Chemistry Letters

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Advance Publication on the web September 18, 2020
doi:10.1246/cl.200535

Usage of Ionic Liquid Electrolyte in Tin and Zinc Oxide Composite Dye-sensitized Solar Cells

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Though Dye-sensitized solar cells (DSCs) made from less photo-catalytically active tin and zinc oxides are inefficient, composite tin-zinc oxide films yield efficiencies comparable to those fabricated out of titanium dioxide films. Studies conducted reveal that DSCs based tin-zinc oxide films are highly stable when high boiling point solvents are incorporated to solubilize the conventional iodide/tri-iodide redox system.

Keywords: Dye-sensitized solar cell, Tin oxide, Zinc oxide

Researchers worldwide have engaged in development of dye-sensitized solar cells (DSCs) for nearly three decades [1–7]. Despite this effort, the device continues to be plagued with issues of long term stability preventing large scale practical application. Instability originates from photo-degradation of the dye and/or the electrolyte, evaporation or leakage of the electrolyte owing to imperfect sealing [8,9]. The latter cause is largely eliminated by the use of electrolytes based on high boiling point ionic liquids instead of volatiles such as acetonitrile [10]. The photo-degradation of the dye and the electrolyte happens mainly due to photocatalytic reactions at the TiO_2 surface, induced by ultraviolet (UV) component of solar radiation in presence of water. The moisture contamination of the electrolyte is practically unavoidable, even with the use of hydrophobic electrolytes [11]. Holes generated via direct absorption of UV photons by TiO_2, produce highly oxidative hydroxyl free radicals via reaction with water molecules [12]. The concomitant electron, reduces iodine discoloring the electrolyte, an effect almost always seen in prolonged illumination of a DSC. The reactions involved can be summarized as follows:

$H_2O + h^+$ (valence band) → $OH^{\cdot} + H^+$ (1)
$OH^{\cdot} + X$ → oxidation products of X (2)
$I + e^-$ (conduction band) → I^- (3)

Where X denote the dye or the electrolyte.

The above problem could be solved by use of a less photo-catalytically active larger band-gap (compared to ~ 3.2 eV for TiO_2) oxide semiconductor having appropriate positioning of the conduction band edge [2,5]. Tin (IV) oxide (band gap ~ 3.8 eV) satisfies the above requirement, however, solar cells based on this material are inefficient and energy conversion efficiency values attained are order of 1% or less. The reason attributed is faster recombination of dye cation with conduction band electrons, probably due to the low effective mass of conduction band electrons in SnO_2. Imposition of ultra-thin barriers of higher band gap oxides over SnO_2 crystallites, relieve this problem greatly, suppressing recombination and efficiencies comparable to that of the TiO_2 system has been achieved with SnO_2 based DSCs, when the crystallite are coated ZnO or MgO [5]. This work examines the stability of a DSC made of SnO_2/ZnO (ZnO coated SnO_2) using an ionic liquid based electrolyte (0.4 M I_2 in 1-methyl-3-propylimidazolium iodide with ~ 1 % by vol 4-tert butyl pyridine) and compares it with a TiO_2 system based on the same electrolyte.

Before making the samples, fluorine-doped tin oxide (FTO) plates (1 cm × 2 cm) were cleaned by ultra-sonication in a detergent for 5 min and thoroughly washed with distilled water. Then the cleaned glass plates were rinsed with isopropyl alcohol and purged with air to dry. Commercially available chemicals of purity 98% or more were used for sample preparation without further purifications. Fabrication method of each film and the construction of solar cell are described below.

First, SnO_2 films were fabricated as follows. Colloidal tin oxide (3 ml, 15% aqueous dispersion Alfa Aesar) and glacial acetic acid (6 drops) were grounded in a mortar. Triton X-100 (5 drops) and ethanol (20 ml) was added to the mixture and the suspension sonicated for 15 minutes were sprayed onto cleaned FTO substrates heated to150 °C. Finally, SnO_2 films were sintered at 500 °C for 30 minutes.

Zinc oxide powder (0.06 g Aldrich), glacial acetic acid (6 drops) and Triton X-100 (5 drops) were mixed with ethanol (20 ml) for the fabrication of ZnO films. The suspension was sonicated for 15 minutes and sprayed onto cleaned FTO substrates heated to 150 °C. ZnO films were sintered at 500 °C for 30 minutes.

SnO_2/ZnO composite films were fabricated grounding colloidal tin oxide (3 ml, 15% aqueous dispersion Alfa Aesar), glacial acetic acid (6 drops), ZnO (0.06 g Aldrich) in a mortar and then adding triton X-100 (5 drops), ethanol (20 ml) to the mixture and the suspension sonicated for 15 minutes was sprayed onto cleaned FTO substrates heated to 150°C. Lastly, composite films were sintered at 500 °C for 30 minutes.

Plates coated with oxides (SnO_2 , ZnO and SnO_2/ZnO) were heated to 80 °C and kept soaked overnight in a $3x10^{-4}$ M solution of N719 dye in 1:1 v/v ratio acetonitrile and tert-butyl alcohol. The Pt counter electrode was clipped firmly to the dye-anchored surface and the space between the two electrodes was impregnated with the ionic liquid based electrolyte (0.4 M I_2 in 1-methyl-3-propylimidazolium iodide with ~ 1 % vol 4-tert butyl pyridine). A mask with a window of 0.25 cm^2 was pasted the working electrode and solar cell characteristics were ascertained using a simulated sunlight using SPD SS-25 LED Solar Simulator and VK-PA-300K PV Power Analyzer (AM 1.5 at 100 mW cm^{-2}).

The IV characteristics of DSCs made of SnO$_2$, ZnO and SnO$_2$/ZnO films are shown in Figure 1 and the IV parameters , short-circuit photo-current (J_{sc}), open-circuit voltage (V_{oc}), fill factor (*FF*) and efficiency (η) are summarized in Table 1. The efficiencies of cells made of SnO$_2$ and ZnO separately are 0.69% and 0.83% respectively, whereas that of SnO$_2$/ZnO is 5.04 %. Clearly conspicuous improvements in J_{sc}, V_{oc} and FF are also seen in the SnO$_2$/ZnO based solar cell.

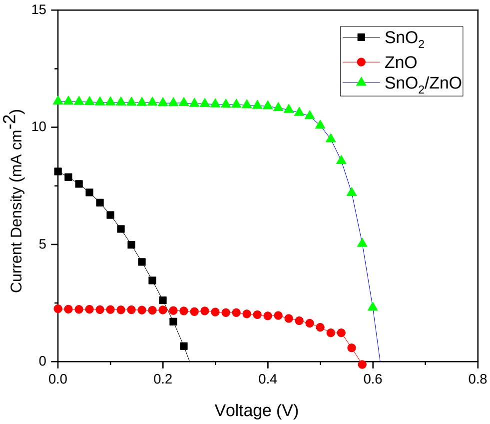

Figure 1. IV characteristics of the DSCs based on SnO$_2$, ZnO and SnO$_2$/ZnO films using the ionic liquid electrolyte constituted of 0.4 M I$_2$ in 1-methyl-3-propylimidazolium iodide with ~ 1 % by vol 4-tert butyl pyridine.

Table 1. IV parameters of DSCs based on SnO$_2$, ZnO and SnO$_2$/ZnO films using the ionic electrolyte constituted of 0.4 M I$_2$ in 1-methyl-3-propylimidazolium iodide with ~ 1 % by vol 4-tert butyl pyridine.

Working Electrode	J_{sc} (mA cm^{-2})	V_{oc} (V)	*FF* (%)	η (%)
SnO$_2$	8.11	0.251	0.34	0.69
ZnO	2.25	0.577	0.64	0.83
SnO$_2$/ZnO	11.10	0.614	0.74	5.04

Figure 2 compares the time variation of the efficiencies of SnO$_2$/ZnO cell that utilizes the high boiling point ionic liquid and volatile electrolytes. The less viscous volatile electrolyte yields higher initial efficiency, but the electrolyte loss causes rapid decline of the efficiency. A detectable decrease in the efficiency of ionic liquid system was not observed during the period of illumination.

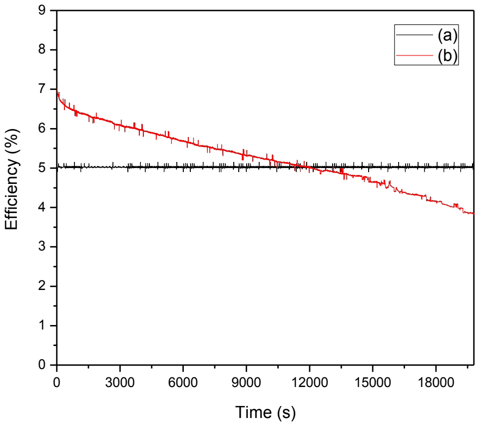

Figure 2. Comparison of the time variation of the efficiencies of SnO$_2$/ZnO DSCs based (a) on ionic liquid electrolyte (0.4 M I$_2$ in 1-methyl-3-propylimidazolium iodide with ~ 1 % by vol 4-tert butyl pyridine) and (b) volatile electrolyte (0.4M LiI/10^{-2} I$_2$ in methoxide acetonitrile containing ~ 1 % by vol 4-tert butyl pyridine).

When SnO$_2$/ZnO and TiO$_2$ based cells with ionic electrolyte were compared, TiO$_2$ system displayed clear evidence for gradual decrease of efficiency (Figure 3). It is also evident that rate of decrease of the efficiency of the TiO$_2$ cell is initially faster and the rate gradually decrease, possibly because, the degradation reactions (1)- (3) eliminate moisture. Figure 3 compares the time variation of the efficiencies of SnO$_2$/ZnO and TiO$_2$ cells using the ionic liquid electrolyte (0.4 M I$_2$ in 1-methyl-3-propylimidazolium iodide with ~ 1 % by vol 4-tert butyl pyridine). TiO$_2$ cell with ionic electrolyte yields higher efficiency, but the efficiency reduces by about 10 % over 2 hour period. However in the SnO$_2$/ZnO system detectable decline in efficiency was not observed. A 10 % reduction in efficiency of TiO$_2$ based solar cell could be attributed to photocatalytic effect of TiO$_2$ induced by ultraviolet component of the solar simulator radiation.

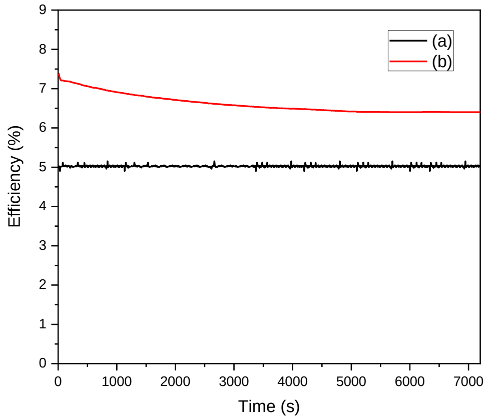

Figure 3. Comparison of the time variation of the efficiencies of the (a)

SnO_2/ZnO and (b) TiO_2 based DSCs using the ionic liquid electrolyte (0.4 M I_2 in 1-methyl-3-propylimidazolium iodide with ~ 1 % by vol 4-tert butyl pyridine).

The work reported above has conducted a comparative study of DSCs made of SnO_2, ZnO, SnO_2/ZnO and TiO_2 films sensitized with the N719 dye, using an I^-/I_3^- redox shuttle in a high boiling point ionic liquid electrolyte . Results indicate that the SnO_2/ZnO cell, yields nearly an order of magnitude higher efficiency compared to the efficiencies of systems based on individual oxides. More importantly findings demonstrate that the DSCs made of SnO_2/ZnO films and the ionic liquid electrolyte are highly stable and resistant to degradation during prolonged illumination.

The authors would like to thank the National Institute of Fundamental Studies, Sri Lanka for financial support.

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