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Letter

Stability of the SnO$_2$/MgO dye-sensitized photoelectrochemical solar cell

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Abstract

Dye-sensitized solar cells made of TiO$_2$ are extensively studied as a cheap alternative to conventional photovoltaic cells. The other familiar stable oxide material of similar band gap suitable for dye sensitization is SnO$_2$. Although cells based only of SnO$_2$ are prone to severe recombination losses, the cells made of SnO$_2$/MgO films where the SnO$_2$ crystallite is surface covered with an ultra-thin shell of MgO, deliver reasonably high efficiencies. It is found that SnO$_2$/MgO cells resist dye and electrolyte degradation better than TiO$_2$ cells. Furthermore, the ultra-thin barrier of MgO on SnO$_2$ remains intact during prolonged usage or storage of the cell.
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1. Introduction

After the pioneering work of Gratzel and O' Regan, dye-sensitized (DS) solar cells are emerging as practically viable systems for conversion solar energy to electricity [1–5]. The long-term stability of the DS solar cells has also been investigated [6]. The main advantage of these devices happens to be the ability to utilize cheap non-toxic high band gap oxide semiconductors. Fabrication procedures are not energy intensive and use of high-purity materials is not a restrictive impediment. DS solar cells extensively tested to assess the practical viability are those based on TiO$_2$. DS photoelectrochemical cells with an active area of 0.25 cm^2 have efficiencies of the order 10% and larger cells and modules of reasonable efficiencies have also been demonstrated [7]. Another promising DS solar cell based on an alternative oxide semiconductor material is the SnO$_2$/MgO cell, where the TiO$_2$ film is replaced by a SnO$_2$ film whose outer crystallite surface is covered with an ultra-thin layer of MgO [8–11]. These cells attain efficiencies of

the order 6.5–7%, although cells made entirely out of SnO$_2$ have efficiencies of the order 1% [8]. The ultra-thin layer of MgO on the surface of SnO$_2$ crystallites seem to acts as a barrier preventing the recombination of the electrons injected to SnO$_2$ with acceptors in the electrolyte. It is important to assess the stability of this cell, especially to see if the ultra-thin MgO barrier remains intact during prolonged storage or operation of the cell. In this note we summarize experiments conducted over the past 4 years to assess the stability of the SnO$_2$/MgO cell. It is found that compared to the TiO$_2$ cell, the SnO$_2$/MgO cell is less sensitive to degradation of the dye and the electrolyte by UV light. Use of an electrolyte containing ethylene carbonate enabled easy comparison of the degradation rates. The effectiveness of the MgO layer on SnO$_2$ remains intact and there is no evidence that it undergo any deterioration during prolonged operation or storage of the cell.

2. Experimental

SnO$_2$/MgO films were deposited on conducting fluorine doped tin oxide glass (FTO) plates (sheet resistance 13 Ω/

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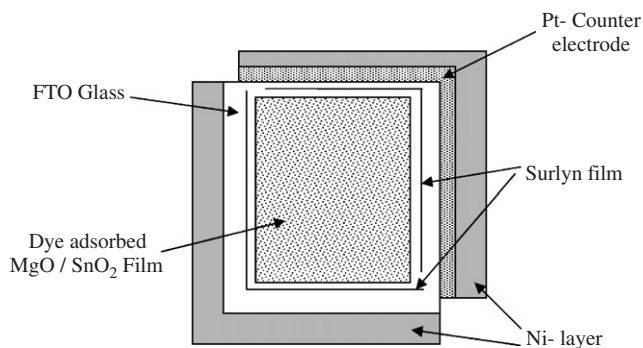
Fig. 1. Schematic diagram showing the construction of the large area dye-sensitized solar cell.

Fig. 2. *I–V* Characteristic of dye-sensitized solar cell made from (a) SnO_2 (b) SnO_2/MgO (c) TiO_2.

sq) by the procedure described below. Colloidal SnO_2 aqueous solution (Alfa Chemicals, 15% SnO_2 colloidal in H_2O, 10 ml) is ground with 75 mg of anhydrous MgO, gradually adding glacial acetic acid to dissolve all MgO. The mixture is dispersed in 100 ml of ethanol and ultrasonically agitated for 30 min. Solution is sprayed onto conducting FTO glass plates (1.5×0.5 and $4 \times 7 \, cm^2$ to form cells of area active area 0.25 and $10 \, cm^2$, respectively) heated to 150 °C and sintered in air at 550 °C for 30 min. The size of SnO_2 crystallites in the film was 3–5 nm and the thickness was maintained at ~10 μm. Films were coated with the dye by soaking them in a 3×10^{-4} M solution of $RuL_2(NCS)_2$: 2TBA (Solaronix) in ethanol for 12 h. Lightly platinized conducting FTO glass counter-electrodes were heat pressed onto the dyed plates interposing a window cut out of Surlyn. The electrolyte (0.5 M 4-tert-butylpyridine, 0.5 M tetrapropylammonium iodide, 0.1 M iodine, in 4:1 ratio mixture of ethylene carbonate and acetonitrile) was introduced through vents in the Surlyn window. Subsequently the vents were also sealed with Surlyn. In the case of the large cells, two adjacent edges of the both electrodes were nickel plated to improve the current collection (Fig. 1). *I–V* characteristics of the cells were recorded using a Keithly source meter (Keithly 2000). Some large area cells were continuously illuminated using OSRAM compact fluorescent lamps (CFL) or exposed to sunlight and short-circuit photocurrent (I_{sc}), open-circuit voltage (V_{oc}) and efficiency (η) were recorded at suitable intervals of time. Light intensities were measured using an Eko Pyranometer. For comparison the efficiency of a TiO_2-based cell with the same electrolyte was measured under identical conditions. The TiO_2 film for these cell was a made by screen printing a paste of Degussa P25 TiO_2 powder and hydrolysed titanium isopropoxide on FTO glass and sintering at 430 °C for 35 min.

3. Results and discussion

Cells of area $0.25 \, cm^2$ were found to have efficiencies of the order 6.5–7% at AM 1.5, $1000 \, W \, m^{-2}$ illumination (*I–V* characteristics of a typical cell is shown in Fig. 2 and
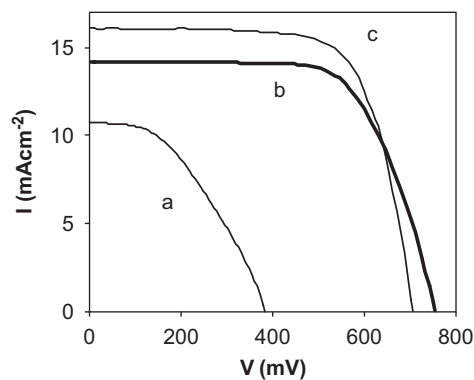
Table 1
I–V parameters of SnO_2, SnO_2/MgO and TiO_2 cells of active area $0.25 \, cm^2$ corresponding to the curves shown in Fig. 2

	V_{oc} (mV)	I_{sc} (mA cm^{-2})	FF%	η (%)
SnO_2	388	10.74	41.9	1.74
MgO/SnO_2	758	14.21	67.0	7.21
TiO_2	705	16.08	70.8	8.03

I–V parameters are summarized in Table 1). For comparison the *I–V* characteristics of a TiO_2 based cell measured under identical conditions are also presented in the same figure. The efficiency reached the highest value when 75 mg of MgO is incorporated into 10 ml of the colloidal SnO_2 solution, corresponding to a MgO layer average thickness of the ~0.2 nm. As the optimum energy conversion efficiency happens to be highly sensitive to the thickness of the MgO shell on SnO_2, the amount of MgO needed to get the highest efficiency may depend on the sample of MgO used (MgO absorbs moisture and carbon dioxide). Fig. 3 shows the time variation of the I_{sc}, V_{oc} and η of a large cell ($10 \, cm^2$) exposed to light from a CFL lamp at intensity ~$400 \, W \, m^{-2}$. Cell was kept under short-circuit conditions and at time of each measurement V_{oc} and the efficiency was also recorded. After 550 days of continuous exposure to light, there was no evidence for deterioration of the cell. When similar cells were exposed to direct sunlight, the Surlyn sealing yielded within few days. As the temperature of the cell reached 45–55 °C on exposure to sunlight, we believe that the yielding of sealing was caused by heating. For comparison, similar cells made from TiO_2 were also examined. Here again sealed cells deteriorated in the same manner as SnO_2/MgO cells. In SnO_2/MgO cells, if one of the vents used to introduce the electrolyte is kept opened, significant changes in *I–V* parameters (apart from up and down fluctuations possibly originating from temperature changes) were not observed after 2 months exposure to direct sunlight (10 a.m. to 5 p.m. daily from February to March in Sri Lanka, intensity varying approximately between 600 and $1000 \, W \, m^{-2}$) provided the electrolyte is replenished. However, TiO_2-based cells
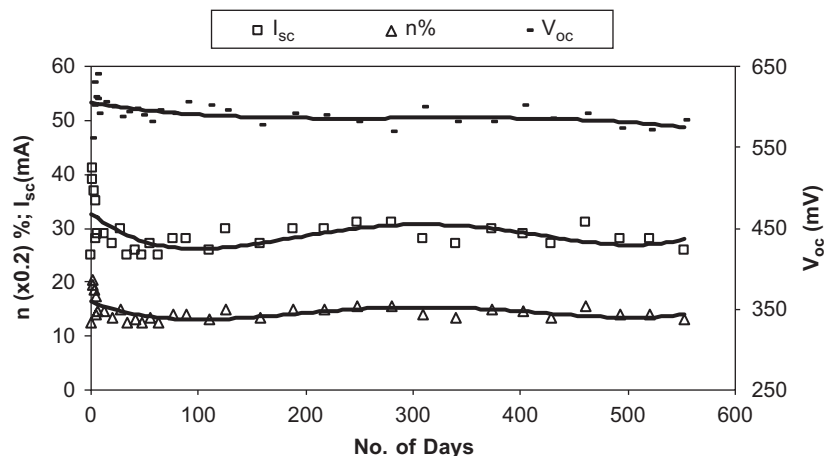
Fig. 3. A plot showing the values of short-circuit photocurrent, open-circuit voltage and efficiency (multiplied by 5) of a large area SnO_2/MgO cell measured during continuous illumination from a CFL lamp at intensity $400\,W\,m^{-2}$ for a period of nearly 550 days.

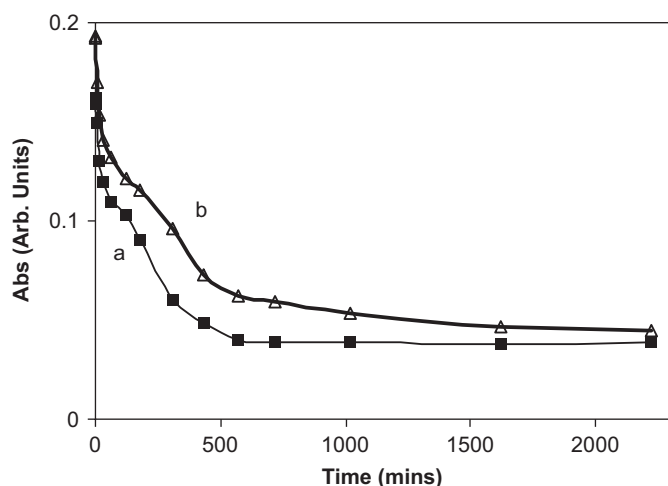Fig. 4. The change in absorbance at $550\,nm$ of (a) TiO_2 (b) SnO_2/MgO films coated with the dye during illumination with a xenon lamp (unfiltered at intensity $\sim 800\,W\,m^{-2}$)

with open vents behaved differently. Here, after few weeks of exposure, fading of the dye and decrease in I_{sc} was noticeable. We believe that fading of the dye is caused by entry of moisture and oxygen through the vent. As TiO_2 is more photo-catalytically active, faster degradation of dye by the UV light occurs in TiO_2 based cells. To test this hypothesis further, we exposed dye-coated TiO_2 and $SnO_2/$ MgO films to a xenon lamp at intensity $800\,W\,m^{-2}$. Fig. 4 compares the absorption spectra of the two films before and after exposure to the xenon lamp (intensity $\sim 800\,W\,m^{-2}$, in air relative humidity $\sim 65\%$) for different intervals of time. It is clear that the SnO_2/MgO film fades slowly compared to the TiO_2 film. When an electrolyte containing ethylene carbonate was used faster electrolyte degradation was noticeable in TiO_2-based cells. Here the yielding of the sealing and dye degradation was faster in TiO_2 cells exposed to direct sunlight. The products of photo-degradation of ethylene carbonate seem to promote photo-catalytic decomposition of the dye as well. In the experiment on photodegradation of the dye coated on SnO_2 and TiO_2 films (Fig. 5), both films reached nearly the same saturation level of absorbance. However, in the outdoor test SnO_2 cells showed better stability even after prolonged exposure to sunlight. The UV component in the xenon lamp is much higher compared to sunlight. Also in the experiment with the xenon lamp, the dye coating is continuously exposed to oxygen resulting in a faster degradation of the dye.

Fig. 5 compares the dark I–V curves of SnO_2 and $SnO_2/$ MgO cells in the presence and absence of the dye. The better rectification of the latter cell is a clear indication influence of the MgO barrier in suppressing recombination. We found that the rectification property of the SnO_2/MgO cell is not altered by prolonged exposure to light, changes of temperature or aging. This observation indicates that the MgO outer shell on SnO_2 is of permanent nature. An unsealed cell that was intermittently tested in sunlight and solar simulator light for more than 2.5 years regained the original efficiency when the cell was washed with acetonitrile and replenished with the electrolyte. An electrolyte based on ethylene carbonate was used as it enabled easier comparisons because of the poor chemical instability of this material. When the efficiency of a SnO_2/MgO cell with a more state-of-the-art electrolyte (0.6 M dimethylpropyl imidazolium iodide + 0.1 M LiI + 0.05 M I_2 + 0.5 M t-butylpyridine in methoxyacetonitrile) was measured, we could notice any improvements.

4. Conclusion

DS SnO_2/MgO cell was found to be stable on storage as well as exposure to direct sunlight. The extent of dye degradation by UV light is found to be lesser compared to the TiO_2-based cell. When an ethylene carbonate containing electrolyte was used, electrolyte decomposition and gas
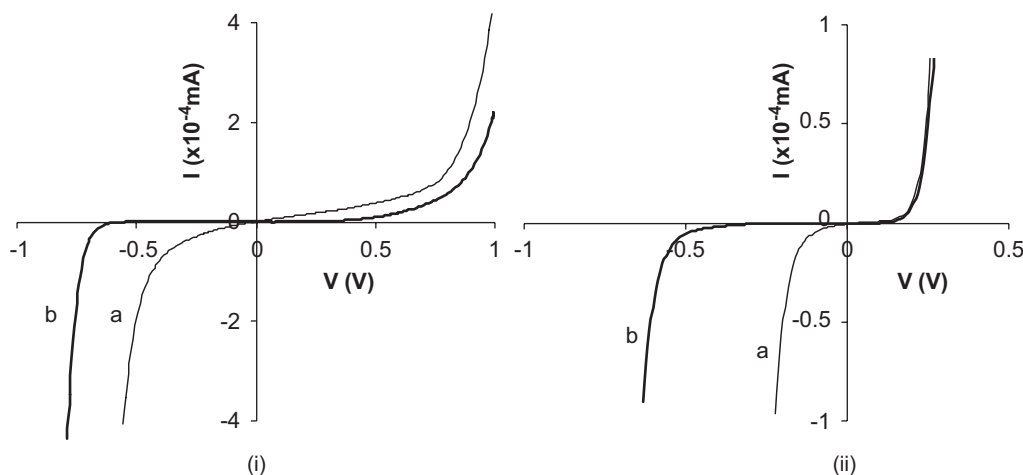
Fig. 5. The dark *I–V* curves of solar cells in (i) the presence of the dye (a) SnO_2 and (b) SnO_2/MgO and (ii) absence of the dye (a) SnO_2 and (b) SnO_2/MgO (cell area = 1 cm^2).

accumulation was found to be less pronounced in the SnO_2/MgO cell.

There is clear evidence that the ultra-thin barrier of MgO on the surface of SnO_2 crystallites is permanent. Efficiencies of the order 6.5–7% are readily achievable, but improvement above this figure seems to require difficult fine tuning of the thickness and the evenness of the MgO layer. Optimum efficiency is critically sensitive to the thickness of the MgO barrier and its uniformity.

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