

TiO₂ pore-filling and its effect on the efficiency of solid-state dye-sensitized solar cells

Lukas Schmidt-Mende*, Michael Grätzel

Institut des Sciences et Ingénierie Chimiques (ISIC), Laboratoire de Photonique et Interfaces (LPI), Ecole Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland

Abstract

Solid state dye sensitized solar cells have been the focus of much attention over the past few years. We have recently been able to demonstrate efficiencies in excess of 4% and further improvements are expected. Here we compare a range of different hole conductor materials and investigate a number of key parameters which affect their performance. Wetting and pore filling of the nanoporous TiO₂ layer by the hole transporter appears to play a critical role in determining the final efficiency of the cell. A comparison of our results shows the importance of complete filling in contrast to just wetting of the nanoporous TiO₂ layer, which is generally underestimated.

Keywords: Solar cells; Organic conductors; Titanium oxide; Scanning electron microscopy

1. Introduction

Liquid electrolyte dye-sensitized solar cells reach power conversion efficiencies of over 11% [1]. This concept is clearly an alternative to conventional amorphous silicon solar cells. However, these liquid electrolyte based solar cells suffer from leakage problems, which can be avoided by replacing the liquid electrolyte with a solid hole-conductor. The first successful implementation of an organic material as a hole-conductor was demonstrated in 1998 by Bach et al. [2]. After much optimization, the efficiency could be improved to 3.2% [3] and recently we have been able to increase the efficiency still further to 4% [4].

In this investigation, we compare this 4% cell with cells, where we replaced the standard hole conducting material 2,2',7,7'-tetrakis-(*N,N*-di-*p*-methoxyphenyl-amine)9,9' spiro-bifluorene (spiro-OMeTAD) with other hole-conductors and present our results.

Solid-state cells with spiro-OMeTAD have been optimized over the last few years. Little further improvement is expected

because the spiro-OMeTAD has a relatively low charge carrier mobility (of the order of 10^{-4} cm²/Vs) which limits the cell performance. Other organic hole-transport materials exhibit an order of magnitude higher mobility. This should be highly advantageous to the device performance as it should facilitate rapid and efficient charge collection. Despite this advantage, we have found that no hole-conductor works as well as the formerly used spiro-OMeTAD, which we mainly attribute to the difficulty associated with filling the pores of the mesoporous TiO₂ layer with the hole conducting material. The best result we achieved with an alternative hole-conductor was an efficiency of 2% under simulated sunlight (AM 1.5 global, 1000 W/m²) which, to our knowledge, is higher than previously reported results using other hole-conductors. The results are very promising and much higher efficiencies are expected, if we are able to improve the pore-filling and optimize other conditions within the cell.

Many groups are looking for new types of organic hole-conductors for solid-state dye-sensitized solar cells [5–14], but the efficiencies lie far behind the efficiencies of cells fabricated with spiro-OMeTAD. It is anticipated that materials with a higher mobility will allow for an increase in efficiency for two reasons [15,16]. Firstly, the generated charge will be transported more quickly to the electrodes and hence reduce the possibility of recombination. The second is

* Corresponding author. Current address: University of Cambridge, Department Materials Science and Metallurgy, Pembroke Street, Cambridge, CB2 3QZ, UK. Tel.: +44 1223 334374.

E-mail address: ljs38@cam.ac.uk (L. Schmidt-Mende).

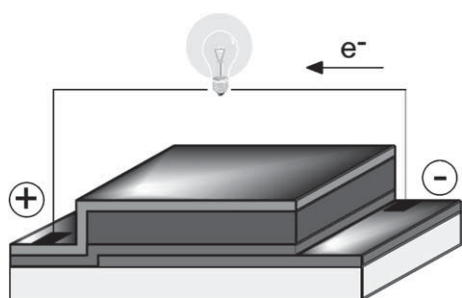


Fig. 1. The device structure consists of a glass substrate coated with F-doped SnO_2 . On top of this a dense layer of TiO_2 is deposited by spray pyrolysis and a nanoporous TiO_2 layer via doctor-blading. The nanoporous layer is soaked in dye and filled with an organic hole conductor. A gold electrode is evaporated on top as counter electrode.

that the higher mobility will allow for a thicker cell to be made, thereby enabling a greater fraction of the incoming sunlight to be absorbed. Hole-conductors for solid-state dye-sensitized solar cells have to fulfill certain conditions to be successful candidates for this type of cell: The materials have to be processable from solution and should form smooth amorphous films. Crystallization would prevent efficient pore-filling, which seems to be one of the limiting problems for some materials. Not only is complete wetting of the dye-covered TiO_2 surface important, but also complete filling of the pores with the hole-conducting material is critical in determining the efficiency of the cells. The *highest occupied*

molecular orbital (HOMO) level of the hole-conductor should be sufficiently offset from that of the dye molecule to ensure hole transfer from the dye into the hole-transporting material.

2. Experimental details

The structure of our cells is shown schematically in Fig. 1. After cleaning F-doped SnO_2 glass substrates (with acetone, methanol and Helmanex), a ~ 100 nm compact layer of TiO_2 was deposited by spray-pyrolysis. A nanoporous TiO_2 layer was fabricated via doctor-blading a TiO_2 paste containing 19 nm-sized anatase particles, followed by sintering at 450 °C. A 0.02 M aqueous TiCl_4 solution was deposited overnight on the TiO_2 films, and afterwards, the substrates were rinsed in water. Prior to dye uptake, the substrates were annealed at 450 °C for 15 min and then cooled down to ~ 80 °C. The thickness of the nanoporous TiO_2 layers used for devices was ~ 2 μm . They were sensitized by soaking in a 3×10^{-4} M solution of amphiphilic polypyridyl ruthenium complex, *cis*- $\text{RuLL}'(\text{SCN})_2$ ($L=4,4'$ -dicarboxylic acid- $2,2'$ -bipyridine, $L'=4,4'$ -dinonyl- $2,2'$ -bipyridine) (in the literature often referred to as Z907) (Fig. 2d) in acetonitrile:tert.-butanol (1:1 vol%) at room temperature. After soaking in the dye solution, the substrates were rinsed in acetonitrile. The hole conductor matrix was applied by spin coating a solution of the hole-conductor in chlorobenzene (0.17 M), containing

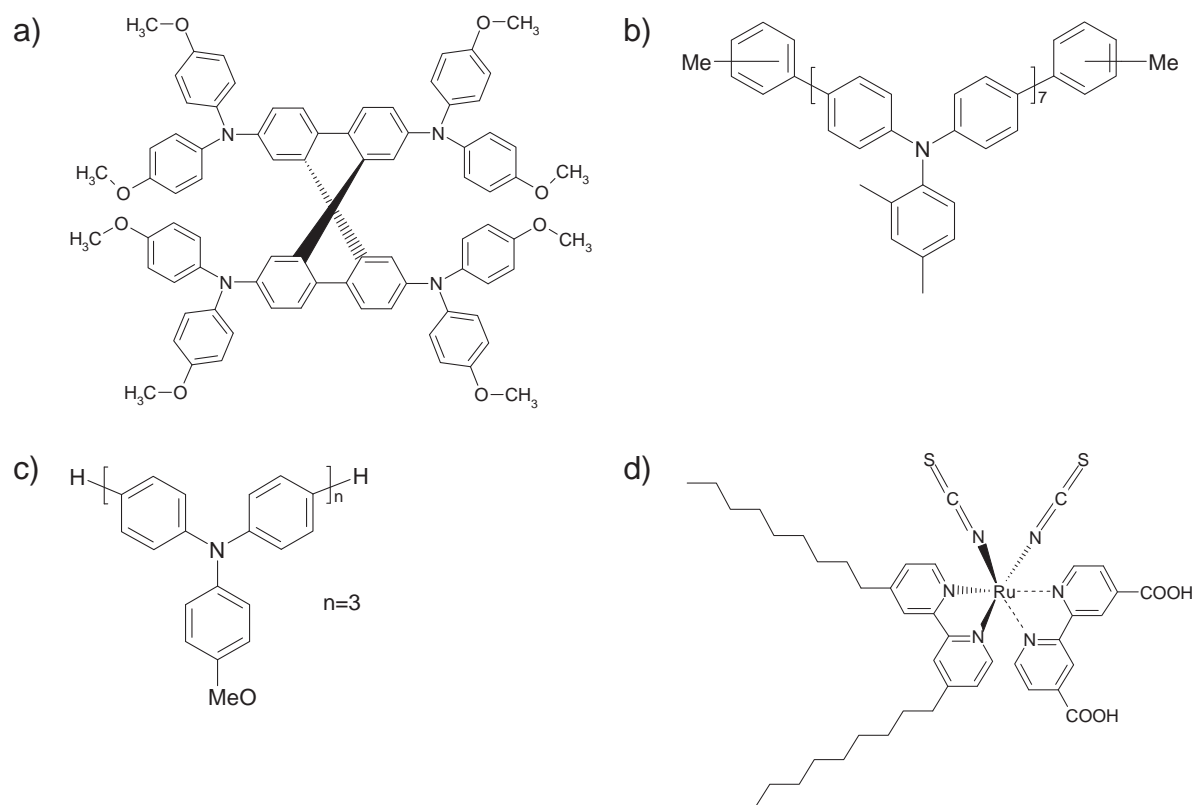


Fig. 2. a) Chemical structure of the hole-conductor spiro-OMeTAD. This material has shown a time of flight mobility of $\mu \sim 2 \times 10^{-4}$ cm^2/Vs . [15]. b) Chemical structure of AV-DM. This material has a mobility of $\mu \sim 2 \times 10^{-3}$ cm^2/Vs (FET mobility). c) Structure of AV-OM. The charge carrier mobility of this material is $\mu \sim 5 \times 10^{-4}$ cm^2/Vs (FET mobility). d) Structure of the Z907 dye used for all solar cells as sensitizer of the nanostructured TiO_2 film.

Li[CF₃SO₂]₂N (13 mM), tert.-butylpyridine (0.13 M) and N(PhBr)₃SbCl₆ (0.3 mM). (The concentration values are given for the spiro-OMeTAD hole-conductor solution.) Before spin-coating, this solution was deposited onto the dye-sensitized substrate and was allowed to penetrate into the pores of the TiO₂ layer for 1 min. To finish the device production, a 30-nm Au electrode was evaporated on top.

The current–voltage characteristics were measured using a Keithley 2400 Source Meter and a 1000 W Oriel solar simulator fitted with an AM 1.5 global filter set as light source. Light intensity was changed with meshes in front of the light source and measured with a Si photodiode and calibrated to 1000 W/m² for 1 sun. All production steps and measurements were performed under ambient conditions. The devices were not sealed or otherwise protected.

The spectral response of the silicon reference was adapted to the spectral sensitivity of the dye-sensitized solar cell with a Schott KG3 filter in front of the reference diode. The efficiency was calculated as $\eta = P_{\text{out}}/P_{\text{in}} = I_{\text{SC}} U_{\text{OC}} \text{FF}/P_{\text{in}}$, with P_{in} and P_{out} the incident and outgoing power, respectively, I_{SC} the short circuit current, U_{OC} the open circuit voltage and FF the fill factor ($\text{FF} = (I_{\text{max}} U_{\text{max}}) / (I_{\text{SC}} U_{\text{OC}})$, with I_{max} U_{max} the maximum power).

Dynamic contact angle measurements were recorded with a Krüss DSA100 drop shape analysis system. The dynamic change of a droplet of 3 μl was observed on a nanoporous dyed TiO₂ film.

Scanning electron microscope images were recorded with a Philips XL30 SFEG scanning electron microscope at 5.00 kV acceleration voltage, ~ 5 mm working distance, $\times 100,000$ magnification.

3. Results

In this work we focused on different triarylamine type hole-transporting material. The chemical structures of the materials used are shown in Fig. 2. All the hole-transporting materials are highly soluble in chlorobenzene, which was used as solvent. The HOMO levels (measured by cyclic voltammetry) of *novel substituted triarylamine oligomers, which we refer to as AV DM* (Fig. 2b) and *AV OM* (Fig. 2c) are around 5.0 eV and for the spiro-OMeTAD ~ 4.8 eV.

We find that the penetration of the hole-conductor into the nanoporous TiO₂ varies with each different material studied. In addition to the results shown here we tried several other hole-conductors and in most cases we found pore-filling to be inadequate as seen, for example, in the case of AV-DM. Here, no penetration at all is visible in the cross-section *scanning electron microscopy* (SEM) image of the device (Fig. 3a).

For the AV-OM device, the cross-section SEM image is different from that of AV-DM. Here, penetration of the hole-conductor into the pores of the TiO₂ layer can be observed as evidenced by the darker areas and the diminished contrast and softened features in the TiO₂ layer (Fig. 3b). Interestingly, in this case it seems that penetration does not appear to be of uniform density throughout the TiO₂ layer, which is one explanation for the lower performance of this material

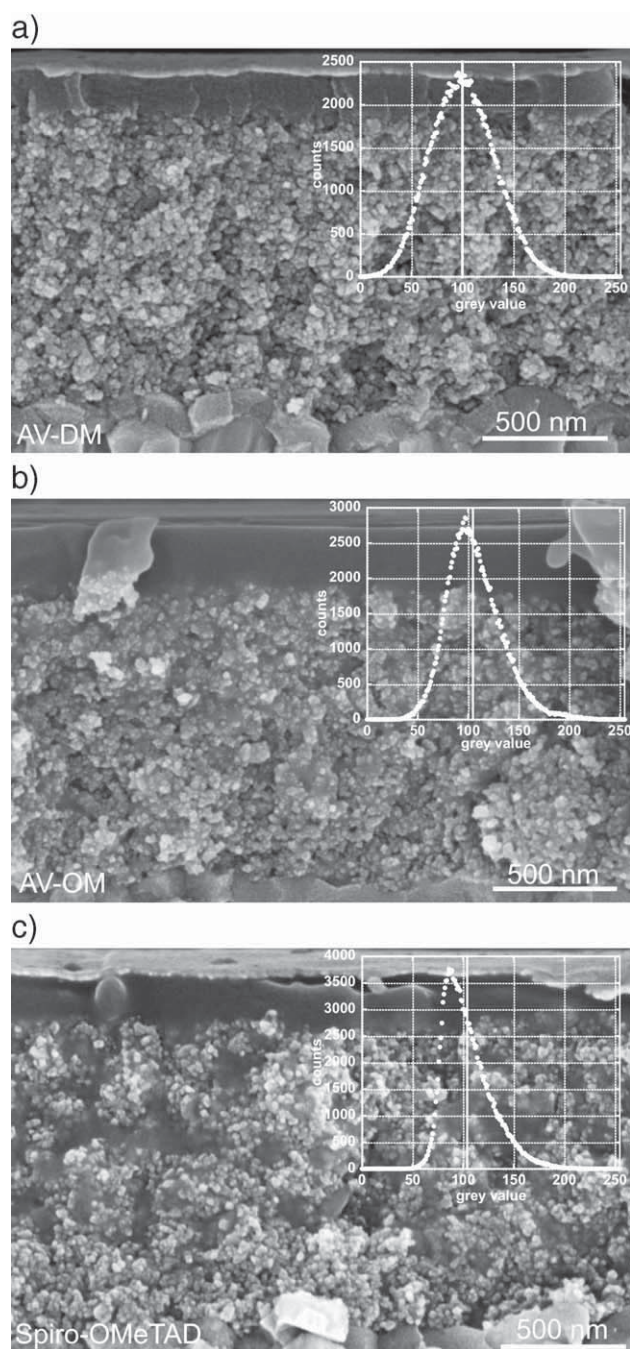


Fig. 3. SEM image of the solar cell with AV-DM (a), AV-OM (b) and spiro-OMeTAD as hole-transporting material. The insets show the histogram of the grey value distribution of the area of the nanoporous TiO₂ layer. (a) No penetration of AV-DM into the nanoporous TiO₂ can be observed. (b) Hole-transporting material AV-OM in the TiO₂ layer. Some penetration can be recognized in this image. However, it seems that the hole-conductor does not appear to be of uniform density throughout the nanoporous TiO₂ layer. The performance of this cell is 2% under standard AM 1.5 global conditions (1000 W/m²). (c) The standard spiro-OMeTAD cell with the best performance of η 4% (AM 1.5 global, 1000 W/m²). Good penetration and filling of the pores can be seen, but there is still scope for further improvement of pore-filling, especially down at the lower levels of TiO₂.

compared with that of the spiro-OMeTAD. However, devices with the AV-OM hole-conductor show a performance of 2% under standard AM1.5 global conditions (1000 W/m²) (Fig.

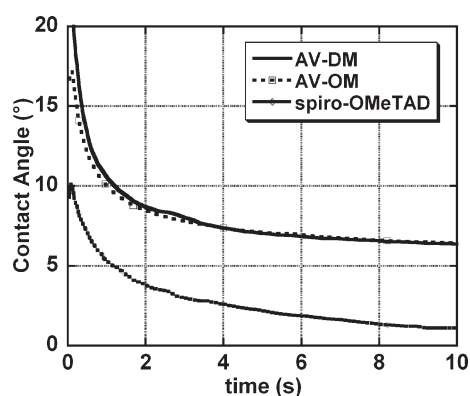


Fig. 4. Dynamic contact angle measurements: The change of the contact angle of a 3- μ l droplet of hole-conductor solution is recorded for the first 10 s after the droplet hits the surface. We observe significantly improved wetting behavior by the spiro-OMeTAD solution compared to the other hole-transporting materials.

5b). This is half the value of the performance obtained with the spiro-OMeTAD cells (Fig. 5c), but twice as much as that obtained with AV-DM.

In case of the spiro-OMeTAD the pore-filling is much more advanced (Fig. 3c). The dark areas within the TiO₂ layer in the SEM cross-section image of the spiro-OMeTAD device cover large areas, where the TiO₂ matrix is covered, which indicates good pore-filling in these areas. In the case of AV-OM (Fig. 3b) the dark areas on the SEM image are smaller and less distinguished, indicating the presence of a smaller amount of hole-transporting material in the nanoporous TiO₂ layer.

Dynamic contact angle measurements (Fig. 4) indicate a different wetting behavior of the different hole-transporter solutions: For the spiro-OMeTAD solution a 3- μ l droplet rapidly spreads out and the contact angle decreases much faster than in the case of the other hole-transporter solutions. The spiro-OMeTAD clearly wets the dye-covered TiO₂ surface much better, which certainly supports the pore-filling.

4. Discussion

The charge carrier mobility of the AV-DM material, at $\sim 2 \times 10^{-3} \text{ cm}^2/\text{Vs}$, is the highest of the three different materials discussed here. The mobilities of AV-OM and spiro-OMeTAD are $\sim 5 \times 10^{-4} \text{ cm}^2/\text{Vs}$ and $\sim 2 \times 10^{-4} \text{ cm}^2/\text{Vs}$, respectively. The values for the charge carrier mobility for AV-DM and AV-OM were obtained by measurement in a field effect transistor (FET) configuration device, whilst the value for spiro-OMeTAD is taken from the literature [15]. Even though the values for the novel materials cannot directly be compared with the literature value of spiro-OMeTAD, because this is measured in a different way, it shows a general trend towards higher mobilities for the novel materials, which is also expected from the molecular structure of the materials. The apparent lack of correlation between efficiency and mobility in the performance of our cells implies that the charge carrier mobility of the hole-transporting material is not the dominating factor for efficiency.

Therefore we suggest that the wetting and pore-filling of the TiO₂ by the hole-transporting material has the dominant influence on the device performance.

We assume that we have – to a certain degree – wetting of the TiO₂ surface with all the materials discussed here, but the level of filling of the pores is quite different and the efficiency of the cells seems to be directly correlated to this wetting and pore-filling behavior as far as it can be seen from the SEM images (Fig. 3). In case of the cross-section SEM image of the AV-DM device (Fig. 2b) the amount of wetting of the pores by this hole-transporting material is too small to be visualized by the SEM. In the absence of any wetting of the TiO₂ pore surfaces, we would expect to obtain for this device an efficiency similar to that of a flat junction cell, i.e., a cell made using just a dense layer of TiO₂ covered by a dye layer and a layer of AV-DM. Our results (Fig. 5) show that a device based on AV-DM gives a performance of almost 1%, which is a factor of 10 greater than that of a corresponding flat junction cell. Analyzing the grey value distribution of the area of the nanoporous TiO₂ layer of the SEM image, a symmetrically shape of the curve can be observed (Fig. 3a inset). The mean value (vertical solid line) and the peak value almost fall together, which would be expected from a non-filled nanoporous TiO₂ film. A comparison with the AV-OM and spiro-OMeTAD filled pores shows that there the peak value is shifted towards lower (darker) values in respect to the mean value (Fig. 3b,c insets). This can be explained by the increase of dark grey values caused by the hole conductor inside the pores. The shift is much more pronounced for the spiro-OMeTAD filled devices than for the AV-OM, which directly reflects the higher degree of pore-filling.

Feng et al. reported an improvement of their solid-state cell efficiency by enlarging the effective interface between the hole-conductor and titanium dioxide [16]. The improvement was achieved by choosing a larger pore size which, despite reducing the surface area of the titanium dioxide, increased the effective interface between the hole-conductor and TiO₂. Models for solid-state cells have to take into account the incomplete interfacial contact between the dye attached to the TiO₂ and the hole-conductor [17]. This certainly is an important issue in our devices as well. The different wetting behaviors seen in the dynamic contact angle measurements (Fig. 4) not only make the differences in pore-filling ability apparent, but also allow us to assume that we are not able to wet all of the pores. We assume that pores of smaller size are probably not covered by the hole-transport materials such as AV-DM and to a lesser extent also AV-OM. Only in case where the dye on the TiO₂ surface is covered with the hole-transporter a charge transfer can be expected. Otherwise the dye will be excited and electron transfer to the TiO₂ will take place, but no regeneration of the dye via hole-transfer to the hole-transporter and no charge collection occur, which will lead to decreased current density of the cell as can be observed in the device performances of these cells (Fig. 5).

In addition, our results suggest that not only a complete interfacial contact, achieved by complete wetting of the TiO₂ surface is essential but also a complete filling of the pores is

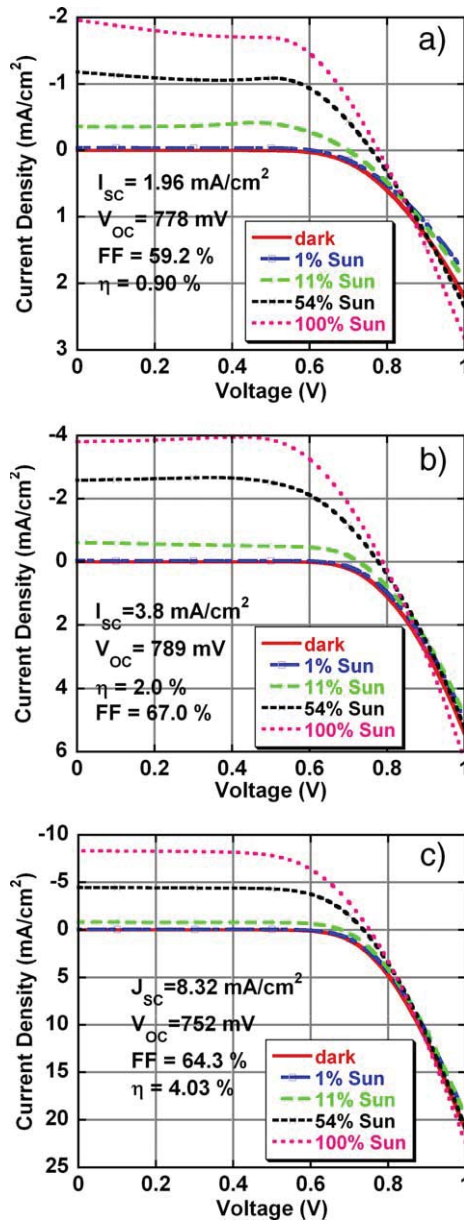


Fig. 5. Current voltage characteristic of a solid-state dye-sensitized solar cell with Z907 as sensitizer and AV-DM (a), AV-OM (b) and spiro-OMeTAD (c) as hole-transporting material. The different curves show the I-V characteristic under different illumination intensities from darkness to 100% sun (AM 1.5 global, 1000 W/m^2).

crucial for high efficiency cells. In cases where the pores are not completely filled with the hole-conductor, the path for the holes to reach the gold electrode is longer. If the hole-conductor just covers the TiO_2 with a thin layer, the positive charges have to travel within this thin film, following the shape of the nanoporous TiO_2 surface, which will be much longer than a direct path. The fact that the charges have to travel by a more circuitous route may also result in a higher chance of recombination. As more hole-conductor material is found in the nanopores, a shorter pathway for the charges towards the electrode becomes available. Therefore, incomplete filling leads to a higher series resistance within the cell, which – in case of AV-DM and AV-OM – seem to be compensated by the

higher charge carrier mobility of these materials. Otherwise we would expect significant higher series resistance and lower fill factors. An effect of higher series resistance caused by a longer pathway can be observed in spiro-OMeTAD devices with thicker TiO_2 layers. Short circuit current and the fill factor decrease, when exceeding an optimal devices thickness, despite the higher fraction of absorbed light in the film. This is a reason why, in solid-state dye-sensitized solar cells, the optimal TiO_2 film thickness is only a few microns, even though only a fraction of the incoming light will be absorbed in these thin layers.

Another experimental evidence for our assumption of the importance of complete pore-filling is given by devices made with spiro-OMeTAD solutions of different concentrations. The higher concentrated the spiro-OMeTAD solution, the higher the performance of the cell.

Our results suggest that pore-filling is a key problem that needs to be addressed with AV-DM and, to a lesser extent, AV-OM. Although the structure of the spiro-OMeTAD-filled TiO_2 layer looks further softened compared to both AV-DM and AV-OM, it would appear from these images that even this material does not seem to fill the TiO_2 pores *completely* down to the bottom. Even though a certain degree of wetting of the TiO_2 pores by the spiro-OMeTAD is expected throughout the entire film, the pores close to the bottom of the film do not seem to be filled to the same extend as the pores closer to the top of the film. A histogram analysis of the top and bottom half of the nanoporous layer of the SEM image clearly indicates a distinct difference in the degree of pore-filling. This may suggest that further performance improvements might be possible by optimization of the pore-filling. Effective pore-filling, although a primary consideration at this stage, is but one factor affecting cell performance. It is anticipated that further optimization work on, for example, charge carrier mobility, hole-conductor HOMO levels and dopant and lithium ion concentration will be required once the difficulties with pore-filling have been successfully overcome. The slightly lower HOMO level of the spiro-OMeTAD might be advantageous for the hole transfer from the oxidized dye to the hole conductor, which might be an additional reason for the better performance of this hole conductor. Transient spectroscopy measurements have to reveal whether the differences in HOMO levels are also crucial to the device performance. In case of AV-DM and AV-OM the HOMO levels are identical and therefore the difference in device performance cannot be explained with this.

5. Conclusions

This work demonstrates the crucial role of pore-filling in the performance of solid-state solar cells. In addition to complete wetting of the dye-covered TiO_2 surface, good pore-filling is also necessary for efficient solid-state dye-sensitized solar cells. It is important to distinguish between wetting of the pores and “real” pore-filling. The series resistance in a cell increases if the pores of the nanoporous TiO_2 are not completely filled and this leads to lower current densities and a poorer performance of the cell under sunlight. We have shown very promising new hole-

conductors, which performed well despite their poorer penetration into the pores. In case of AV-OM a device performance of 2% could be achieved with a high fill factor and open circuit voltage, which shows the high potential of this material. It is expected that the efficiency will be higher than for the spiro-OMeTAD material, if a complete wetting and good filling of the nano-pores can be achieved. For the future, it will be important to find methods, which facilitate pore-filling and to identify materials that fill the pores more efficiently, since this would appear to have a major influence on the overall device performance. Only after resolving the current issues relating to pore-filling can other aspects associated with cell performance such as charge carrier mobility and the level of other additives be effectively optimized.

Acknowledgment

The authors would like to thank Dr. Kathryn Carr, Dr. Simon Ogier and Dr. Charles Orizu of Avecia Limited, Blackley, Manchester, UK for the synthesis and characterisation of all the novel organic hole conductors used in this work and for their valued input to the project. The authors would also like to thank Geoff Parr of Intertek for the SEM imaging work.

We wish to acknowledge partial funding by the European Commission (MolyCell project, SES6-CT-2003-502783). LSM thanks the German Research Foundation (DFG) for funding (Emmy-Noether Stipendium).

References

- [1] M. Grätzel, *J. Photochem. Photobiol., A Chem.* 164 (2004) 3.
- [2] U. Bach, D. Lupo, P. Comte, J.E. Moser, F. Weissörtel, J. Salbeck, H. Spreitzer, M. Grätzel, *Nature* 395 (1998) 583.
- [3] J. Krüger, R. Plass, M. Grätzel, H.J. Matthieu, *Appl. Phys. Lett.* 81 (2002) 367.
- [4] L. Schmidt-Mende, S.M. Zakeeruddin, M. Grätzel, *Appl. Phys. Lett.* 86 (2004) 13504.
- [5] R. Cervinia, Y.B. Cheng, G. Simon, *J. Phys., D, Appl. Phys.* 37 (2004) 13.
- [6] P. Ravirajan, S.A. Haque, J.R. Durrant, D. Poplavskyy, D.D.C. Bradley, J. Nelson, *J. Appl. Phys.* 95 (2004) 1473.
- [7] Y. Saito, N. Fukuri, R. Senadeera, T. Kitamura, Y. Wada, S. Yanagida, *Electrochem. Commun.* 6 (2004) 71.
- [8] Y. Saito, T. Kitamura, Y. Wada, S. Yanagida, *Synth. Met.* 131 (2002) 185.
- [9] C.D. Grant, A.M. Schwartzberg, G.P. Smestad, J. Kowalik, L.M. Tolbert, J.Z. Zhang, *J. Electroanal. Chem.* 522 (2002) 40.
- [10] K.R. Haridas, J. Ostrauskaite, M. Thelakkat, M. Heim, R. Bilke, D. Haarer, *Synth. Met.* 121 (2001) 1573.
- [11] S. Spiekermann, G. Smestad, J. Kowalik, L.M. Tolbert, M. Grätzel, *Synth. Met.* 121 (2001) 1603.
- [12] Y.G. Kim, J. Walker, L.A. Samuelson, J. Kumar, *Nano Lett.* 3 (2003) 523.
- [13] K. Peter, H. Wietasch, B. Peng, M. Thelakkat, *Appl. Phys. A Mater.* 79 (2004) 65.
- [14] B. O'Regan, F. Lenzmann, R. Muis, J. Wienke, *Chem. Mater.* 14 (2002) 5023.
- [15] D. Poplavskyy, J. Nelson, *J. Appl. Phys.* 93 (2003) 341.
- [16] W. Feng, T. Umeda, A. Fujii, X.G. Wang, K. Yoshino, *Jpn. J. Appl. Phys.* 43 (2004) 3473.
- [17] S. Tanaka, *Jpn. J. Appl. Phys.* 40 (2001) 97.