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The effect of electrolyte filling method on the performance of dye-sensitized solar cells

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Abstract

The effect of electrolyte filling method on the performance of the dye-sensitized solar cells is investigated with the segmented cell method, a recent technique which is very simple but effective as it can be used to examine all the photovoltaic characteristics. The electrolyte filling techniques compared were single injection, which is typically used in small laboratory cells, and pumping the electrolyte through the cell several times, which is often used for larger cells and modules. Significant photovoltage and photocurrent variations occur with the repeated pumping of the electrolyte in the cell preparation. Transient and charge extraction measurements confirmed that the differences in open circuit voltage were due to the shifts of the TiO₂ conduction band and time correlated single photon counting confirmed that the reduction of short circuit current was largely due to reduced electron injection correlated with the increasing conduction band edge in the studied cases. This was interpreted as an effect of molecular filtering by the TiO₂ causing an accumulation of electrolyte additives (*4-tert*-butylpyridine and benzimidazole) near the electrolyte filling hole, the concentration of which increased with repeated pumping of the electrolyte. Interestingly, spatial variations were seen not only in the relative TiO₂ conduction band energy but also in the density of trap states. In this contribution it is demonstrated how the changes in the conduction band can be separated from the changes in the density of trap states which is an essential for the correct interpretation of the data.

Keywords: Dye-sensitized; Electrolyte filling; Up-scaling; Spatial distribution; Conduction band.

1. Introduction

Dye-sensitized solar cells (DSSC) are an emerging photovoltaic technology and their commercial manufacture has begun. One of the key benefits of DSSCs is that they can be produced using several different materials and methods. To optimize the device performance, the response to material and preparation choices should be understood. One important area is the impact of electrolyte composition and the method of its deposition for which several different methods have been suggested in the literature. Simple injection using either two holes or just one hole and a vacuum pump is typically employed in small scale. In large scale manufacturing of glass based modules, the electrolyte is often pumped through the cell several times.¹⁻³

Whilst a significant amount of research has investigated the effect of different electrolyte compositions in laboratory sized cells, neither the effect of electrolyte composition on up-scaling nor the effect of electrolyte filling method have been appreciated prior to our initial study.⁴ That work indicated that electrolyte filling caused spatial variation in performance which led to 20 % efficiency loss in larger cells (active area ~4 cm long) compared reference cells (active area ~1 cm long).⁴ In typical DSSC modules, the electrolyte passes an even longer distance (from ~10 cm up to 2 m)¹⁻³ and thus the effects could be even larger. The main effect was gradual loss of open circuit voltage from the electrolyte filling hole to the other end of cell. This effect was related to the uneven distribution of 4-tBP that arose from the molecular filtering effect of the TiO₂ during a single fill. The spatial distribution did not equalize over time demonstrating the

permanence of the effect.⁴ Our later study indicated that effect could be reduced but not avoided by selection of suitable electrolyte composition.⁵

Since the spatial variations are related to electrolyte filling (as well as electrolyte composition), it suggests that the selection of electrolyte application method could affect the cell performance in particular at larger scale. The purpose of this study is to examine the effects of two most commonly used electrolyte filling methods: simple injection and repeated pumping. Here two electrolytes are employed one has additives similar to those often used in high performance cells (tBP, LiI, GuSCN, PMII) whereas the other is a composition typically used for high stability electrolytes (BI, GuSCN, PMII).⁶ The latter one of these is similar to the electrolyte that resulted in one of smallest spatial performance distribution and the highest overall efficiency in our previous work.⁵

In this investigation we apply the segment method ⁴ which was developed in our initial evaluation of the spatial distribution losses and discussed in detail in our previous study.⁵ The main advantage of the technique compared to the only other approaches for detecting spatial variations (such as photocurrent imaging)⁷⁻¹⁰ is that segmented cell method allows the examination of all the photovoltaic parameters separately in the different parts of the cell. The other major benefit of segmented cell method is that neither specialized equipment nor complex analysis is needed to define the spatial distribution. The segmented cells are used to examine the conditions present in a single strip cell for example as used in a series connected module and are thus related to the changes in performance seen in the up-scaling of DSSCs.

Time correlated single photon counting (TC-SPC) and transient optoelectronic characterization with charge extraction measurements are used to explain the influence of electrolyte injection procedure on device performance. We show that the density of electronic trapping states and conduction band position in the TiO₂, the electron injection efficiency, and electron recombination kinetics can all be influenced by molecular filtering. These factors contribute to the observed spatial variations in performance.

2. Experimental methods

2.1. *Cell preparation*

The photoelectrodes were deposited with doctor blading using commercial TiO₂ paste (18NR-T, Dyesol) on fluorine-doped tin oxide (FTO) glass substrates (TEC-15, 3 mm thick, Hartford Glass Co inc.) that were sintered at 450 °C for 30 min (resulting thickness $7.6 \pm 0.4 \mu\text{m}$). The sintering was followed by a TiCl₄ treatment after which the films were sintered again at 450 °C for 30 min as in literature.¹¹ When the films had cooled down to about 70 °C, they 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 (N-719, DyeSol) in ethanol (99.5 wt-%). The counter electrodes were prepared on FTO glass substrates using 5 mM H₂PtCl₆ (Sigma-Aldrich) in 2-propanol solution and heat treated at 390 °C for 15 min. 25 μm thick Bynel ionomer resin films were employed.

Here two different electrolytes were studied: One referred here-in as tBP-LiI contains 0.5 M 4-*tert*-butylpyridine (4-tBP, Aldrich, 99 %), 0.03 M Lithium iodide (LiI, Aldrich, 99.9 %), 0.1 M Guanidinium thiocyanate (GuSCN, Fluka \geq 99 %), 1.0 M 1-propyl-3-methylimidazolium iodide (PMII, AlfaAesar, 98 %), and 0.03 M with Iodine (I₂, Sigma-Aldrich, \geq 99 %) in 3-methoxypropionitrile (MPN, Dixie Chemical Company). The one as referred to here-in as BI consists of 0.3 M benzimidazole (BI, Aldrich, 98 %), 0.05 M GuSCN, 0.8 M PMII, and 0.05 M with I₂ in MPN.

The electrolytes were injected through filling holes drilled in the counter electrode substrate. The effect of pumping electrolyte through the cell was examined in some cells by the injecting to completely fill the device followed by removing the electrolyte from the other end of the cell using a manual vacuum pump. This cycle was repeated 10 times. After the final filling cycle, the filling holes were sealed with another Bynel foil and a thin cover glass. The sequential pumping (fill/remove) used here differs slightly continuous flow filling which is used commercially. The former was employed here as the cells were measured during the filling process to investigate the filling process in more detail and required sequential steps in the filling. The names for the cells with the two electrolyte compositions and filling methods are listed in Table 1.

The spatial performance variations in the cells were examined using segmented cells (Figure 1). To achieve this, the transparent conducting layer (TCO) on the glass substrates was cut to form the electrically isolated sections. Here we employed 4-segmented cells and the different segments are numbered consecutively starting from that

closest to the electrolyte filling hole. Multiple cells of each kind were made to verify the repeatability of the effects.

2.2. *Measurements*

The photovoltaic performance was measured using a solar simulator providing 1000 W/m² AM1.5G equivalent light intensity described in detail in elsewhere.¹² The performance of the cells (J_{SC} and V_{OC}) was studied during the cell assembly using a 10 W metal halogen lamp (Solarc) giving approximately 0.7 Sun equivalent light intensity.

The time-correlated single photon counting (TC-SPC) method and the system settings are described in detail elsewhere.¹³ The measurements were carried out with Jobin Yvon IBH Fluorocube laser system using 467 nm laser for excitation and a 695 nm long pass filter for emission detection.

Small perturbation photovoltage and photocurrent transients and charge extraction measurements were made to assess the transport and recombination of electrons in the device at a range of bias light intensities. The concentration of charge n in the device for each condition (short circuit (SC) and open circuit (OC)) was also estimated using charge extraction. This technique involves running a device under steady-state conditions at either OC or SC conditions, the light source is then rapidly switched off and the cell set to short circuit conditions (if it is not already at short circuit). The current that is collected from the device after switching the light off is then measured as it drops to zero.

Integrating this current transient with respect to time yields an estimate of the concentration of charge stored in the device if electron collection losses are relatively minor. In other words n_{SC} and n_{OC} are the density of electrons in the TiO_2 phase under those conditions (SC and OC), relative to the dark condition at short circuit. Detailed descriptions of the measurement setup, course of measurements and the theory behind the measurements are given elsewhere.¹⁴⁻¹⁸

3. Results and discussion

3.1. *Photovoltaic performance*

The effect of pumping electrolyte through the cell was examined during the cell preparation. The short circuit density (J_{SC}) and open circuit voltage (V_{OC}) were recorded after each cycle using a 0.7 sun light source (Figure 2). When the electrolyte was inserted to the cell the first time (i.e. filling cycle 1), there was a decrease of V_{OC} along the electrolyte filling direction from segment 1 to segment 4 with both tested electrolytes (Figures 2a and 2b). Pumping the electrolyte repeatedly increased V_{OC} significantly in all of the segmented and reference cells as shown in Figures 2a and 2b. The local increase of V_{OC} varied from 50 mV to over 200 mV during the filling procedure i.e. the difference between filling cycle 1 and 10. The V_{OC} increase became smaller with every filling cycle and hence at 10 cycles the change in V_{OC} was only minor.

Although the effect of pumping on V_{OC} was similar for both electrolytes, the effect on J_{SC} varied significantly: With BI electrolyte, there was an increasing trend of J_{SC} from

segment 1 to segment 4 at the first cycle (Figure 2c). The photocurrent increased up to 15 % following with repeated pumping of the electrolyte through the cell. Contrary to BI cells for the tBP-LiI-10F cells, J_{SC} was quite similar in the segments at filling cycle 1 and it dominantly decreased as a function of filling cycles (Figure 2d). There is also some initial increase in the segment 4 of the tBP-LiI-10F cells, but after the first few cycles it also started to decrease. In segment 1 of the tBP-LiI-10F, there was practically a linear decrease of J_{SC} (total 20 %).

The photocurrent and photovoltage variation in the cells with single electrolyte fill (i.e. those with SF electrolyte) was very similar to that shown by the 10F cells at the first filling step as to be expected. Thus it is not shown in Figure 2.

After a stabilization of a few days, the photovoltaic performance of the cells (Table 2) followed the trends measured during the cell preparation (Figure 2) with some minor differences. It is common that the performance of the cells changes to some extent before reaching their steady state; this typically takes at least overnight. After the stabilization period the performance of typical DSCs such as these does not change much/quickly if not placed under significant stress (e.g. temperatures of 80 °C). Note that Table 2 values are measured with standard AM1.5 solar simulator opposed to Figure 2. Overall, the segmented 10F cells were average about 10 % higher efficiencies compared to the corresponding segmented SF cells. This is dominantly due to the higher V_{OC} in these cells. This improved efficiency of the 10F segmented cells may explain the reason why the pumping has become a common procedure in fabrication of larger cells. The fact such

significant improvements can be gained by pumping electrolyte through the cell have not, however, been presented previously in the literature and consequently the mechanisms behind this improvement have not been investigated either.

One difference between the data collected during preparation and after stabilization is that while 10F cells appear quite stable, SF cells evolve with time for example the V_{OC} in all segments of the SF cells increased about 100 mV. Another interesting difference is that the performance of the small reference cells changed more during the stabilization period (i.e. larger increase in V_{OC} and larger decrease in J_{SC}) compared to the segmented ones. This suggests that the performance of a cell may also depend on cell geometry in addition to electrolyte filling method. Detailed analysis of the possible geometrical effects is, however, out of the scope of this contribution and in the later sections the focus is on understanding the spatial variations in the segmented cells.

3.2. *Molecular filtering effect*

There are two main trends in the photovoltaic data on the stabilized cells (Table 2): Firstly, in all the segmented cells, the V_{OC} is initially the highest near the electrolyte injection hole (i.e. in the case of single fill) and further increases when the electrolyte was pumped through the cell (i.e. in the case of 10 fills). Secondly, contrary to this, the photocurrent is initially quite similar across the cell but pumping electrolyte through the cell mainly decreases J_{SC} in particular near the electrolyte filling hole. As suggested in our studies,^{4,5} it appears that the TiO_2 layer can be thought as kind of a molecular filter which adsorbs some of the electrolyte components leaving an inhomogeneous electrolyte

composition and TiO₂ surface across the cell. This effect is known to occur in chromatography, but other than in our previous studies,^{4,5} its significance for DSSC manufacture has not been recognised. Spatial variations in the electrical performance of the cell would then be caused by the spatial variations in the electrolyte composition induced by the electrolyte filling.

Whilst the direct measurement in the changes in the electrolyte composition would be desirable, that has been difficult to achieve: Basically only non-destructive methods are suitable for these cells as the opening procedure of the cells and the preparation of the sample for the measurements would likely corrupt the result. In our previous work, in-situ Raman measurements were conducted on the segmented cells to investigate the surface composition.⁵ Unfortunately, the key electrolyte components such as tBP or N-methyl-benzimidazole (NMBI) did not show a characteristic response in the Raman spectra of a complete DSSC and thus their spatial distribution could not be directly verified.⁵ In this contribution the focus is on the understanding the mechanisms causing photovoltage and photocurrent variation. The electrolyte components affect the electrical performance of the cell in a particular manner and from that it is possible to evaluate which electrolyte components are dominating the effect. This approach is used in the later sections for investigations of the electrolytes.

Whilst the molecular filtering phenomenon is not in this contribution directly proven in the case of the (colourless) electrolyte additives, the existence of the phenomenon can be easily shown by using a colourful agent. To demonstrate the effect, a dye solution (1 mM

Coumarin 343 (Aldrich) in MPN) was added to the cell in a similar way to the electrolyte filling process. Figure 3 shows that there was a visible spatial distribution as the dye solution was inserted to the cell. The highest concentration of dye was near the electrolyte filling hole which decreased towards the other end of the cell as to be expected based on our hypothesis on the filtering effect. With repeated pumping the overall amount of dye could be increased and difference between the segments decreased (Figure 3). This demonstration with the dye solution illustrates clearly the concept of the molecular filtering effect by the TiO₂ film.

It should be remembered that although the filtering is a good simplified model to understand the phenomena, the actual processes are in reality more complex: Firstly the spatial distribution of each electrolyte component depends on their individual adsorption time in relation to the speed in which the electrolyte is filled. In other words if the adsorption time is very short compared to the electrolyte filling procedure, the spatial distributions are likely to be very large. Secondly, there is only limited amount of sites to which to electrolyte components can adsorb creating the situation of competing adsorbents.

3.3. *Photovoltage variation*

The photovoltage in a device is limited by the recombination of charge (electrons), the maximum photovoltage is reached when the total rate of electron recombination is equal to the rate at which electrons are injected. The photovoltage corresponding to the point where this equilibrium is reached is determined by two factors – the recombination

lifetime of the free electrons, and the position of the TiO₂ conduction band relative to the electrolyte redox level. A description of this process can be found elsewhere.¹⁹ The maximum photovoltage would not exceed the TiO₂ conduction band edge because the high concentration of free electrons corresponding to the high voltage would lead to an increasingly high recombination rate. Thus changes in a cell V_{OC} can be considered in terms of two factors: a shift in the TiO₂ conduction band (CB) position relative to the electrolyte redox couple, and a change in the recombination kinetics of the electrons in the film (including current leakage via photoelectrode substrate to the electrolyte). Electrolyte additives which shift the CB up relative to the electrolyte potential will lead to an increase in the V_{OC} if electron recombination kinetics are not influenced significantly. The relative CB position can be estimated by the total charge concentration or its derivative the chemical capacitance.

Before going to the actual analysis of the CB edge shift, the density of trap states is investigated. The total electron density n is composed of trapped electrons n_T and conduction band electrons n_c and the two populations are thought to be in dynamic equilibrium. Figures 4a and 4b show the typical power law relationship between total charge density at short circuit (n_{SC}) and J_{SC} in all the devices, this is consistent with an exponential distribution of trapping states below the CB edge which is commonly seen in DSSCs (Figure 4c). In this model the concentration of trapped electrons is thought to be much greater than the concentration of conducting electrons ($n_T \gg n_c$). The key issue to note in Figure 4a is that the mean (trapped) electron concentration as a function of photocurrent was basically unchanged by the filling procedure of BI in the segments. In

contrast, the segmented cells with tBP-LiI electrolyte in Figure 4b show that the charge density for a given current decreases along the electrolyte filling direction and is increased as a result of repeated electrolyte pumping. This factor of three difference in n_{SC} between the first segment of the tBP-LiI-10F cell and the fourth segment of tBP-LiI-SF cell is indicated in Figure 4b with an arrow. The important conclusion of this is that in the case of tBP-LiI cells the electrolyte additives appear to be changing electron trap states. It is critical to take this into account for the correct interpretation of the data as the changes in the density of trapped states interfere with the measurements of CB. Next it is shown how the data can be corrected by examining the charge concentration extracted from short circuit operating conditions as a function of photocurrent.

This information can be interpreted by using J_{SC} as a proxy for the mean concentration of conduction band electrons n_c . This can be justified by Fick's first law of diffusion if we assume that the free (conduction) electron diffusion coefficient (D_0) is constant in all devices so that

$$J_{SC} = qD_0 \frac{dn_c(x=0)}{dx} \quad (1)$$

where q is the electronic charge and x is the distance from the photoelectrode substrate. The term $dn_c(x=0)/dx$ represents the gradient of electrons flowing through the substrate/TiO₂ film contact, this is proportional to the current of the device when taking into account the diffusion constant and the electron charge. Since under short circuit conditions the concentration of electrons at the substrate ($x = 0$) is approximately zero we may make a further assumption: that $dn_c(x=0)/dx$ is proportional to the mean

concentration of conducting electrons. This is reasonable since the film thickness and D_0 are constant so that more conducting electrons should lead to a higher electron gradient given the constraint that $n_c(x=0) \approx 0$. The assumption is valid if the recombination losses during electron collection are relatively minor. Thus the short circuit photocurrent should be proportional to the mean conduction band electron concentration ($n_c \propto J_{SC}$).

Under most operating conditions, the concentration of conducting electrons is thought to be directly related to the total concentration of electrons in the device. As mentioned above the majority of the charge is thought to reside in sub conduction band traps at dynamic equilibrium with the conducting charge. Evidence suggests (confirmed by the data presented here) that the concentration of trapped charge (which is approximately equal to n_{SC} at short circuit or n_{OC} at open circuit since n_{SC} or $n_{OC} \gg n_c$) is related by a power law to the concentration of conducting charge, n_c .²⁰

Differences in the total electron concentration at short-circuit n_{SC} as a function of J_{SC} can thus be interpreted in terms of changes in the density of trapping states. This is because if J_{SC} is a measure of n_c and we do not expect that the total density of conduction band states in will be influenced by the electrolyte composition or filling procedure then any changes in n_{SC} for a given current are likely to be related to a variation in the density of trapping states below the conduction band. Hence the increased concentration of total charge in the first relative to fourth segments and in the segments with repeated electrolyte pumping relative to those with only a single fill seen in Figure 4b implies that

molecular filtering of additives from the tBP-LiI electrolyte leads to an increase in the density of trap states.

If no change in the total density of trap states is inferred from the J_{SC} vs. n_{SC} data, then any changes in the total charge density at open circuit (n_{OC}) plotted vs. V_{OC} imply that the TiO_2 conduction band has shifted relative to the electrolyte redox potential. The magnitude of this shift (ΔE_c) is then given by the change in V_{OC} for a given concentration of charge (n_{OC}) in the device since the concentration of charge is proportional to the density of electronic states. If there are changes in the density of trap states, they also affect n_{OC} in proportion to the change of n_{SC} . Thus changes in the density of trap states overlap the changes in CB in a plot of n_{OC} vs. V_{OC} and the changes in the density of trap states could be therefore easily mistaken for changes in CB. Therefore it is important to separate these two effects for correct interpretation of the data. Similar approach is used also in our other publication.²¹

The charge extraction data from open circuit plotted against V_{OC} plotted in Figure 5a shows that there are only small shifts in the conduction band position between the different segments in the case of the BI electrolyte. Larger differences are observed however between the relative CB positions of the BI-SF and BI-10F cells. The accuracy of the ΔE_c evaluation based on this data is about 10 mV and thus it is not purposeful to make comparison more accurately than that. Taking into account this error margin, the data in Figure 5a is in excellent agreement with the differences in the V_{OC} seen in the photovoltaic measurements shown in Table 2. This suggests that the changes in V_{OC} are

indeed due to shifts of the TiO_2 conduction band (illustration in Figure 5b) in the case of the BI electrolyte.

In the case of cells with the tBP-LiI electrolyte, the analysis of the electron concentration vs. V_{OC} data in Figure 5c is complicated by the changes in the density of trapping states inferred from Figure 4b. For quantitative comparison the changes in the total density of states need to be compensated for; in other words the Δn_{T} illustrated in Figure 4c needs to be corrected to determine credibly the changes in ΔE_{c} shown in Figure 5e. This can be done by using the ratio of charge at given J_{SC} (here 10 mA/cm^2) to multiply the charge density values at V_{OC} . Here tBP-LiI-10F segment 1 data was used as the reference point for these corrections. This effectively normalizes density of trapping states to the same value in all cell segments.

Figure 5d describes the charge density after correcting to normalize the density of trapping states values as function of photovoltage with tBP-LiI electrolyte. For a given normalized total electron concentration (e.g. $4 \cdot 10^{18} \text{ cm}^{-3}$) significant differences are observed as indicated by the arrow in Figure 5e. These shifts in the CB correlated quite well with the differences in V_{OC} measured in Table 2. For example the measured difference in photovoltage between tBP-LiI-10F segment 1 and tBP-LiI-SF segment 4 in Table 2 is 130 mV while Figure 5d indicates a difference of 135 mV. The shifts in Figure 5d imply again that shifts in CB are the cause of the V_{OC} differences (Table 2) between segments and between 10F and SF cells for tBP-LiI electrolyte except for the difference in segment 1 and 4 in the tBP-LiI-10F electrolyte. Thus overall the results imply that the

CB edge relative to the electrolyte redox potential is increased by the accumulation of tBP by molecular filtering.

For both electrolytes the large differences in final V_{OC} can be primarily explained by shifts of the TiO_2 conduction band, however it is also useful to check whether any variation in the electron recombination rate might also be expected to influence V_{OC} . Whilst the actual changes in the electron lifetime can be easily accessed in the case of BI electrolyte, this is not the case for the tBP-LiI electrolyte due to the changes in the density of trap states. That is because we want to compare recombination from the conduction band while the measurement is for all electrons. The ratio of trapped electrons changes in the case of tBP-LiI electrolyte between different segments and therefore the measured electron lifetime data does not allow direct comparison of the electron lifetimes. In contrast in the case of BI electrolyte, the ratio of trapped electrons remained constant between the different segments enabling a quantitative comparison of the electron lifetimes. Thus the electron lifetime analysis is here limited only to BI electrolyte. Figure 6 shows that with the cells containing BI electrolyte there is less than a factor of 2 difference in electron lifetime τ_n . This suggests that there are only minor differences in recombination in the BI cells which implies that recombination plays a less significant role in the changes of V_{OC} . In other words, the variations between the measured V_{OC} (Table 2) could be largely explained with the shifts of the TiO_2 conduction band and the mismatch between those was in the order of 10 mV for the BI electrolyte. Therefore the mismatch falls in the range of measurement accuracy (10 mV) for the evaluation of band shifts but it could alternatively/partly relate to the small differences in

τ_n . In general the conduction band shifts (Figure 5a) were perhaps slightly smaller (about 10 mV) compared to variation in measured V_{OC} (Table 2) and the minor effect of recombination could bridge the gap. The differences in recombination were qualitatively in the same direction as the unexplained part of the variation in V_{OC} for the BI electrolyte. In the case of tBP-LiI electrolyte, the electron lifetime analysis could not be made so we cannot confirm if there were such effects in that case.

We now briefly consider the effects of the electrolyte components we have used which can increase V_{OC} as reported in the literature. BI and tBP have been shown to shift TiO_2 conduction band up thus increasing V_{OC} .^{22,23} GuSCN has also been shown to increase V_{OC} , in contrast it is thought this occurs due to a significant reduction in the electron recombination rate which dominates over a secondary effect where the CB is shifted down.²⁴ As the increase of V_{OC} was due to a raised CB and not a reduction in recombination rate, it suggests the filling process predominantly affects photovoltage due to the accumulation tBP and BI by molecular filtering. In the context of the results presented here the decrease of the photovoltage range resulting from repeated electrolyte pumping (Figure 2a and b) would then relate to the saturation of the amount of tBP or BI (c.f. buffered solution) on the TiO_2 surface. Previously, it has been speculated that by increasing the concentration of tBP and BI, the amount of Li^+ able to intercalate to the TiO_2 decreases due to complex formation between Li^+ and tBP.²⁵ Hence in addition to actual an increase in the amount of tBP or BI, there could be additional loss of intercalated or surface bound Li^+ shifting the TiO_2 conduction band up further. The

effects of LiI are a likely cause to the larger spatial performance variations in the case of tBP-LiI electrolyte compared to BI (without LiI).

3.4. Photocurrent variation

Increases in the TiO₂ conduction band position relative to the electrolyte redox potential are likely to cause electron injection limitations and reduce photocurrent. Besides changes in the electron injection,²⁶⁻³² there are also other reactions which have been reported to affect photocurrent when changing the concentration of tBP, BI and Li⁺ such as regeneration of dye, light harvesting and electron collection.^{5,25,33,34} In our previous study, the relation between the thiocyanate (SCN) in the Raman spectra and the J_{SC} suggests that some of segmented cells may have suffered from dye regeneration problems.⁵ However in the present study this is not likely to be an issue since the presence of GuSCN in both electrolytes significantly increases the amount of SCN surrounding the dyes.⁵ In this section we investigate to what extent variation in electron injection efficiency influences the observed changes in J_{SC} . For this purpose we employ the time-correlated single photon counting (TC-SPC) measurements which allow quantification of electron injection efficiency.

The rate of photoluminescence from a cell is proportional to the population of excited dye molecules remaining following a short excitation pulse. Since dyes with excited states may either inject an electron into the TiO₂ substrate (with rate k_{inj}) or decay back to the ground state (with rate k_0) the observed rate of photoluminescent decay (k_{obs}) corresponds to the sum of these two processes: $k_{obs} = k_{inj} + k_0$. We define the observed decay rate as

being given by $k_{\text{obs}} = 1/\tau$ where τ is the mean lifetime derived by fitting a stretched exponential function convolved with the instrument response function to the TC-SPC data (see Figure 7 caption for details). By measuring the photoluminescent decay of an identical cell fabricated using a ZrO_2 film instead of TiO_2 an estimate of k_0 can be obtained. This is because the high CB edge of ZrO_2 prevents electron injection from the LUMO level of an excited dye ($k_{\text{inj}} = 0$), thus the only process contributing to the TC-SPC signal is decay to the ground state such that $k_0 = k_{\text{obs}} = 1/\tau$. By combining these measurements an estimate of the injection efficiency, η_{inj} , can be found:

$$h_{\text{inj}} = \frac{k_{\text{inj}}}{k_{\text{inj}} + k_0} = \frac{k_{\text{obs}} - k_0}{k_{\text{obs}}} \quad (2)$$

Figure 7 shows examples of measured TC-SPC data describing the tBP-LiI-SF segments and the appropriate zirconia reference with corresponding stretched exponential reconvolution fits. There was some relatively small variation in the k_0 values with different filling methods and electrolytes as described in detail in the supporting information (Section 1S).

Figure 8a indicates that there is a correlation between τ and J_{SC} which suggest that electron injection is apparently a factor causing the differences in J_{SC} . This relation can be more quantitatively studied by employing eq. (2) and taking into account also the variation in k_0 with the different electrolytes and filling methods (i.e. the data from the ZrO_2 cells). It can be seen that the calculated η_{inj} explains a significant fraction of the

variations in J_{SC} as illustrated in Figure 8b. There is, however, scatter in Figure 8b which implies that there may also be other mechanisms causing the differences in the photocurrent generation as expected based on the literature.^{5,25,33,34} To investigate the remaining variation in the photocurrent, IPCE (data not shown) and optical (Figure S1, supporting information) measurements were carried out and analysed similarly as in our previous work.³⁵ The IPCE and optical data indicate that the scatter in Figure 8b is due the combined effect of several factors such as electron collection and light harvesting having minor variations typically in the order of a couple of percents. In addition the IPCE data shows significant variations of η_{inj} in agreement with TC-SPC results.

4. Conclusions

Electrolyte filling method was shown to have a significant effect on the spatial performance distribution of the cell, in particular on that of V_{OC} . The effect was explained by the porous TiO_2 film acting as a molecular filter (c.f. chromatography) causing spatial variation in the distribution of the electrolyte components arising during the electrolyte filling process. The commonly used electrolyte additives tBP and BI appear to accumulate near to the electrolyte filling hole causing a decreasing photovoltage in the cell along the electrolyte filling direction. When pumping the electrolyte through the cell several times, which is the typical filling technique used in larger size modules, V_{OC} was increased through the cell and additionally spatial differences of V_{OC} decreased. This is understood as an increase and saturation of tBP or BI across the whole photoelectrode. These deductions were supported by charge extraction and transient measurements which demonstrated a spatial variation of the TiO_2 conduction band that matched the observed

changes in V_{OC} . The analysis of that data indicated that the electrolyte filling could introduce/remove trap states and here it was shown how the changes in the trap state distribution can be taken into account to evaluate the differences in the conduction band edge accurately. The shifts of TiO_2 conduction band, which we associate with changes in the adsorbed quantity of tBP and BI, also caused changes in the electron injection efficiency affecting also the spatial variation of J_{SC} .

Whilst the differences in V_{OC} were largely reduced with the electrolyte pumping treatment, the overall performance did not become homogenous because spatial variation in J_{SC} was increased by the treatment. Repeated electrolyte pumping did improve the average efficiency of the segmented cells but reduced that of the small reference cells. This leads to the practical conclusion that in order to reach the maximum device performance the filling procedure needs to be separately optimized for different types of electrolytes and cell geometries. This in turn motivates work on the development of novel electrolyte filling methods that would lead to an inherently even distribution of electrolyte components.

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Figure captions:

Figure 1. Image of a segmented cell (on the right) and a small reference cell. The numbering of the segments relative to electrolyte insertion hole is marked also. With the pumping treatment the electrolyte was removed by taking it out from the hole at the opposite end of the cell compared to the electrolyte insertion hole.

Figure 2. Typical V_{OC} vs. filling cycle number for a) BI and b) for tBP-LiI electrolytes. Typical J_{SC} vs. filling cycle number for c) BI and d) for tBP-LiI electrolytes. The marker points refer to measured data and the same colored curves to corresponding fits. These measurements were carried out in ~ 0.7 Sun during the cell preparation. The trend lines for curves in a, b and c are logarithmic fits in d linear or second order polynomial. Note that the data of the SF cells is similar to the 10F cells at first filling cycle.

Figure 3. a) The absorption spectra of the different segments at 470 nm when repeating the filling of Coumarin dye into the segment cell. A photo of the segmented cell with Coumarin dye b) after the first filling and b) after 10 filling cycles with marked segment numbering.

Figure 4. Variation of charge density at short circuit vs. J_{SC} a) for BI electrolyte (points are overlapping) and b) for tBP-LiI electrolyte. The variation is the density of conduction band electron Δn_T for a given J_{SC} value is indicated with an arrow. While this Δn_T is

insignificantly small with the BI electrolyte (case a), Δn_T is large for the tBP-LiI electrolyte. c) Schematic of density of states (DOS) as a function of energy E illustrating the affect of Δn_T .

Figure 5. Measured charge density at open-circuit vs. V_{OC} in the case of a) BI electrolyte and c) tBP-LiI electrolyte. d) shows the data of c corrected with the changes in the trap density. The arrows indicate the real (a,c) or apparent (b) shift of the conduction band. Schematics of density of states (DOS) as a function of energy E illustrating b) the effect of ΔE_c in the case of BI electrolyte and e) the combined effect of ΔE_c and Δn_T in the case of tBP-LiI electrolyte.

Figure 6) Electron lifetime τ_n compared to the charge at open-circuit for the BI electrolyte.

Figure 7. An example of time resolved photoluminescent measurements of the tBP-LiI-SF₆ cell for different segments compared with the decay of a ZrO₂ control cell. The excitation pulse wavelength was 467 nm and the photoluminescence detection wavelength was 750 nm. The markers refer to the measured data while the continuous lines show the corresponding reconvolution fit. A stretched exponential function was used as the decay model so that the rate of photoluminescence is given by $n = n_0 e^{-(t/t_{90})^b}$

where v_0 , τ_{wv} and β are fit parameters.^{12,13} The table below the figure shows the fit

parameters and calculated mean lifetime values given by $t = (t_{\text{wv}} / b) \exp(\frac{v_0}{b})$.

Figure 8. a) The measured mean time constant measured from the TC-SCP measurements compared to J_{SC} from the photovoltaic measurements. b) The calculated injection efficiency calculated based on eq. (2) and data shown in a and defining τ_0 based on the cells made with ZrO_2 films with the same electrolytes and filling methods (τ_0 varied between 20-27 ns). The lines represent linear fits and in case of b the line is set to cross at origin.

Table 1. The shortened names for the electrolyte filling method and electrolyte combinations. Both segmented and reference cells were made with all the combinations.

Filling method → Electrolyte ↓	10 filling cycles (10F)	Single fill (SF)
tBP, LiI, GuSCN, PMII, I2 (tBP-LiI)	tBP-LiI-10F	tBP-LiI-SF
BI, GuSCN, PMII, I2 (BI)	BI-10F	BI-SF

Table 2. Photovoltaic parameters of the individual segments and small reference cells measured at 1 Sun (AM1.5) which have stabilized for a few days after the cell preparation.

	J_{sc} (mA/cm ²)	V_{oc} (mV)	FF (%)	η (%)
tBP-Lil-10F, seg 1	9.1	755	64	4.4
tBP-Lil-10F, seg 2	10.7	771	62	5.2
tBP-Lil-10F, seg 3	10.9	773	59	4.9
tBP-Lil-10F, seg 4	11.6	773	63	5.4
tBP-Lil-10F, ref	8.8	773	67	4.6
tBP-Lil-SF, seg 1	10.7	713	61	4.7
tBP-Lil-SF, seg 2	11.7	675	55	4.4
tBP-Lil-SF, seg 3	11.4	651	51	3.8
tBP-Lil-SF, seg 4	11.3	643	57	4.2
tBP-Lil-SF, ref	11.2	743	62	5.2
BI-10F, seg 1	9.9	787	64	5
BI-10F, seg 2	10.4	771	63	5.1
BI-10F, seg 3	11.3	769	62	5.4
BI-10F, seg 4	11	775	60	5.1
BI-10F, ref	9	830	56	4.2
BI-SF, seg 1	10.6	746	62	4.9
BI-SF, seg 2	11.4	705	58	4.7
BI-SF, seg 3	11.2	684	58	4.4
BI-SF, seg 4	11	697	60	4.6
BI-SF, ref	10.3	774	64	5.1