements for Pt CEs include carbon materials [3], CoS [4], TiN [5] and conductive polymers [6]. Recently, tungsten carbide (WC) [7] and tungsten oxide (WO_x) [8] have been introduced as CEs and have exhibited good catalytic performance.

Wu et al. reported that the use of WO_2 nanorods embedded in mesoporous carbon (MC) as the counter electrode in DSSCs generated a conversion efficiency as high as 7.76%, which is higher than that of a Pt DSSC, 7.55% [9]. This was attributed to a combination of the excellent conductivity of carbon and the high catalytic activity of WO_2 . Tungsten trioxide (WO_3) or stoichiometric tungsten oxide and substoichiometric tungsten oxide (WO_{3-x})

nanostructures have also been intensively investigated for a wide range of applications including photocatalysis [10-12], electrochromic devices [13], gas sensors [14] and DSSC photoanodes [15]. The crystal structure of WO_3 is based on corner-sharing WO_6 octahedra [16]. Non-stoichiometric tungsten trioxide (WO_{3-x} , where $0 < x \leq 1$), which is oxygen deficient, contains tungsten in a number of differing formal oxidation states. It has been reported that a slight deficit of oxygen i.e. $x = 1/6$ is more energetically stable in standard atmospheric conditions than stoichiometric WO_3 [17]. Stoichiometric WO_3 is a wide band gap semiconductor ranging from 2.6 - 3.0 eV [13, 18], with a conductivity that increases with increasing oxygen deficiency [13].

Tungsten oxides can be synthesized by many different routes including vapor phase techniques such as physical vapor deposition (PVD) [19] including thermal evaporation [20], chemical vapor deposition (CVD) [21] or liquid phase methods such as sol-gel and hydrothermal techniques [22]. Other chemical methods for synthesizing sub-stoichiometric tungsten oxides are; for example, thermal decomposition of $\text{W}(\text{CO})_6$ at 250–270 °C in $\text{Me}_3\text{NO}\cdot 2\text{H}_2\text{O}$ and oleylamine mixture to produce colloidal $\text{W}_{18}\text{O}_{49}$ nanorods [23]. WO_2 nanorods were also produced by adding urea to a solution of WCl_6 and alcohol, then the solution was dried and sintered at 800 °C for 4 hours under a N_2 atmosphere [9]. In general, vapor phase routes are rapid and high-yield processes, but they usually require high temperatures 700-1400 °C and low pressures [24]. Liquid phase methods are generally more time consuming but offer lower production costs and better control of morphology; however, they suffer from impurities that require further post-synthesis treatments to eliminate them.

Development of high performance CEs by a facile synthesis route without sophisticated equipment, harsh experimental conditions or dealing with hazardous chemicals would be very beneficial to the solar cell manufacturing industry. In this work, we have prepared and characterized WO_{3-x} counter electrodes for DSSCs by direct annealing of pure

tungsten metal under an Ar atmosphere with low oxygen content. The tungsten oxide films produced were found to exhibit a good catalytic activity with I^-/I_3^- redox species and a promising DSSC energy conversion performance of 5.25%, however the performance of the resulting DSSCs was found to vary with annealing temperature. To explain the changes in DSSC efficiencies, cyclic voltammetry and electrochemical impedance spectroscopy were also conducted.

2. Experimental

2.1 Counter electrode preparation

DSSC counter electrodes were prepared using tungsten metal sheet with a thickness of 0.25 mm (99.95 % purity, Goodfellow) cut into pieces of 0.7 x 1.5 cm². The tungsten foils were cleaned in a series of deionized water, ethanol and acetone solutions. After drying in air, the tungsten foils were annealed in a tube furnace under an Ar atmosphere (99.9% purity containing less than 25 ppm O₂ and less than 25 ppm water vapor) at 100, 200, 300, 400, 500 and 600 °C for 2 hours at a heating rate of 2 °C/min. Then the samples were allowed to cool down to room temperature under Ar atmosphere.

2.2 Cell assembly

DSSCs were assembled using the pure tungsten or annealed tungsten foils as counter electrodes, TiO₂-coated dye-sensitizer films on Fluorine Tin Oxide (FTO, sheet resistance 7 Ω/sq, Solaronix, USA)) were used for the working electrodes, and an I^-/I_3^- solution was used as the electrolyte. The working electrodes were prepared using a screen printing method as previously reported [25] using commercial TiO₂ powders: PST-18NR and PST-400C (JGC Catalysts and Chemicals Company, Japan). The TiO₂ films were sintered at 500 °C for 1 hour, and treated with UV radiation for 10 min and then immersed into a 0.3 mM cis-bis-

(isothiocyanato)bis(2,2-bipyridyl-4,4-dicarboxylato)-ruthenium(II)-bis-tetrabutylammonium (N-719, Solaronix) solution for 24 hours. Pt counter electrodes were prepared by spin coating 20 mM of $\text{H}_2\text{PtCl}_6\text{H}_2\text{O}$ (Aldrich) and 0.01 g of ethylcellulose (Aldrich) in ethanol onto FTO glass, and then annealing at 500 °C for 1 hour in an ambient environment.

2.3 Film characterization

The morphology and structure of the pure (unannealed) and annealed tungsten sheets were characterized using transmission electron microscopy (TEM) (FEI Tecnai G2 20, LaB₆ filament, operating at 200 kV) and X-ray photoelectron spectroscopy (XPS) (AXIS-His, Kratos Analytical with aluminum K-alpha X-ray source (1486.71 eV, 150W). The XPS spectra were fitted with asymmetric mixed Gaussian–Lorentzian sum functions using the XPS peak fitting programme XPSpeak (version 4.0). XPS analyses were undertaken on the bulk structures of the as-prepared tungsten sheets. TEM samples were prepared by scratching off the film surface, the particles being dispersed in ethanol and dropped onto TEM grids. The electrode catalytic activity was measured using Cyclic Voltammetry (CV, Gamry Instrument Reference 3000, U.S.A) with a three-compartment cell at a scan rate of 20 mV/s in solutions of 10 mM LiI, 1 mM I₂, and 0.1 M LiClO₄ in acetonitrile. A Pt plate and an Ag/AgCl electrode were used as a counter electrode and a reference electrode, respectively. The DSSC characteristics were analyzed using a solar simulator (PEC-L11, Japan) under an air mass of 1.5 and a light intensity of 100 mW/cm². The impedance of the symmetric-electrode cells was measured using Electrochemical Impedance Spectroscopy (EIS, Gamry Instrument Reference 3000, U.S.A.) under dark conditions by varying the frequency from 0.1 Hz to 100,000 Hz at an AC amplitude of 10 mV.

3. Results and discussion

3.1 Tungsten oxide (WO_x) Film characterization

Figure 1(a) shows a photograph of the pure and annealed tungsten electrodes, showing a clear color change to golden brown and dark blue at the annealing temperatures of 500 and 600 °C, respectively. This color change suggests a transformation in stoichiometry [26, 27].

The crystal structures of the films were examined by TEM analysis of the scratched surface parts of the 400, 500 and 600 °C samples. No oxide content was detected by TEM selected area electron diffraction of the 400 °C sample [Fig. 1(b)], only cubic tungsten metal was present (JCPDS file No. 47-1319). Orthorhombic WO_3 and the cubic tungsten background were detected at the annealing temperature of 500 °C (JCPDS file No.20-1324) implying that annealing between 400-500 °C is sufficiently high a temperature to activate tungsten oxide formation [Fig. 1(c)]. Crystalline nanorods of various sizes were observed in the 600 °C annealed film [Fig. 1(d)]. TEM selected area electron diffraction indicated that the surface of the 600 °C sample also contained orthorhombic WO_3 (diffraction pattern inset in Fig. 1(d) and indexed to JCPDS file No.20-1324) and some reflections from cubic tungsten can still be observed. Orthorhombic WO_3 is typically stable at 330-740 °C [28]. The detailed indexing of the electron diffraction patterns can be found in section S1 of the supplementary material.

Fig. 1. (a) Photograph of the pristine and annealed tungsten sheets after annealing at temperatures ranging from 100-600 °C. (b), (c) and (d) are TEM images and inset selected area electron diffraction patterns of the annealed tungsten foils at 400, 500 and 600 °C, respectively.

Detection of both W metal and WO_3 in the 500 °C film could be due to the formation of only a thin oxide layer, with the specimen preparation route of simply scratching the film surface possibly resulting in particles of both the oxide and bulk tungsten metal being sampled [Fig. 1(c)].

To further identify the valence state and stoichiometry of the tungsten oxides, surface analysis using X-ray photoelectron spectroscopy (XPS) was performed. The W 4f spectra of the pristine tungsten and tungsten annealed at 100-300 °C (not shown) are similar, consisting of a superposition of peaks of various tungsten oxide states [Fig. (2)]. These peaks were deconvoluted into 5 doublet components as a result of spin-orbit coupling corresponding to W 4f_{5/2} and W 4f_{7/2} states. Binding energies of these doublet peaks are centered at ~35.7 and ~37.8 eV for W⁶⁺, at ~34.6 and ~36.7 eV for W⁵⁺ and at ~33.7 and ~35.7 eV for W⁴⁺ [29-31]. The peaks at 31.5 and 33.5 eV are assigned to metal tungsten peaks, which were not detectable at the annealing temperatures of 500 and 600 °C presumably due to an increase in thickness of the oxide film at these temperatures. The peaks at ~32 and 34 eV visible in the unannealed and the 400 °C annealing are suspected to be a mixture of tungsten in a low oxidation state (W²⁺) and possibly tungsten carbide [32].

The XPS results suggest that oxides containing W⁶⁺, W⁵⁺, W⁴⁺ and W²⁺ readily form as the native oxide at ambient temperature and remain unchanged up to an annealing temperature of 300 °C, albeit with the presence of W²⁺, W⁴⁺ and W⁵⁺ in relatively small amounts compared to W⁶⁺ (Table 1). The detectable oxides presumably form a very thin layer [33] which would explain the dominance of tungsten metal in the electron diffraction patterns of specimens prepared for TEM by scratching the sample surface. After the 400 °C annealing, the ratio of total tungsten oxide peak areal intensity to tungsten metal peak areal intensity increased and at 500 °C the tungsten metal peaks almost disappeared. After the 600 °C annealing, only W⁶⁺ and W⁵⁺ were detected by XPS.

The areal intensities and relative ratios of W⁶⁺, W⁵⁺ and W⁴⁺ (W⁶⁺: W⁵⁺: W⁴⁺) of the unannealed and the annealed tungsten sheets are presented in Table 1. When annealing above 300 °C the W⁶⁺ content rises sharply from ~ 45% to ~ 80 % by 600 °C. Similarly the W⁵⁺ content also increased sharply from ~ 5% at 300 °C to 22% at 600 °C while the W⁴⁺ and W²⁺ contents were at the highest in the pure W (10 and 20 % respectively) and gradually decreased with the rising annealing temperature (to 4 and 11 % respectively at 600 °C), suggesting a shift to a more stoichiometric WO_{3-x} oxide layer.

Table 1

The fitted peak area as a percentage of the total 4f_{7/2} peak area and the ratio of W⁶⁺, W⁵⁺ and W⁴⁺ (W⁶⁺: W⁵⁺: W⁴⁺) of the unannealed and the annealed tungsten sheets at 100-600 °C

The combination of the TEM electron diffraction and XPS analysis suggest that a substoichiometric tungsten oxide (WO_{3-x}, containing W⁶⁺, W⁵⁺ and W⁴⁺ in the ratio of 5.18 : 1 : 0.24) forms and fully covers the tungsten metal foil after annealing at 500 °C. The O/W was quantified using O 1s and W 4f_{7/2} XPS peak areas (the detail is described in section S2 in the supplementary material) indicating a ratio of 2.57 after the 500 °C annealing suggesting a WO_{3-x} oxide layer with x = 0.4. The 600 °C annealed tungsten contained only W⁶⁺ and W⁵⁺ (W⁶⁺: W⁵⁺ = 3.46 : 1) giving an O/W ratio of 2.76 suggesting the presence of WO_{3-x} with x ≈ 0.2 nanorods

Fig. 2. W 4f X-ray photoelectron spectra of the pristine and annealed tungsten foils at 400, 500, and 600 °C (in black) with peak fitting to metal W (grey), W²⁺/WC(blue), W⁴⁺ (purple), W⁵⁺ (green) and W⁶⁺ (orange) components.

3.2 DSSC performance

Photocurrent (J) - photovoltage (V) characteristics of the tungsten and tungsten oxide DSSCs are presented in Figure 3(a). The short-circuit current density (J_{SC}), the open-circuit voltage (V_{OC}), the fill factor (FF), and the energy conversion efficiency (η) have been extracted from Fig. 3 and are summarized in Table 2. It was found that the efficiency, short-circuit current density, open-circuit voltage, fill factor of the tungsten oxide based DSSCs depended on the annealing temperature. The efficiency dramatically increased from 0.17% for the pristine tungsten metal DSSC to 5.25% for the 500 °C annealed tungsten DSSC, which is approaching that of Pt DSSCs (6.96%). When the annealing temperature was further increased to 600 °C, the DSSC performance dropped to 4.16%.

Fig. 3. (a) J-V characteristics and (b) Nyquist plot of the I^-/I_3^- symmetrical cells for the various annealing temperatures of the tungsten counter electrodes and compared to those of a Pt based DSSC. (c) The equivalent circuit used to fit the EIS spectra.

Table 2

Summary of J_{sc} , V_{oc} , FF, η , R_s , R_{ct} , $V_{red}(1)$, $I_{red}(1)$, $V_{red}(2)$ and $I_{red}(2)$ values for the tungsten CE DSSC devices annealed at the various temperatures and compared to that of a Pt CE DSSC.

To explain the observed variation in efficiency, electrochemical impedance spectroscopy (EIS) was undertaken on symmetric-electrode cell, CE||electrolyte||CE, as shown in Fig. 3(b). The impedance spectra were fitted according to the equivalent circuit in Fig. 3(c). In the figure, R_s , R_{ct} and C represent series resistance, charge-transfer resistance and interface capacitance of the electrodes, respectively. Z_w represents the Nernst diffusion impedance in the electrolyte. Electrodes with large impedance values (i.e. large R_s and R_{ct}) indicate an inferior conductivity and electrocatalytic activity, consequently suppressing the solar cell performance [34]. The impedance of the symmetric-pure and the symmetric-annealed (at 100, 200 and 300 °C) tungsten cells were relatively large, of the order of kΩ as seen in Fig. 3(b) and Table 2. This represents low catalytic activity with I_3^- , which results in an efficiency of 0.17%-1.10%. The charge transfer resistance of the symmetric-annealed (at 400, 500, and 600 °C) tungsten cells were significantly reduced to 1.36×10^3 , 44.33, and 160.15 Ohm, respectively, suggesting that the annealing process does promote the catalytic activity of the surface films, especially on annealing at 500 °C. This reduction of impedance is accounted for the enhanced cell efficiency.

Cyclic voltammetry (CV) was also conducted to analyze the CE catalytic activities. In general, two pairs of redox peaks are found in the Pt curve [Fig. 4] which can be assigned to the reaction in equation (1) and equation (2).



Reduction at the counter electrode surface is $I_3^- + 2e^- = 3I^-$ (reduction 1) and $3I_2 + 2e^- = 2I_3^-$ (reduction 2) as seen in Figure 4.

Fig. 4. (a) and (b) cyclic voltammetry curves of Pt, pristine tungsten and the annealed tungsten electrodes (at 100-600 °C), the measurements were performed in 10 mM LiI, 1 mM I₂ and 0.1 M LiClO₄ in acetonitrile solutions at a sweep rate of 20 mV.s⁻¹.

There was however no reduction peak generated for the pure tungsten and 100-200 °C annealed tungsten electrodes [Fig. 4(a)]; indicating the absence of any reduction reaction on these films. The well-defined peaks detected on the 300, 400, 500 and 600 °C annealed tungsten electrodes in Fig. 4(b) imply a promotion of the I₃⁻ reduction rate, i.e. an enhancement of the film catalytic activity. Taking the EIS and CV results together, one can infer that an annealing temperature between 500-600 °C would produce the greatest enhancement of the tungsten based electrode catalytic activity.

The high catalytic activity of the 500 °C annealed tungsten electrode could be attributed to the presence of W⁶⁺, W⁵⁺ and W⁴⁺ detected by XPS in the substoichiometric tungsten oxide surface layer. In the case of the 600 °C annealed tungsten film, only W⁶⁺ and W⁵⁺ were detected by XPS and its catalytic activity was found to be lower than that of the film annealed at 500 °C. Improved properties of a WO_{3-x} oxide film over a stoichiometric WO₃ device has also been reported in terms of electrochromic performance [35]; the presence of W⁶⁺, W⁵⁺ and W⁴⁺ species in WO_{3-x} were considered to be the key to a higher coloration efficiency than that of WO_{3-x} with only W⁶⁺ and W⁵⁺ [36]. This is consistent with our findings of an inferior energy conversion efficiency for the 600 °C annealed tungsten CE DSSC which is attributed to the absence of W⁴⁺ observed by XPS [Fig. 2]. This implies that the superior energy conversion efficiency of the WO_{3-x} CE DSSC is due to an improved electrical conductivity resulting from increased oxygen vacancies in the structure [37]. The improved electrical conductivity is supported here by measurement of a low impedance value of 44.33 Ω in the 500 °C annealed tungsten or WO_{2.6} layer (containing W⁶⁺, W⁵⁺ and W⁴⁺) which rises

to $160.15\ \Omega$ in the $600\ ^\circ\text{C}$ annealed tungsten or $\text{WO}_{2.8}$ layer as it becomes more stoichiometric (containing only W^{6+} and W^{5+}).

The high electric conductivity of the annealed tungsten sheet at $500\ ^\circ\text{C}$ can be explained by a small polaron hopping conduction mechanism that is known to operate in WO_3 [38]. S.K. Deb [39] presented a polaronic model to explain the coloring mechanism in WO_{3-x} , which is consistent with the electrical conductivity mechanism established for WO_3 . The presence of oxygen vacancies in substoichiometric WO_{3-x} creates localized defect states; V_o^0 (W^{4+} or 2W^{5+}), $V_o^+(\text{W}^{5+})$ and $V_o^{2+}(\text{W}^{6+})$, located at the top of the valence band, within the band gap and at the bottom of the conduction band, respectively (see Fig. 2. in reference [39]). These promote charge transfer and enhance the electrical conductivity in the 500°C annealed tungsten where mixed valence states of W^{4+} , W^{5+} and W^{6+} were shown to be present whereas in the 600°C material there were fewer mixed valence states (only W^{5+} and W^{6+}) so the conductivity dropped accordingly (Tables 1 and 2).

To ensure reproducibility of the DSSCs, 4 cells of the tungsten oxide DSSCs were produced at each annealing condition (except for the unannealed and the $100\ ^\circ\text{C}$ annealed tungsten DSSCs where only 2 cells each were prepared). The individual performance figures can be found in section S3 of the supplementary material. The standard errors of the measured efficiencies of almost all annealing conditions were within 10% of the mean values and those of the 400 , 500 and $600\ ^\circ\text{C}$ annealing were within less than 5% error, indicating reproducible and reliable mean values for each annealing condition.

4. Conclusions

High performance WO_{3-x} counter electrodes for DSSCs have been prepared by simple, thermal annealing of tungsten foils under an Ar and low O_2 atmosphere. The highest dye-sensitized solar cell performance of 5.25% energy conversion efficiency was achieved

using a 500 °C annealed containing a $\text{WO}_{2.6}$ surface layer CE DSSC, where the oxide film structure contained W^{6+} , W^{5+} and W^{4+} . The reported efficiency is approaching that of a Pt DSSC (6.96%) yet the production costs would be significantly lower. The cell efficiency of a 600 °C $\text{WO}_{2.8}$ coated CE DSSC, where the oxide film structure contained only W^{6+} and W^{5+} ($\text{W}^{6+} : \text{W}^{5+} = 3.46 : 1$), was lower at 4.16% consistent with the drop in impedance expected for the more stoichiometric oxide layer. It is suggested that the presence of W^{6+} , W^{5+} and W^{4+} valence states in the substoichiometric WO_{3-x} produces excellent catalytic activity and electrical conductivity as inferred by cyclic voltammetry and electrical impedance spectroscopy.

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