Importance of Blocking Layers at Conducting Glass/TiO_2 Interfaces in Dye-sensitized Ionic-liquid Solar Cells

Jiangbin Xia,[1] Naruhiko Masaki,[1] Kejian Jiang,[1] Yuji Wada,[2] and Shozo Yanagida*[1]
[1] *Center for Advanced Science and Innovation, Osaka University, Suita, Osaka 565-0871*
[2] *Material and Life Science, Graduate School of Engineering, Osaka University, Suita, Osaka 565-0871*

(Received November 30, 2005; CL-051484; E-mail: yanagida@mls.eng.osaka-u.ac.jp)

Thin Nb_2O_5 film works as a potential blocking layer when deposited between fluorine-doped tin oxide and nanocrystalline TiO_2 layer, improving V_{oc} and conversion efficiency of the dye-sensitized TiO_2 solar cells using ionic liquid electrolytes.

In dye-sensitized TiO_2 solar cells (DSCs) that compose of a dye-adsorbed nano-TiO_2 layer on fluorine-doped tin oxide (FTO) glass cathode as the window electrode, redox electrolytes as charge carrier and the counter anode electrode, unidirectional charge flow with no electron leakage at the interfaces is essential for the high energy-conversion efficiency. Recently, much attention[1–3] has been paid to improve the performance of the ionic-liquid DSCs because of their features such as high ionic conductivity, nonvolatility, electrochemical stability, and nonflammability.[4–6]

According to the unidirectional electron-transporting principle of DSCs, there are four important interfaces in the devices as shown in Figure 1. These are, the interface of FTO/TiO_2, TiO_2/dye, dye/electrolyte, and electrolyte/counter electrode (usually platinized FTO electrode). Recently, many researchers pay much attention to the interface of TiO_2/dye especially through core–shell structured electrodes by introducing Nb_2O_5, $SrTiO_3$, and Al_2O_3[7–11] for TiO_2 electrode surface modification. However, except for the establishment of model for DSCs,[12–15] few groups investigate the modification of the interface of FTO/TiO_2 and its effectiveness by employing a compact TiO_2 layer.[12b,15]

In this letter, we first develop Nb_2O_5 as blocking layer which gives an improvement in open-circuit photovoltage (V_{oc}) and fill factor, leading to respectable energy-conversion efficiency in ionic-liquid DSCs. The improvement may come from the Nb_2O_5 forming potential barrier between FTO and TiO_2, which can suppress back electron transfer from FTO to electrolytes without lowering conductivity between them as shown in Figure 1.

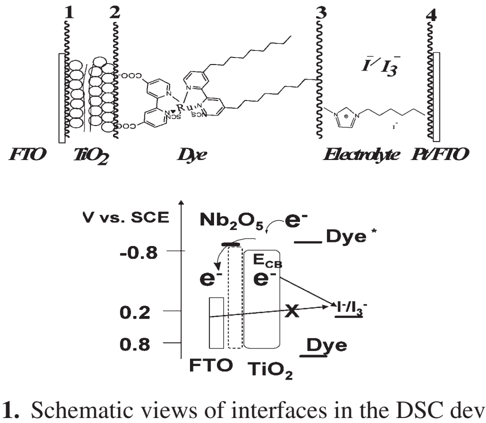

Figure 1. Schematic views of interfaces in the DSC device and the electron transfer of the new structured electrode.

The spray pyrolysis method[12a] with different precursors listed in Table 1 has been applied to form the corresponding metal oxide layers on FTO during the fabrication of the structured FTO/*metal oxide*/porous TiO_2 (Nanoxide-T, Solaronix, 5.5 μm) electrodes. The general procedure is as follows; each ethanol solution (0.02 M) of the precursor was sprayed layer-by-layer appropriate repetitions onto the FTO substrate keeping over 400 °C. Then, the substrates with the blocking layers were annealed at 500 °C for 1 h (some XRD data refer to supplementary information). The Ru dye, Z-907 (Ru-520 DN, Solaronix) and the ionic-liquid electrolyte composed of HMImI (1-hexyl-3-methylimidazolium iodide) with iodine ($[I^-]:[I_2] = 10:1$) are employed for ionic-liquid DSCs. The cells without any blocking layer or with liquid electrolyte based on methoxyacetonitrile are also fabricated for comparison.

As shown in Table 1, while the blocking MgO, ZnO, Al_2O_3, Eu_2O_3, and SiO_2 layers do not give any improvement of V_{oc}, the Nb_2O_5 blocking layer improves V_{oc} effectively, with keeping respectable fill factors (FF), giving the high conversion efficiency as well as the TiO_2 blocking layer. Figure 2 presents the *J*–*V* curve of the novel type solar cell and that of nonblocked reference under AM 1.5 irradiation of 100 mW/cm^2.

Table 1. Comparison of the parameters of the ionic-liquid DSCs using mesoporous TiO_2 electrodes with several metal oxide blocking layers on FTO after optimization

Precursors	Blocking materials	V_{oc} /mV	J_{sc} /mA	FF	η/%
—	none	580	8.30	0.57	2.8
[a]	TiO_2	641	7.85	0.65	3.3
$Nb(OCH_2CH_3)_5$	Nb_2O_5	649	7.43	0.67	3.2
$Mg(OCH_3)_2$	MgO	590	7.38	0.64	2.8
$Sn(CH_3COCHCOCH_3)_4$	SnO_2	578	8.63	0.57	2.8
$Zn(CH_3COCHCOCH_3)_2$	ZnO	572	4.44	0.54	1.4
$Al(OCH(CH_3)_2)_3$	Al_2O_3	579	5.35	0.69	1.8
$EuCl_3$	Eu_2O_3	621	6.06	0.61	2.3
Tetramethylcyclotetrasiloxane	SiO_2	567	6.75	0.57	2.2
—	none[b]	704	10.17	0.68	4.9
$Nb(OCH_2CH_3)_5$	Nb_2O_5[b]	710	9.54	0.72	4.8

[a] Diisopropoxytitanium bisacetylacetonate as precursor.
[b] Liquid electrolyte: 0.1 M LiI, 0.3 M 2,3-dimethyl-1-propylimidazolium iodide, 0.05 M I_2, 0.5 M 4-*tert*-butylpyridine in methoxyacetonitrile.

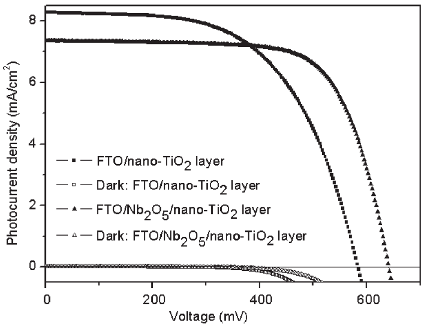

Figure 2. *J–V* curves of cells employing Z-907 sensitized FTO/nano-TiO$_2$ (■) and FTO/Nb$_2$O$_5$/nano-TiO$_2$ electrodes (▲) under AM 1.5 irradiation. (Electrolyte:HMImI:I$_2$ = 10:1).

When the thicker Nb$_2$O$_5$ layer (obtained by 50-times pyrolyses, being estimated as around ≈50 nm) is employed, the device gives a great improvement of V_{oc} about 70 mV and better fill factor with the compensation of some lower J_{sc} and finally gives a 3.3% energy-conversion efficiency which is 15% higher than that of the reference. The great improvement of V_{oc} can be explained by the diode equation:[16,17]

$$V_{oc} = (nRT/\mathrm{F})\ln[(J_{sc}/J_0) - 1] \qquad (1)$$

where n is the ideality factor whose value is between 1 and 2, J_{sc} and J_0 are the photocurrent density under short circuit and reverse saturation current, respectively, R and F have the common meaning. The literature[16] suggested that charge recombination at the nanocrystalline/redox electrolyte interface is expected to play a significant role in lowering the photovoltage. Acceptably, there are two recombination pathways occurring at the interface. The injected conduction-band electrons recombine with oxidized dye or triiodide and polyiodide redox species in the electrolyte. And usually the former reaction is ignored because of the rapid rate of reduction of oxide dye molecules by I$^-$ ions. Many attempts have been done to suppress such back transfer reaction taken place at the surface of TiO$_2$ in the last several years using surface treatment of TiO$_2$ electrode.[7–11] On the other hand, the porous interfaces between FTO substrate and TiO$_2$ can also act as electron recombination sites, i.e., electron leakage sites especially in solid- or quasi-solid-state electrolytes like ionic-liquid electrolytes. Our newly structured FTO/Nb$_2$O$_5$/TiO$_2$ electrode that should form 100-mV[18] potential barrier can prohibit the recombination of injected electron in FTO with the redox electrolyte effectively, which means the enhancement of the electron collection at FTO, giving an improvement of shunt resistance and V_{oc} for the accumulation of injected electrons.

On the other hand, the improved fill factor maybe due to the lower series resistance.[19] Such an explanation is supported by the evidence that the sheet resistance of Nb$_2$O$_5$-doped SnO$_2$ is decrease compared with SnO$_2$ after high temperature calcination.[20]

It should be noted that such kinds of structured electrode have less influence in liquid-electrolyte system and that this assures the fluid solvent molecules can easily penetrate into the porous FTO/TiO$_2$ interfaces, working as separators from the redox species. Since in solid state DSCs, or ionic-liquid DSCs, it is not easy to change the surface potential of TiO$_2$ by adding additives like TBP (4-*tert*-butylpyridine) to improve the V_{oc} of the cell, such kind of modified substrate is a good choice for the improvements of V_{oc}. Other facile methods for construction of the effective blocking layer are currently being undertaken.

In summary, we have demonstrated that among the examined metal oxides, Nb$_2$O$_5$ can form an effective blocking layer at FTO/nano-TiO$_2$ interfaces and greatly improve V_{oc} and fill factor, proving the importance of blocking layer at FTO and TiO$_2$ interfaces in ionic-liquid DSCs.

This research was supported by the New Energy and Industrial Technology Development Organization (NEDO) under the Ministry of Economy, Trade and Industry.

References

1 P. Wang, B. Wenger, R. Humphry-Baker, J.-E. Moser, J. Teuscher, W. Kantlehner, J. Mezger, E. V. Stoyanov, S. M. Zakeeruddin, M. Grätzel, *J. Am. Chem. Soc.* **2005**, *127*, 6850.
2 H. Matsumoto, T. Matsuda, T. Tsuda, R. Hagiwara, Y. Ito, Y. Miyazaki, *Chem. Lett.* **2001**, 26.
3 N. Yamanaka, R. Kawano, W. Kubo, T. Kitamura, Y. Wada, M. Watanabe, S. Yanagida, *Chem. Commun.* **2005**, 740.
4 R. Hagiwara, Y. Ito, *J. Fluorine Chem.* **2000**, *105*, 221.
5 T. Welton, *Chem. Rev.* **1999**, *99*, 2071.
6 A. B. McEwen, H. L. Ngo, K. LeCompte, J. L. Goldman, *J. Electrochem. Soc.* **1999**, *146*, 1687.
7 A. Zaban, S. G. Chen, S. Chappel, B. A. Gregg, *Chem. Commun.* **2000**, 2231.
8 S. M. Yang, Y. Y. Huang, C. H. Huang, X. S. Zhao, *Chem. Mater.* **2002**, *14*, 1500.
9 Y. Diamant, S. G. Chen, O. Melamed, A. Zaban, *J. Phys. Chem. B* **2003**, *107*, 1977.
10 T. Taguchi, X. T. Zhang, I. Sutanto, K. Tokuhiro, T. N. Rao, H. Watanabe, T. Nakamori, M. Uragami, A. Fujishima, *Chem. Commun.* **2003**, 2480.
11 E. Palomares, J. N. Clifford, S. A. Haque, T. Lutz, J. R. Durrant, *J. Am. Chem. Soc.* **2003**, *125*, 475.
12 a) L. Kavan, M. Grätzel, *Electrochim. Acta* **1995**, *40*, 643. b) S. Ito, P. Liska, P. Comte, R. Charvet, P. Péchy, U. Bach, L. Schmidt-Mende, S. M. Zakeeruddin, A. Kay, M. K. Nazeeruddin, M. Grätzel, *Chem. Commun.* **2005**, 4351.
13 B. A. Gregg, F. Pichot, S. Ferrere, C. L. Fields, *J. Phys. Chem. B* **2001**, *105*, 1422.
14 a) P. J. Cameron, L. M. Peter, *J. Phys. Chem. B* **2003**, *107*, 14397. b) P. J. Cameron, L. M. Peter, *J. Phys. Chem. B* **2005**, *109*, 7392.
15 B. Peng, G. Jungmann, C. Jäger, D. Haarer, H. W. Schmidt, Thelakkat, *Coord. Chem. Rev.* **2004**, *248*, 1479.
16 S. Y. Huang, G. Schlichthörl, A. J. Nozik, M. Grätzel, A. J. Frank, *J. Phys. Chem. B* **1997**, *101*, 2567.
17 M. Grätzel, *Prog. Photovoltaics* **2000**, *8*, 171.
18 K. Sayama, H. Sugihara, H. Arakawa, *Chem. Mater.* **1998**, *10*, 3825.
19 G. Kron, U. Rau, J. H. Werner, *J. Phys. Chem. B* **2003**, *107*, 13259.
20 N. Kikuchi, E. Kusano, E. Kishio, A. Kinbara, *Vacuum* **2002**, *66*, 365.

Published on the web (Advance View) January 28, 2006; DOI 10.1246/cl.2006.252