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Effect of molecular filtering and electrolyte composition on the spatial variation in performance of dye solar cells

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ABSTRACT

It is demonstrated that the molecular filtering effect of TiO_2 has a significant influence on dye solar cell (DSC) performance. As electrolyte is injected to a DSC, some of the electrolyte components adsorb to the surface TiO_2 (here 4-*tert*-butylpyridine and 1-methyl-benzimidazole) and accumulate near the electrolyte filling hole resulting in varying electrolyte composition and performance across the cell. The spatial performance distribution was investigated with a new method, the segment cell method. Not only is the segmented cell method simple and cheap when compared to the only other method for examining spatial variation (photocurrent mapping), it also has the major advantage of allowing the spatial variation in all other operating parameters to be assessed. Here the molecular filtering effect was to influence the cell performance in case of all the five studied electrolytes causing up to 35% losses in efficiency. Raman spectra indicated that the loss in photocurrent in the electrolyte filling was in correlation with the loss of thiocyanate ligands suggesting that dye regeneration may also be a significant factor in addition to electron injection in some of the cells. There were also shifts in the absorption spectra the photoelectrodes which further supported changes in the thiocyanate ligands. Besides absorption changes, there were additional shifts in the IPCE spectra which may relate to deprotonation of the dye. The efficiency losses were reduced to ~10% with contemporary electrolyte compositions.

1. Introduction

Dye solar cells (DSCs) are an attractive alternative to conventional *pn*-junction solar cells due to their cheap materials and easy manufacturing methods which can even be transferred to roll-to-roll mass production. Over 10% efficiencies have been demonstrated in small scale [1] and the transferring of the DSC technology to large scale has begun. The efficiencies are lower in large scale [1,2] as in part due to resistive losses from current collection as the cell size increases. In some studies, the differences in the performance of small cells (2.5 cm^2 active area) and modules (900 cm^2 active area) have actually been relatively small [2–4]. However this appears not be generally the case, for example our earlier results showed that significant efficiency losses (~20%) occur due to the electrolyte filling when the cell size is increased from 0.4 cm^2 to only 1.2 cm^2 [5], the smaller area is typical of the size tested for record efficiency cells. The changes were independent of resistive losses.

That initial study indicated that 4-*tert*-butylpyridine (4-tBP), a common additive in DSC electrolytes, adsorbs to the TiO_2 unevenly so that the area near the electrolyte filling hole had the highest concentration which decreases in the regions further away from the hole [5]. Moreover, it was noted that these differences did not decrease over time but rather increased [5]. The spatial variation of cell performance that results from electrolyte filling represents a major challenge for the commercialization of DSCs. Even relatively minor reductions in the efficiency of manufactured modules can have a very significant impact on the economic viability of the technology. To avoid these performance losses, either the electrolyte composition or its application method need to be developed.

In this contribution we focus on modification of the electrolyte composition to avoid, or at least reduce, the spatial losses caused by the conventional electrolyte filling method without compromising the cell efficiency. The main task is to investigate which of the commonly used electrolyte components have tendency to cause spatial performance variation. We use the segmented cell method that was introduced briefly in our previous study shown in the context of the initial results [5]. The dimensions of the segmented cells used in this study are roughly similar to a single stripe of a

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DSC mini module such as the ones used in our previous study [6]. In addition to detecting the spatial variation in the photovoltaic performance with segmentation, Raman and incident-photon-to-current-efficiency (IPCE) measurements are executed to further investigate the underlying causes of the performance variation.

2. Experimental methods

2.1. Cell preparation

The different electrolyte compositions are given in Table 1. The chemicals used for the preparation of the electrolytes were: iodine (I_2, Sigma–Aldrich, ⩾99.8%), 4-*tert*-butylpyridine (4-tBP, Aldrich, 96%), 1-Methyl-benzimidazole (NMBI, Aldrich, 99%), Lithium iodide (LiI, Aldrich, 99.9%), 1-propyl-3-methylimidazolium iodide (PMII, Solaronix), Guanidinium thiocyanate (GuSCN, Sigma, ⩾99%), 3-methoxypropionitrile (MPN, AlfaAesar, 99%). A commercial electrolyte high stability electrolyte (HSE) by DyeSol was also tested.

The photoelectrodes consisted of a screen printed thermally treated TiO_2 film (DyeSol 18NR-T, two layers with total thickness ~7 μm) deposited on fluorine-doped tin oxide (FTO) coated glass substrates that were sintered at 450 °C for 30 min. After that the films were sensitized in a dye bath using a dye solution consisting of 0.32 mM *cis*-bis(isothiocyanato)bis(2,2′-bipyridyl-4,4′-dicarboxylato)-ruthenium(II) bis-tetrabutylammonium (DyeSol) in ethanol (99.5 wt.%). The counter electrodes were thermally platinized FTO glass substrates. Detailed specifications of the electrode preparation are given elsewhere [5]. The electrodes were sealed with a 25 μm thick Surlyn ionomer resin film spacer (DuPont) and the electrolyte was injected to the cell through filling channels drilled in the counter electrode substrate. The filling holes were sealed with a Surlyn foil and a thin cover glass.

2.2. Segmented cells

In the analysis we used 4-segment cells in which the conductive FTO layer of the substrates was divided into electrically isolated segments with laser scribing (Fig. 1). The 4-segment cells are compared with simultaneously prepared small single cells having the same geometry and size of the dyed TiO_2 layer as in an individual segment. The segments are numbered from 1 to 4, the one nearest to the electrolyte filling hole is marked as segment 1 as indicted in Fig. 1a. The segmented cells were prepared with sufficient randomization to avoid systematic errors in the examination of the main effect, here the electrolyte filling direction. In this work special care was taken in this regard: for instance the electrolyte was filled from different ends of the different cells so that neither the application of the TiO_2 film nor the position in the oven during the heat treatments can have any effect even though their effect is expected to be negligible. Furthermore, it was tested that the measurement order of the segmented cell does not affect the results.

The basic idea of the method is to section the electrodes of the cell to electrically isolated areas that share the same electrolyte layer, and from each of them all the photovoltaic parameters can be measured independently. This is a major advantage compared to previous techniques; for instance with photocurrent imaging only spatial variations in the short circuit current can be observed [7,8]. There are, however, some limitations that need to be taken into account: If the electrical cuttings on the photoelectrode and counter electrode are not aligned accurately enough, ions in the electrolyte can move between the different segments when current is drawn from the cell and it can cause drifts in the data. We calculated using a 2D dye solar cell model [10] that the maximum tolerance for the misalignment is in the range of 10 μm. In practice this means that it is not practically possible to get the electrodes aligned that well and there will be drifts. The drifts are, however, relatively slow; it takes almost 10 min for the ions to diffuse over the distance of 0.5 mm between the adjacent segments [9] and here the distance between the segments was even larger (2 mm). This means that short measurements (in the range of a couple of minutes) such as IV and IPCE are not significantly affected whereas hours long electrochemical impedance spectroscopy (EIS) measurements very likely are. The drift of ions, as it affects also tri-iodide, will cause a clear change in the electrolyte color meaning that besides modeling, their effect can be also visually monitored. With proper selection and monitoring of the measurements, the segmented cell method is very efficient in the study of spatial variation in particular when the changes between the segments are very large as in this study.

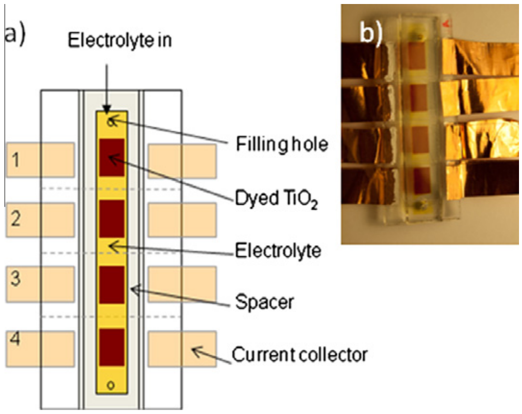

Fig. 1. (a) Schematics and (b) a photo of a four segment cell. The segments are electrically isolated (marked by dashed lines in the schematics) but share the same electrolyte layer.

Table 1
Electrolyte composition given as molar concentrations.

Electrolyte name	I_2	TBP	NMBI	LiI	PMII	GuSCN	Solvent
TBP–LiI	0.05	0.5		0.5			MPN
NMBI–LiI	0.05		0.5	0.5			MPN
NMBI–PMII	0.05		0.5		0.5		MPN
NMBI–PMII–GuSCN	0.05		0.5		0.5	0.1	MPN

2.3. Measurements

The photovoltaic performance was measured using a solar simulator providing 1000 W/m^2 AM1.5G equivalent light intensity.

IPCE measurements and transmission spectra were taken using Model QEX7 Solar Cell Spectral Response Measurement System from (PV Measurements, Inc.) in DC mode without bias illumination. IPCE Spectra were measured in the range of 300–800 nm with intervals of 20 nm from both counter-electrode (CE) and photoelectrode (PE) side at the short circuit conditions. A silicon photodiode was used for calibrating the system in the 300–1000 nm wavelength range.

The Raman spectra of the DSCs were measured using a HORIBA Jobin Yvon LabRam 300 micro-Raman spectrometer equipped with a 514 nm argon laser. The power of the argon laser was 1.24 mW which was reduced to 1% using a filter in the measurements. The spot size was approximately 5000 μm^2 leading to laser light intensity of about 2500 W/m^2. Here we used the same laser source with same incident power, using the same detecting system, the same 5 s time for a single measurement, and following all the measurement procedures in a similar fashion for all the samples in order to maximize the comparability of the data. The FTO glass in the actual segmented cells was too thick to get enough scattered