J Sol-Gel Sci Technol (2008) 48:156–162
DOI 10.1007/s10971-008-1763-7

REVIEW PAPER

Development of TiO_2 pastes modified with Pechini sol–gel method for high efficiency dye-sensitized solar cell

Mateja Hočevar · Urša Opara Krašovec · Marko Berginc · Goran Dražič · Nina Hauptman · Marko Topič

Received: 15 January 2008 / Accepted: 1 May 2008 / Published online: 16 May 2008

Abstract A titanium oxide layer used for a dye-sensitized solar cell (DSSC) has to meet two opponent properties to assure a high efficiency DSSC: good connection between TiO_2 grains and a large inner surface area. Three different paste formulations based on commercial nanocrystalline TiO_2 powder (Degussa P25) are studied. Results confirm that modification of the TiO_2 paste with the Pechini sol–gel method increases the surface area of the TiO_2 layer while maintaining good connections between the nanocrystalline grains, consequently the efficiency of the DSSC increases from 1.8% to 5.3%. The structure and morphology of the TiO_2 layers are described by scanning electron microscopy (SEM), high resolution transmission electron microscopy (HR-TEM) and X-ray diffraction (XRD).

Keywords Dye-sensitized solar cells · TiO_2 layer · Pechini method · Sol–gel

1 Introduction

Dye-sensitized solar cells (DSSCs) have been extensively studied in the last decade as a promising photovoltaic technology, because of their potentially inexpensive manufacturing technology compared to silicon solar cells [1]. The front photoactive electrode of a DSSC is a transparent conductive oxide (TCO) glass coated with nanoporous TiO_2 and covered with a monolayer of the Ruthenium complex based dye while the counter electrode is a TCO glass coated with platinum. The gap between the two electrodes is filled with an electrolyte containing an iodide/tri-iodide (I^-/I_3^-) redox couple. Under illumination, the dye molecules are excited and the initial charge separation occurs by the injection of an electron from the dye into the conduction band of the TiO_2. This electron is then transported to the external load via the nanostructured TiO_2 and the front TCO. Nanocrystalline TiO_2 in anatase modification with a band gap of $\sim$3.2 eV has been identified as the most appropriate material to use, since its conduction band lies just beneath the LUMO level of the ruthenium complex dye. To realize a high efficiency DSSC, a large inner surface area of the nanostructured TiO_2 layer is essential, because it allows adsorption of a sufficiently large number of dye molecules needed for efficient harvesting of light. Beside the high surface area of the TiO_2 layer, good connections between the TiO_2 grains as well as a good adhesion to the TCO are necessary to diminish the reactions of photogenerated electrons with the tri-iodide species present in electrolyte and to assure a good electrical conductivity. Therefore to optimize the morphology of the TiO_2 layer according to the demands outlined above is a prerequisite for the realization of a high efficiency DSSC [2–4].

The TiO_2 layer in a DSSC is usually screen printed from TiO_2 paste. The highest efficiency for a small area DSSC ($\sim$0.2 cm^2) using an ionic liquid (IL) electrolyte reported so far is 7% [5]. However to obtain this a three or fourfold layer deposition of TiO_2 was needed [6]. First, the TCO was treated with an aqueous solution of $TiCl_4$ at 70 °C for 30 min in order to make a thin compact TiO_2 layer that

M. Hočevar (✉) · U. Opara Krašovec · M. Berginc · M. Topič
Faculty of Electrical Engineering, University of Ljubljana,
1000 Ljubljana, Slovenia
e-mail: mateja.hocevar@fe.uni-lj.si

G. Dražič
Jozef Stefan Institute, 1000 Ljubljana, Slovenia

N. Hauptman
National Institute of Chemistry, 1000 Ljubljana, Slovenia

would assure a good mechanical contact between the following printed TiO_2 layer and TCO substrate. In a second step, a transparent layer consisting of 20 nm sized TiO_2 particles was screen printed on the $TiCl_4$-treated TCO, which was further coated with third screen printed layer of 400 nm light scattering TiO_2 particles. The layers are then gradually heated to 500 °C in order to achieve a nanostructured porosity of the TiO_2 layer with a high surface area. The fourth step involves treating a triple TiO_2 layer with an ethanol solution of $TiCl_4$ to improve the connections between the TiO_2 grains present in a thick nanoporous layer [6]. Clearly, this preparation procedure of a fourfold layer of TiO_2 is rather complex, since different TiO_2 precursors as well as different deposition techniques are used. Therefore, our aim was to simplify the preparation of the TiO_2 layer into a single screen printing step of TiO_2 paste followed by the annealing of the layer to produce a highly efficient TiO_2 layer. Therefore we have focused on the development of a new TiO_2 paste formulation that would unify the requirements mentioned above.

A standard TiO_2 paste for a DSSC is composed of TiO_2 nanoparticles, a dispergant for TiO_2 nanoparticles (e.g. methoxy-benzoic acid in ethanol solution), a solvent (e.g. terpineol) and a binder (e.g. methyl cellulose) [7]. The paste is screen printed and the TiO_2 layer is annealed at 450–500 °C in order to burn out the organic additives to leave pores in the layer, which significantly contribute to an increase in the layer's surface area. However, the annealing process does neither assure good connections between the nanocrystalline grains nor good adhesion to the TCO. In order to improve the connections between the TiO_2 grains in the layer as well as the adhesion of TiO_2 grains to the TCO substrate, we add Ti-isopropoxide [$Ti(iOPr)_4$] as a binder into the standard paste. A similar approach has been reported by Chittibabu et al. [8], who introduced the polymeric linking agent Ti-butoxide into the paste based on a nanocrystalline powder. In order to stabilise the paste i.e. to avoid the precipitation of the TiO_2 from the $Ti(iOPr)_4$, we also add a chelating agent to the paste formulation.

In parallel, a new paste formulation was developed by applying the Pechini type sol–gel method [9]. The Pechini method consists of the preparation of polyester, which is achieved by mixing ethylene glycol with citric acid in which the metal alkoxide [e.g. $Ti(iOPr)_4$] is dissolved [9]. During the annealing process the polyester decomposes leading to the formation of a highly porous, but at the same time well connected, metal oxide network. The Pechini method has already been successfully used for the preparation of metal oxide based electrodes for Li-ion battery applications with a high and reversible charge capacity [10] and for the preparation of different electrocatalytic electrodes used either for the electro-reduction of nitro-compounds [11] or for low cost pH meters [12]. In all these applications a high surface area of the electrode and good electrical conductivity of the grains are essential to create highly efficient devices, as is the case for DSSCs.

This paper describes the development of a new TiO_2 paste formulation by introducing a binder into the standard paste and/or by mixing the polyester prepared by the Pechini method with TiO_2 nanoparticles. The structure and morphology of the TiO_2 layers, prepared from the different paste formulations, are described by scanning electron microscopy (SEM), high resolution transmission electron microscopy (HR-TEM) and X-ray diffraction (XRD). Additionally, the TiO_2 layers have been used to assemble a series of DSSCs. The performance of DSSCs employing different TiO_2 layers has been evaluated under standard test conditions [25 °C, 1 sun illumination (100 mW/cm^2), AM 1.5].

2 Experimental

2.1 Preparation of TiO_2 pastes and layers

A standard TiO_2 paste has been prepared by mixing 10 g of TiO_2 powder (P25, Degussa) with 12 ml of an ethanol (98%, Riedel-de Haen) solution of 4-hydroxybenzoic acid (1 wt.%, Merck) together with 10 g of 5 wt.% ethyl cellulose (Fluka) in terpineol (Fluka) [7]. Furthermore, 10 g terpineol was added and mixed in a mortar grinder (RM 200, Retsch) for 1 h (paste A).

Ti-isopropoxide (Fluka) was mixed with acetylacetone (Fluka) in a molar ratio of 1:1.5 and added to the paste A. The molar ratio between the TiO_2 powder and $Ti(iOPr)_4$ was: 7:1. This paste is marked as paste B.

A third paste formulation, by applying the Pechini type sol gel method (paste C), was obtained using a precursor molar ratio of 1:4:16 [$Ti(iOPr)_4$:citric acid:ethylene glycol] as suggested by C.M. Ronconi et al. [11]. The solution was prepared by heating ethylene glycol (Riedel-de Haen) to 60 °C and during stirring the $Ti(iOPr)_4$ was added. Finally, a corresponding amount of citric acid (Fluka) was added and the temperature increased to 90 °C. The solution was stirred at this temperature until it turned clear. The paste C has been prepared by mixing the TiO_2 powder and sol–gel solution in a mortar grinder for 1 h. The molar ratio between TiO_2 and $Ti(iOPr)_4$ was 7:1.

All three types (A, B and C) of TiO_2 paste were deposited on the conduction electrode (TCO) i.e. a fluorine-doped SnO_2 on glass substrate, using the "*doctor blade*" technique. Layers (A, B or C) were sintered at 450 °C for 1 h. Afterwards, the layer thickness was determined by a surface profilometer (Taylor-Hobson Ltd.) and the thickness of a single layer was 13.5 μm for all three types of layers.

2.2 Production and characterisation of DSSC

The TiO_2 layers were immersed in an ethanol solution of the Ruthenium complex dye [Ru(2,2′bipyridyl-4,4′dicarboxylate)$_2$ (NCS)$_2$, Solaronix] for 12 h. For a counter electrode, platinum (thickness ~5 nm) was sputtered onto a SnO_2:F glass substrate. Both electrodes were sealed with a 25 μm thick polymer foil (Surlyn, DuPont) that acts also as a spacer between the electrodes. After sealing, the electrolyte was injected through two holes pre-drilled into the counter electrode. The electrolyte was a binary ionic liquid mixture of 1-ethyl-3-methyl-imidazolium dicyanamide (EMI-DCA, University of Erlangen; viscosity: 21 mPas at 25 °C [13]) and 1-propyl-3-methyl-imidazolium iodide ionic liquid (PMII-Iolitec; viscosity: 1620 mPas measured at 20 °C) in a volume ratio 60:40 with 0.032 M of I_2 (Fluka). For each type of the TiO_2 layer, three identical samples of DSSCs each with an active area of 0.7 cm^2 were assembled. Before characterization, the cells were stored in the dark at open circuit conditions for 24 h to allow the electrolyte to penetrate the TiO_2 pores. Tungsten–halogen lamps were used as a light source as they mimic the black body spectrum with a colour temperature of 3,200 K. We calculated the short circuit current mismatch parameter and in conjunction with a calibrated c-Si reference solar cell determined the level of standard (1 sun, 100 mW/cm^2) irradiance. During irradiance and characterization, the cells were covered with a black mask fitting the active area of the cell [14]. To set the cell temperature to standard test conditions STC (25 °C), the temperature was stabilized with a cooling/heating Peltier setup designed for solar cell characterization. Current–voltage characteristics (*I/V*) were measured using a Keithley 238 source meter by applying voltage and measuring current. The *I/V* measurements were scanned from 0 V (short circuit condition) to 0.9 V (beyond open circuit voltage), with 10 mV steps. Before characterization, each cell was placed on a white paper back reflector placed on a copper plate.

2.3 Instrumental and measuring techniques

The particle size and the surface morphology of the TiO_2 layers were analysed with Hitachi S 4,700 scanning electron microscope (SEM) and a JEOL 2010 F high resolution transmission electron microscope (HR-TEM) operating at 200 keV. The X-ray diffraction (XRD) measurements were done using a Phillips PW1710 (automated) X-ray diffractometer.

The amount of the dye adsorbed on the TiO_2 layer, which correlates with the active surface area of the TiO_2 layer, was determined with UV-VIS spectroscopy [15]. The Ruthenium complex based dye was desorbed from the TiO_2 layers (A, B and C) with 0.02 M NaOH (Merck), the dye solution had been diluted with 0.02 M NaOH to 50 ml before obtaining UV-VIS spectra. In order to determine the amount of the dye adsorbed on the TiO_2 layers, firstly a calibration curve was made for different dye solutions varying in the dye concentration (5.0×10^{-7} M, 1.0×10^{-6} M, 5.0×10^{-6} M, 1.0×10^{-5} M, 5.0×10^{-5} M, 1.0×10^{-4} M) in 0.02 M NaOH. The measurements were scanned in decrements of 5 nm from 600 to 320 nm, where two peaks (370 and 500 nm) characteristic for the dye are present in the spectrum. For the calibration curve and the evaluation of the samples concentration the absorbance of the second peak of the dye i.e. at 500 nm (Fig. 1) has been considered.

3 Results and discussion

In our study three different TiO_2 layers (marked as layer A, B and C) have been deposited from the corresponding pastes. Paste A is a standard TiO_2 paste [7], paste B is the standard paste with a binder added, while paste C is a completely new formulation based on a mixture of polyester prepared by the Pechini method and TiO_2 nanoparticles. The structure and morphology of the sintered TiO_2 layers have been analysed and are described in 3.1. The layers have been sensitized with a Ruthenium complex dye in order to determine the amount of dye molecules adsorbed to the layer as well as to test their influence on DSSC performance. The results of the dye loading and the performance of the DSSC are presented and discussed in 3.2.

3.1 Structure and morphology of the TiO_2 layers

3.1.1 Scanning electron microscopy (SEM)

The SEM pictures of the TiO_2 layers (A, B and C) are presented in Fig. 2. They show that all layers consist of

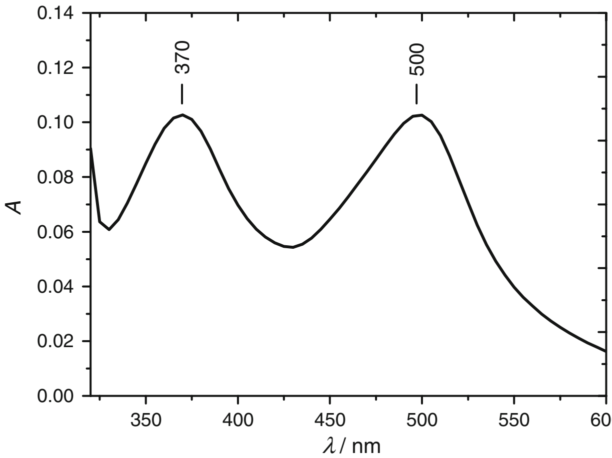


Fig. 1 Absorbance spectrum of the dye solution (1.0×10^{-5} M) with two maximums peaks (370 and 500 nm)

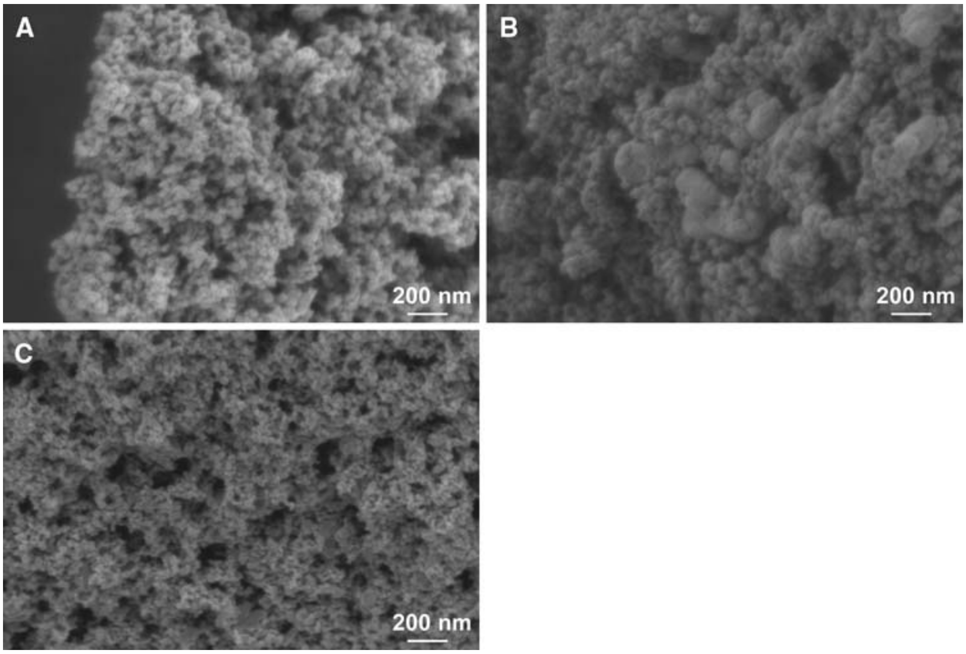


Fig. 2 SEM micrographs of A, B and C TiO_2 layers

homogeneously distributed spherical TiO_2 grains (~20 nm). The connections between the TiO_2 grains in layer B (Fig. 2B) are improved when compared with layer A (Fig. 2A), suggesting that the $Ti(iOPr)_4$ added into the paste acts as a binder connecting the TiO_2 grains in the layer. The SEM micrograph of layer C (Fig. 2C) shows an increase in porosity when compared with layers A and B, while the connections between the TiO_2 grains are comparable with those characteristic for layer B. These findings confirm that during sintering of paste C at 450 °C for 1 h, the polyester, which is obtained by the Pechini sol–gel method, exothermally decomposes [16], resulting in the formation of a highly porous, but at the same time well connected, TiO_2 network.

3.1.2 *High resolution transmission electron microscopy (HR-TEM)*

In Fig. 3 high resolution transmission (HR-TEM) micrographs of the TiO_2 layers (A, B and C) are presented. The micrograph of the TiO_2 layer A (Fig. 3A) shows that the layer consists of poorly connected homogeneously dispersed spherical grains, with a size around 20–25 nm, which agrees well with the results obtained from SEM. Detailed analysis shows that TiO_2 crystalline grains are coated with a 1 nm layer, which could be due to the presence of hydroxyl groups attached to the surface of the TiO_2 grains. Layers B and C (Fig. 3B, C) consist of basic TiO_2 crystals approximately 20–25 nm in size, but smaller crystals (<10 nm) are also present. Furthermore, the shape of the crystal grains in layers B and C are irregular and the roughness of their surface is increased compared to that of layer A. We can assume that the $Ti(iOPr)_4$ present in paste B and C during annealing process converts to small TiO_2 crystals and to some extent also attaches to the basic TiO_2 crystals' surface which leads to the increased roughness observed in HR-TEM micrograph of layers B and C.

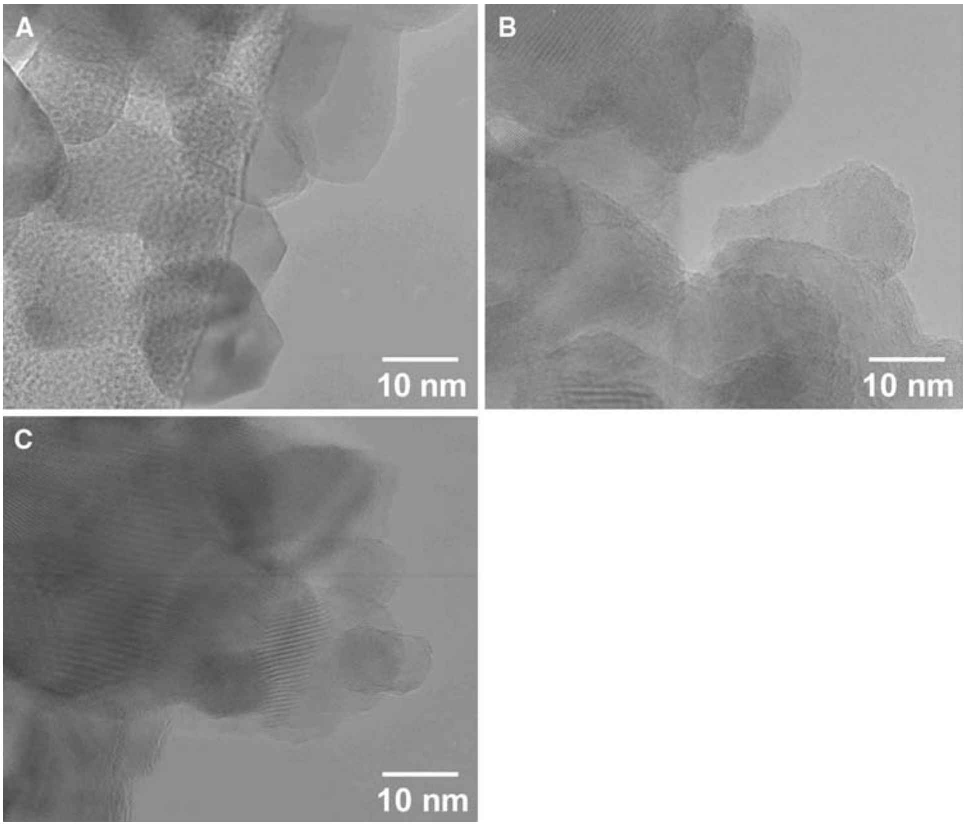
3.1.3 *X-ray diffraction (XRD)*

The XRD spectra of the TiO_2 layers (A, B and C) are given in Fig. 4. The results confirm the presence of anatase TiO_2 phase with small amount of rutile TiO_2 phase for all three layers. The ratio between the anatase and rutile modifications of TiO_2 in all three layers remains similar to that found for TiO_2 powder (P25, Degussa), which has been used as a precursor for the preparation of the pastes. This suggests that the addition of $Ti(iOPr)_4$ (layer B) and Pechini based sol–gel method for the preparation of the paste (layer C) does not influence the ratio between different modifications of TiO_2 in the annealed layers. The spectra also show a peak around 51.5° and two smaller peaks, which are characteristic for the SnO_2 based glass substrate.

3.2 Dye loading and dye sensitized solar cell

The thickness of the layers, the amount of dye molecules attached to the surface of TiO_2 layers together with the short circuit current (J_{SC}) and conversion efficiency (η) of the corresponding DSSCs evaluated under STC (100 mW/cm^2, 25 °C) are presented in Table 1. The thickness of the layers was 13.5 μm, regardless of the type of the layer. For layer A the amount of attached dye molecules was 6.0×10^{-8} mol(dye)/cm^2, however for layer B the value is decreased

Fig. 3 TEM micrographs of A, B and C TiO_2 layers



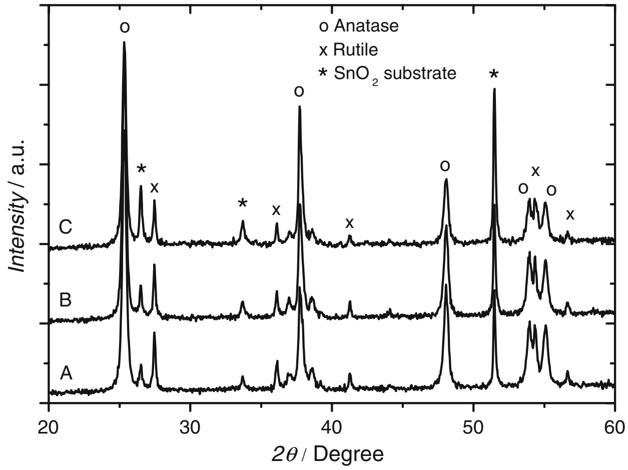


Fig. 4 XRD patterns of A, B and C TiO_2 layers as denoted in the graph

with 17%. The highest amount of dye molecules i.e. 7.1×10^{-8} mol(dye)/cm^2 is found for the layer C. The lowest dye loading characteristic for the layer B could be correlated with the decreased surface area of the layer when compared with layer A, because the addition of Ti(iOPr)$_4$ to the paste improves the connections between the crystalline grains. The highest dye loading found for layer C could be correlated to the highest surface area of the layer that is formed during annealing process when decomposition of titanium polyester present in the paste C takes place.

In order to evaluate the influence of different morphology and dye loading on the TiO_2 layers A, B and C on the performance of DSSCs, the dye sensitized TiO_2 layers were used to assemble three sets of DSSCs with the EMI-DCA/PMII 60:40, 0.032 M I_2 electrolyte. The performance of the DSSCs was measured under standard test conditions

Table 1 The layer thickness (d), the amount of the dye molecules attached to the surface of TiO_2 layers [n(dye)/A], short circuit current (J_{SC}) and conversion efficiency (η) of the DSSCs evaluated under STC (100 mW/cm^2, 25 °C) and the effectiveness of the dye molecules [n(dye)/A]/J_{SC} attached to the TiO_2

	D [µm]	n(dye)/A [mol/cm^2]	J_{sc} [mA/cm^2]	η [%]	[n(dye)/A]/J_{sc} [mol/mA]
Layer A	13.6	6.0×10^{-8}	3.88	1.8	1.5×10^{-8}
Layer B	13.3	5.0×10^{-8}	7.69	4.0	6.5×10^{-9}
Layer C	13.4	7.1×10^{-8}	10.72	5.3	6.6×10^{-9}

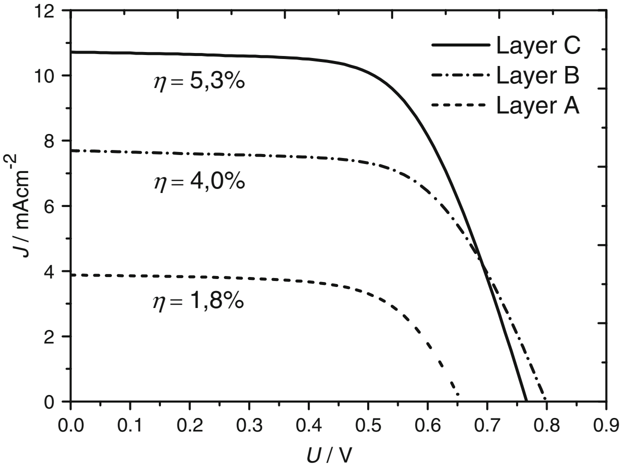


Fig. 5 Current to voltage characteristic of DSSCs (IL electrolyte: EMI-DCA/PMII 60:40, 0.032 M I_2) using layers A, B or C

(100 mW/cm^2, 25 °C) and corresponding *I/V* measurements are presented in Fig. 5. The values of short circuit current densities (J_{SC}) and efficiency (η) determined under STC are gathered in Table 1. The highest value of J_{SC} is 10.7 mA/cm^2 measured for layer C, which means a relative increase of 175%, when compared with the J_{SC} obtained with layer A, although the difference in dye loading is only 18%. An interesting observation is that the difference in dye loading between layers B and C is 40% in favor of layer C, as is also the case for the difference in J_{SC}. The effectiveness of the dye molecules [n(dye)/A]/J_{SC} attached to the TiO_2 layer have been evaluated by normalizing the amount of dye molecules [n(dye)/cm^2] with J_{SC} (Table 1). The results show that almost the same number of dye molecules needs to be adsorbed on layer B and C to generate a J_{SC} of 1 mA/cm^2, while this value is more than double for layer A. An increase of open circuit voltage (V_{OC}) is found for layers B and C as evident in Fig. 5. An improvement of V_{OC} could be linked to the improved adhesion of TiO_2 layer to the SnO_2:F electrode that is achieved by the addition of Ti(iOPr)$_4$ into the TiO_2 pastes. A small difference in V_{OC} between layer B and C, that is in favour to layer B, suggests that exothermic decomposition of the polyester in layer C leaves a small amount of the TCO uncovered. However, the layer C, which is improved by Pechini sol–gel method, makes the highest performance DSSC with the efficiency of 5.3%. This is due to good connections between TiO_2 grains as well as a higher surface area characteristic for layer C. Even though the amount of dye molecules on layer B is the lowest [5.0×10^{-8} mol(dye)/cm^2], the values of J_{SC} and η are still much higher than for layer A due to better connections of the grains allowing a good electron transport through the TiO_2 layer to the SnO_2:F electrode. Further studies are in progress to optimize the TiO_2 paste formulation based on the Pechini method.

4 Conclusions

The results confirmed that the paste formulation has a strong influence on the TiO_2 layer morphology and consequently on the performance of the DSSC. Improved connections between the TiO_2 grains have been obtained by adding Ti(iOPr)$_4$ into the paste formulation (layer B and C) which is found to be beneficial for electrical conductivity and consequently the V_{OC} and J_{SC} of DSSC are increased. The best results were obtained using a layer based on a paste prepared by the Pechini type sol–gel method (layer C). The layer exhibits the highest dye-loading due to high inner surface area and the highest efficiency of DSSC suggesting that the TiO_2 grains are well connected and well attached to the SnO_2:F electrode. If layer C is used in a IL based DSSC, its conversion efficiency could be improved by at least 190% compared to one made of layer A. The efficiency of 0.7 cm^2 DSSC based on the electrolyte mixture of EMI-DCA/PMII (60:40) at 25 °C under 1 sun illumination (100 mW/cm^2) is 5.3%.

Acknowledgements The authors would like to thank Jože Stepan for his help in fabricating the cells. Peter Panjan and Miha Čekada (Josef Stefan Institute, Ljubljana, Slovenia) are acknowledged for measurements of the layers' thickness. We are also grateful for the financial support given by the Slovenian Research Agency (P2-0197). M. Hočevar and M. Berginc would personally like to acknowledge the Slovenian Research Agency for providing them with Ph.D. funding. University of Erlangen is gratefully acknowledged for providing ionic liquid used in this article.

References

1. O'Regan B, Grätzel M (1991) Nature 353:737
2. Fotsa Ngaffo F, Caricato AP, Fernandez M, Martino M, Romano F (2007) Appl Surf Sci 253:6508
3. Park NG, Van de Lagemaat J, Frank AJ (2000) J Phys Chem B 104:8989
4. Barbe CJ, Arendse F, Comte P, Jirousek M, Lenzmann F, Shklover V, Grätzel M (1997) J Am Ceram Soc 80:3157
5. Kuang D, Wang P, Ito S, Zakeeruddin SM, Grätzel M (2006) J Am Chem Soc 128:7732
6. Wang P, Zakeeruddin SM, Comte P, Charvet R, Humphry-Baker R, Grätzel M (2003) J Phys Chem B 107:14336
7. Wienke J, Kroon JM, Sommeling PM, Kinderman R, Spath M, Van Roosmalen JAM, Sinke WC, Baumgärtner S (1997) Proceedings of 14th European photovoltaic solar energy conference and exhibition, Barcelona, Spain
8. Chittibabu KG, Gaudiana R, Beckenbaugh B, Li L, Lee M (2006) US Patent 7 094 441
9. Pechini M (1967) US Patent 3 330 697
10. Gou ZP, Zhong S, Wang GX, Walter G, Liu HK, Dou SX (2002) J Electrochem Soc 149:A792

11. Ronconi CM, Pereira EC (2001) J Appl Electrochem 31:319
12. Pocrifka LA, Goncalves C, Grossi P, Colpa PC, Pereira EC (2006) Sens Actuators B 113:1012
13. MacFarlane DR, Golding J, Forsyth S, Forsyth M, Deacon GB (2001) Chem Commun 16:1430
14. Berginc M, Opara Krašovec U, Jankovec M, Topič M (2007) Sol Energy Mater Sol Cells 91:821
15. Pavasupree S, Jitputti J, Ngamsinlapasathian S, Yoshikawa S (2008) Mater Res Bull 43:149
16. Galceran M, Pujol MC, Aguilo M, Diaz F (2007) J Sol Gel Sci Technol 42:79