Flexible Metallic Substrates for TiO_2 Film of Dye-sensitized Solar Cells

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The effects of metallic supporting substrates in nanocrystalline TiO_2 working electrodes of dye-sensitized solar cells on photocurrent–voltage (*J*–*V*) characteristics were investigated. For W, Ti, stainless steel, and Zn that can produce semiconductor oxides during annealing, the short-circuit photocurrent density (J_{sc}) is related to the conduction band energy levels of the metal oxides. The metals that produce insulating oxides, Al, Co, and Ni, were found to be also useful supporting substrates when both thin layers of ITO and SiO_x were sputtered on the metal surfaces.

Over the past decade, dye-sensitized solar cells (DSSCs) have emerged as a viable substitute for solid-state silicon solar cells.[1] The DSSCs have risen in importance primarily because of their high light-to-electricity conversion efficiency (η, 11%),[2] low production cost and eco-friendly nature. However, such cells have the inherent disadvantage of having glass as a substrate material, which makes the cells unsuitable for certain applications such as cellular phones, ID cards, or watches, in addition to the high material cost. Replacing the glass substrate with plastic materials makes possible the fabrication of lightweight, thin, and low cost DSSCs through roll-to-roll mass production. A variety of methods have been devised to fabricate nanoparticle TiO_2 film on plastic films.[3] However, it is known that η values of the plastic-based DSSCs irrespective of fabrication method are low compared with those utilizing glass substrate because of the poor necking of TiO_2 particles arising from low-temperature heat treatments below 150 °C.[3d,4]

Compared with the great attention that has been paid to plastic materials, only a few studies have been pursued on metallic substrates. A patent involved the use of Ti and Zn foils as electron-collecting substrates with TiO_2 and ZnO, respectively, but no further quantitative photovoltaic properties is available.[5] One earlier work, albeit not intended for a flexible cell, was reported with a Ti sheet covered with TiO_2 film.[6] In this paper we present the effect of eight metallic substrates for the TiO_2 film on *J*–*V* characteristics of DSSCs. The differences in the *J*–*V* curves were related primarily to the formation of metal oxide layers possibly formed between the metal substrates and the TiO_2 film during annealing in air.

Preparation of anatase (TiO_2) colloid and its deposition on a supporting substrate by the doctor blade technique to produce TiO_2 film were described elsewhere.[7] Eight metallic supporting substrates (Goodfellow, England) were evaluated: stainless steel (StSt, SUS 304), W, Ti, Co, Ni, Pt, Al, and Zn of ≈100 µm thickness. Annealed TiO_2 films (10 µm) at 450 °C for 1 h (except Zn at 400 °C for 30 min) in air were coated with sensitizing dye by immersion in 3×10^{-4} M Ru(II)LL′$(NCS)_2$ (L = 2,2′-bipyridyl-4,4′-dicarboxylic acid, L′ = 2,2′-bipyridyl-4,4′-ditetrabutylammonium carboxylate, Solaronix) ethanol solution overnight. FTO glass was used as a counter electrode. The liquid electrolyte was composed of 0.70 M 1-vinyl-3-methyl-immidazolium iodide,[8] 0.10 M LiI (Aldrich), 40 mM iodine (Aldrich) and 0.125 M 4-tert-butylpyridine (Aldrich) in 3-methoxypropionitrile (Aldrich). The active area of the cell was about 0.20 cm^2. The *J*–*V* curves were measured with a Keithley 2400 source meter and a 1000 W Xenon lamp (Oriel, 91193). The light intensity was adjusted with a reference Si cell (Fraunhofer Institute for Solar Energy System) for approximating 1 sun light intensity of 100 mW/cm^2.

Figure 1 compares the *J*–*V* curves of the DSSCs fabricated with eight metal-supported working electrodes with 10-µm thick TiO_2 film. The corresponding J_{sc}, V_{oc}, fill factor (FF) and η, are listed in Table 1. With respect to the *J*–*V* characteristics, the metal substrates can be divided into two classes: W, Ti, StSt, and Zn (Class I) show typical *J*–*V* curves obtainable from solar cells, while Al, Ni, Co, and Pt (Class II) show almost ohmic behaviors. The reason for these behaviors is presumably originated from the formation of metal oxide layers between metallic substrates and TiO_2 layers, which likely occurs during the annealing at 450 °C in air. It is noted that the oxides produced by the Class I metals, unlike the Class II metals, are n-type semiconductors.

The J_{sc} values of the Class I metals can be related to the position of the conduction band edge (E_{cb})[9] for the corresponding semiconductors as shown in Figure 2, although the E_{cb} values show a large scatter due to the variability of surface properties of the materials.

The largest J_{sc} is obtained with Ti because of the absence of energy barrier at the TiO_2/oxide interface. The results with W and StSt substrates indicate that the larger J_{sc} is observed when the E_{cb} of the oxide layer lies closer to that of the TiO_2 layer. Under such closer mutual disposition, electron transfer from the TiO_2 layer to the oxide layer is associated with the dissipation of a lesser amount of energy.[10] However, electron transfer

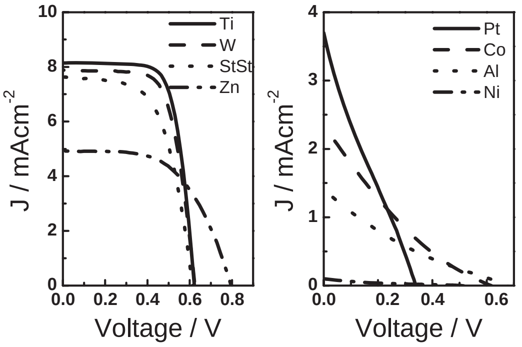

Figure 1. *J*–*V* curves measured at 1 sun level for DSSCs prepared with 10-µm thick TiO_2 films on various metallic substrates.

Table 1. Photovoltaic properties of DSSCs at 1 sun light intensity for the porous TiO_2 layers of 10 µm thickness coated on different metallic supporting substrates[a]

Supporting substrate	V_{oc} (V)	J_{sc} (mA/cm^2)	FF	η (%)
Ti	0.62	8.14	0.71	3.60
W	0.62	7.88	0.68	3.32
StSt[b]	0.61	7.63	0.60	2.79
Zn	0.80	4.92	0.56	2.20

[a] Illuminated through FTO glass counter electrodes. [b] Stainless steel.

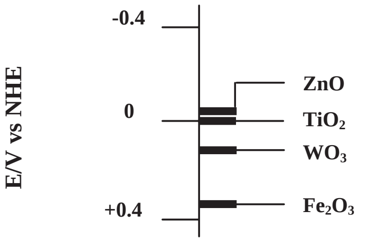

Figure 2. Position of conduction band edges of semiconductors in aqueous electrolyte at pH 1.0.

is considerably retarded, when the E_{cb} of the oxide layer lies above that of TiO_2 as seen in the case of Zn. The FF of the cells shows a similar trend as the J_{sc}, suggesting that the FF may reflect electrical resistance across the TiO_2/oxide/metal layers. Further investigations on the properties of the oxide layers are in progress. As a result of these changes in the J_{sc} and FF with the Class I metals, the η of the DSSCs decreases in the order: Ti > W > StSt > Zn.

Contrary to the J_{sc} and FF, the near invariance of the V_{oc} values of the cells with W, Ti, and StSt substrates can be attributed to almost identical TiO_2 films and TiO_2/electrolyte interfaces in the DSSCs. However, an extraordinary high V_{oc} value with Zn can be explained by the negative shift of the flat band potential of TiO_2 due to the adherence of evaporated Zn in the TiO_2 layer, which occurred during annealing.[11]

The Class II metals can also be utilized as flexible supporting substrates when their surfaces were sputtered with thin layers of ITO and SiO_x prior to the deposition of the TiO_2 colloid. Figure 3 demonstrates that an insulating SiO_x layer of the cell with a TiO_2/SiO_x/ITO/Al electrode improves the J_{sc} by almost fivefold compared with the cell with a TiO_2/ITO/Al electrode. The SiO_x layer apparently isolates the ITO layer from the Al substrate, preventing possible photocurrent leakage from the Al to the electrolyte that penetrated through the ITO layer toward the Al of the TiO_2/ITO/Al electrode. Thus, the role of the SiO_x layer is analogous to that of a TiO_2 blocking layer formed by treatment with Ti(IV) butoxide in conventional DSSCs.[12] In addition, the SiO_x layer prevents the I_2 induced corrosion, which is considered as a cause of the low photocurrent with Al. Similar enhancements of the J_{sc} were observed with the DSSCs consisted of SiO_x- and ITO-sputtered Ni and Co substrates.

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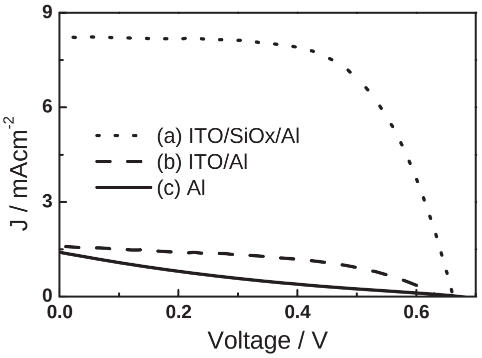

Figure 3. *J–V* curves measured at 1 sun level for DSSCs prepared with 10-µm thick TiO_2 films on supporting substrates: (a) ITO/SiO_x/Al, (b) ITO/Al, and (c) Al.

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