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Dynamic preparation of TiO_2 films for fabrication of dye-sensitized solar cells

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Abstract

Preparation of nanocrystalline porous titanium dioxide (TiO_2) films with roll-to-roll compatible methods was studied. Gravure printing was used for spreading TiO_2 paste and paper calendering for pressing TiO_2 nanoparticle films. Influence of different preparation methods on performance of fabricated dye-sensitized solar cells (DSSCs) was investigated. The attained light into electricity conversion efficiency was compared with DSSCs fabricated on conductive plastic substrates by doctor-blading spreading with subsequent static pressing. The latter method achieved a light conversion efficiency as high as 5.1%. The efficiency of the cells with a gravure printed TiO_2 film was found to be rather low. The highest conversion efficiency was 1.7%; this is concluded to be due to insufficient thickness of the gravure printed TiO_2 films. Calendering of the doctor-bladed films on the other hand attained a light conversion efficiency of 4.7%.

Keywords: Dye-sensitized solar cell; Dynamic press; Calender; Gravure; Roll-to-roll

1. Introduction

Dye-sensitized solar cells (DSSCs) have attracted great attention over the past decade since they have been reported to have a high light-into-electricity conversion efficiency (up to 11%) [1,2] and potential for low-cost production [3–6]. A typical DSSC consists of two conductive transparent glasses, ruthenium dye-sensitized TiO_2 film, a platinum catalyst layer and a liquid electrolyte containing I^-/I_3^- redox couple. In studies reported in the literature, attempts have been made to replace the components with new electrode materials [7–20], alternative sensitizers [21–28] and different types of electrolytes [29–41]. In most cases the studies were aimed at achieving advanced properties and usability of DSSC in order to meet the requirements of commercial applications and/or to reduce the production cost. An important issue in cost reduction is DSSC fabrication on flexible, transparent, conductive plastic substrates [42–45]. Obvious advantages against the conductive glass plates are those of light weight, versatile shape, easy handling and compatibility with a roll-to-roll type of production. In conventional fabrication of DSSCs a nanoporous TiO_2 film is formed by sintering at a high temperature, typically 450 °C. The high temperature removes organic surfactants and improves the film quality. However, this precludes the use of plastic substrates; thus, alternative methods to interconnect the TiO_2 particles into a porous film have been studied during recent years. The studies were focused on compression [42–46] and firing the TiO_2 film at lower temperatures (<150 °C) [47–52]. A light conversion efficiency as high as 6.1% (0.1 Sun) has been reported for static pressing [42] and 3.4% (0.1 Sun) for dynamic pressing in a roller mill [44].

In the present paper we studied the dynamic preparation of nanoporous TiO_2 films for the fabrication of DSSCs. The dynamic preparation includes spreading and pressing of the films with roll-to-roll compatible methods. For spreading of the TiO_2 paste, gravure printing was chosen, since it is a technique used in packing and printed matter industry, and it is a roll-to-roll type of preparation method [53]. Furthermore, gravure printing is not as critical for paste (ink) preparation as

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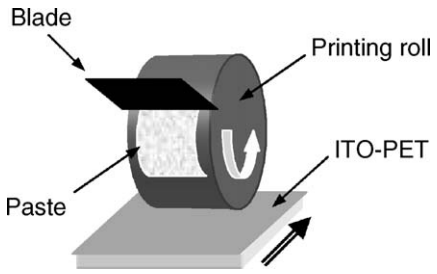

Fig. 1. Schematic presentation of gravure printing. The paste is transferred from the printing roll to the ITO–PET surface.

some other printing techniques, such as off-set and flexographic methods, and it also allows preparation of relatively thick films. In gravure printing, the paste is transferred from the patterned printing roll on top of a substrate; see Fig. 1. To form a stable nanoporous film, a rolling press, a laboratory sized paper calender, was used to compress the dry nanoparticle film on the surface of transparent conductive plastic substrate.

2. Experimental

2.1. Preparation of the photoactive electrode

Dye-sensitized TiO_2 films were made on conductive plastic, ITO-coated polyethylene terephthalate (PET) provided by Bekaert Specialty Films with a mean sheet resistance of 53 Ω/sq. The films were spread over the substrate either by doctor-blading or gravure printing as described in the following sections.

2.1.1. Spreading by doctor-blading

Titanium dioxide (TiO_2) paste was prepared by mixing 25 wt% of TiO_2 nanopowder (Degussa P25) in ethanol. After stirring, the paste was spread on the substrate using an adhesive tape as a frame. Following spreading, the film was left to dry in air for a few minutes and afterwards the substrate with the TiO_2 nanoparticle film was pressed. Two pressing methods were used: (1) applying static pressure of 10 kN/cm^2 and (2) calendering with Enfoplan laboratory calender EP-210 (steel rolls) at a linear load of 300 kN/m, a speed of 10 m/min and a temperature of 30 °C. Calendering nip pressure, in units of kN/cm^2, depends on the nip length when the pressed material is between the rolls. The nip length with steel rolls was of the order of 3 mm, which gives a calendering pressure of 10 kN/cm^2. This is the same as that used in the static pressing. In static pressing a Teflon sheet and in calendering a Tedlar sheet was used between the pressing plate/roll and the TiO_2 film. After pressing, the TiO_2 films were left for ∼18 h in a 0.3 mM ruthenium 535-bis TBA (Solaronix) solution (solvent: *tert*-butanol and acetonitrile, 1:1 vol%) for dye-sensitization. Sensitized films were rinsed with acetonitrile prior to the cell assembly.

2.1.2. Spreading by gravure printing

Three TiO_2 pastes were used in preparation: ∼16 wt%, ∼25 wt% and ∼30 wt% TiO_2 powder (Degussa P25) in 1 wt% ethyl cellulose solutions in a toluene/hexanol (1:5) mixture. The paste dried relatively slowly during the gravure printing, which ensures that the gravure roller did not clog. Gravure printing was performed with apparatus IGT G1 equipped with a printing cylinder which had 40 lines/cm and 80 μm deep cells. See Fig. 1 for schematic presentation of the gravure printing. The printing speed was 36 m/min and an applying force was either 150 N or 250 N. After TiO_2 spreading, the same pressing and dye-sensitization methods were used as for the samples prepared by the doctor-blading technique.

2.2. Preparation of the counter electrode

Sb-doped SnO_2 powder (Milliken Chemical, Zelec ECP-3010-XC) was platinized by mixing 700 μl 5 mM H_2PtCl_6 (Aldrich) in 2-propanol with 0.5 g SnO_2:Sb powder and heating in an oven for 15 min while the temperature increased from room temperature to 385 °C and then keeping the mixture at the final temperature for 10 min [44,54]. After this, the powder was stirred with 2 ml ethanol for about 12 h, spread by the doctor-blading technique on a conducting ITO–PET and subsequently pressed statically in a hydraulic press. This type of counter electrode was used in all samples, except one study in which pressing of counter electrode film was made by calender instead of static press (a study of totally calendered DSSC in Section 3.2).

2.3. Electrolyte and the cell assembly

A hotmelt polymer foil (Surlyn 1702, DuPont) was used as a spacer frame between the electrode substrates. The empty volume between electrodes was filled with an electrolyte consisting of 0.1 M LiI (Aldrich, 99.9%), 0.05 M I_2 (Aldrich, 99.8%), 0.3 M *tert*-butylpyridine (Aldrich, 99%) and 0.5 M 1-hexyl-3-methylimidazolium iodide (HMII was synthesized according to ref. [55]) in 3-methoxypropionitrile (Fluka, 99%). The electrodes were pressed together and heat-sealed at 95 °C. Finally, a silver paste was added on clean areas of ITO–PET to enhance conductivity and to ensure good contact during measurements. The fabricated DSSCs had a surface area of 0.8–1.0 cm^2.

2.4. Characterization of the cell

A calibrated mono-Si reference solar cell with KG3 filter was used to adjust the illumination. The samples were illuminated with a halogen lamp (Solux) of intensity corresponding to 0.1 Sun (10 mW/cm^2). No mask was used around the photoactive area, the dye–TiO_2 film, or the reference solar cell in the measurements. Current–voltage curves were measured by using a Keithley 2400 source measurement unit with Lab View 6.1 software.

3. Results and discussion

Influence of preparation method employed for TiO_2 spreading and compression on the performance of fabricated dye-sensitized solar cells was studied. The following roll-to-roll type preparation methods were selected in the study: spreading by gravure printing (Fig. 1) and pressing with a rolling press, i.e. paper calender. Samples made with these techniques were

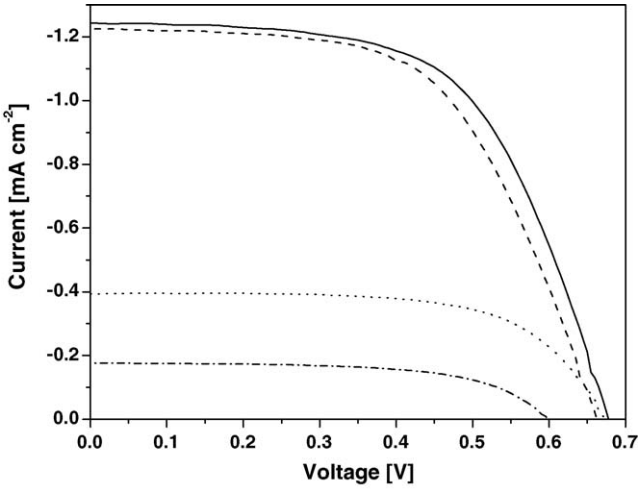

Fig. 2. Current–voltage curves measured on DSSCs with TiO_2 films fabricated by doctor-blading and static pressing (—), doctor-blading and calendering (- - -), gravure printing and static pressing (···) and gravure printing and calendering (-·-).

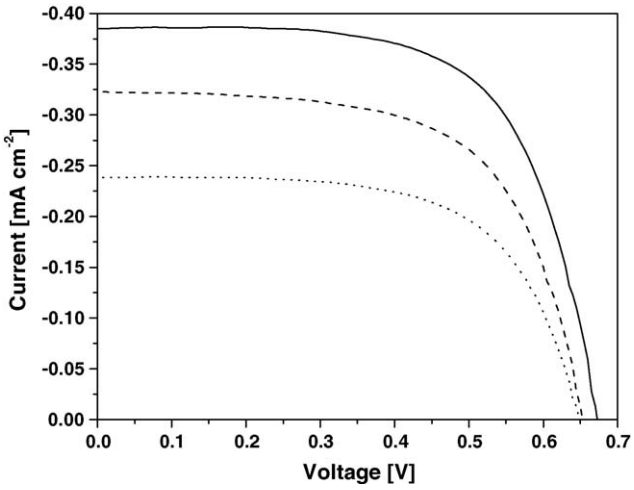

Fig. 3. Current–voltage characteristics measured for DSSCs with gravure printed TiO_2 films. Different content of TiO_2 nanoparticles in hexanol was used in the paste preparation: ∼30 wt% (—), ∼25 wt% (- - -) and ∼16 wt% (···). The corresponding light conversion efficiencies of the cells were 1.7%, 1.3% and 1.0%, respectively.

compared with those prepared by the doctor-blading and pressed statically in a hydraulic press. Fig. 2 shows the current–voltage characteristics measured on DSSCs fabricated by different TiO_2 preparation methods. Corresponding measured light conversion efficiencies and other characteristics are listed in Table 1.

3.1. Gravure printing

Pastes containing 16 wt%, 25 wt% and 30 wt% of TiO_2 nanoparticles were spread and tested in DSSCs. Higher solid content in the paste leads to thicker TiO_2 film and thus to a better absorption of the incoming light after dye-sensitization. Our study of how thickness of gravure printed TiO_2 film influences the performance of fabricated DSSCs showed that the higher content of TiO_2 in the paste, the higher light conversion efficiency attained (see Fig. 3). The highest efficiency of 1.7% was measured for a DSSC containing 30 wt% of TiO_2. Thickness of this TiO_2 film was ∼2 μm. Obviously, the optimum thickness was not achieved and thicker TiO_2 films are needed in order to increase the efficiency towards values measured for doctor-bladed and statically pressed films (see Table 1). However, there was a limit to the maximum amount of TiO_2 material that could be deposited by gravure printing so that we were not able to form any thicker films. Increasing the TiO_2 solid content in the paste was also not possible since this would increase its viscosity and eventually affect the printing quality. High solid content could also clog up the roller. Consequently, the light conversion efficiency of the best cell with gravure printing was only 1.7%. As this is due to insufficient thickness, it is, far from optimal conditions for a maximal absorption of light in dye-sensitized films.

Table 1
Characteristics of DSSCs based on differently spread and pressed TiO_2 films

Spreading method	Pressing method	Efficiency (%)[a]	FF	V_{oc} (V)	I_{sc} (mA/cm^2)
Gravure	Calender	0.7	0.62	0.60	0.18
Gravure	Static press	1.7	0.66	0.67	0.39
Doctor-blading	Calender	4.7	0.59	0.66	1.22
Doctor-blading	Static press	5.1	0.60	0.68	1.24

[a] Efficiency of the best performing cell.

3.2. Calendering

Calendering of the films was performed using a laboratory paper calender. In calendering, the pressure is applied on the TiO_2 film for a relatively short time. In this study pressing was done at a speed of 10 m/min, which gives a pressing time of 18 ms (nip length of 3 mm). This is a very short time compared to static pressing, where the pressure is applied for much longer time, ca. 30 s. Despite the difference in pressing conditions, quite similar results were attained for the different compression method; see Table 1 and Fig. 2. An efficiency as high as 4.7% was reached when doctor-bladed and calendered TiO_2 film was used in DSSC. This is close to that attained for DSSC based on statically pressed TiO_2 film, 5.1%. This implies that pressure in the calender was high enough to produce interconnected, good TiO_2 films for DSSCs. The cells based on gravure printed and calendered TiO_2 film showed clearly poorer performance than the statically pressed reference cells (0.7% versus 1.7%). This could arise from the fact that the thin gravure printed film was not as well compressed in the calender as thicker films. Another reason might be the use of Tedlar sheet between TiO_2 film and calender roll, since a tiny amount of TiO_2 material was transferred onto the protective plastic sheet during calendering. We also fabricated a totally calendered cell, where both electrodes were spread by doctor-blading and pressed in the calender (in the above studies counter the electrode was made by doctor-blading and static pressing). In the best case an efficiency of 3.2% was achieved, that is, however, somewhat lower than in the case of statically pressed counter electrode. The reason for

this lower performance is presently unclear and further study to clarify this point is needed.

4. Conclusions

Dynamic preparation of TiO_2 films for fabrication of dye-sensitized solar cells has been studied. Two spreading and pressing techniques were employed close to room temperature ($\leq$30 °C) to produce porous nanocrystalline TiO_2 films on conductive plastic substrates. Doctor-blading or gravure printing was used to spread TiO_2 paste and a static press or calender was used to compact the TiO_2 nanoparticles together in order to form a stable porous film.

The efficiency of cells with gravure printed TiO_2 film was found to be quite low. The best light conversion efficiency was only 1.7%. This was concluded to be due to insufficient thickness of the gravure printed TiO_2 film and thus a poor light absorption of the sensitized film in DSSC. Although thicker films were required, there was a limit of TiO_2 material that we were able to transfer by gravure printing on the ITO–PET substrate. A rolling press (paper calender) was found to be suitable for compressing nanoporous TiO_2 films. An efficiency as high as 4.7% was reached when doctor-bladed and calendered TiO_2 film was used in DSSC. This is close to what was attained for DSSC based on statically pressed TiO_2 film, for which an efficiency of 5.1% was measured.

The present work is aimed at developing methods that are compatible with roll-to-roll fabrication of DSSCs. The performance of the studied cells demonstrates that gravure printing and calendering can be used in making electrodes of DSSCs in a roll-to-roll process. To our knowledge this is the first report on employing a gravure printing in producing TiO_2 nanoporous films for DSSCs. Although dynamic pressing of TiO_2 films has been studied and patented by Hagfeldt and co-workers [43,44,56], in our approach a laboratory sized paper calender was employed for compression.

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