NANO-MICRO LETTERS ARTICLE
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Dye-sensitized Solar Cells with Higher J_{sc} by Using Polyvinylidene Fluoride Membrane Counter Electrodes

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(Received 16 August 2011; accepted 21 September; pulished online 29 September 2011.)

Abstract: A flexible counter electrode (CE) for dye-sensitized solar cells (DSCs) has been fabricated using a micro-porous polyvinylidene fluoride membrane as support media and sputtered Pt as the catalytic material. Non-conventional structure DSCs have been developed by the fabricated CEs. The Pt metal was sputtered onto one surface of the membrane as the catalytic material. DSCs were assembled by attaching the TiO_2 electrode to the membrane surface without Pt coating. The membrane was with cylindrical pore geometry. It served not only as a substrate for the CE but also as a spacer for the DSC. The fabricated DSC with the flexible membrane CE showed higher photocurrent density than the conventional sandwich devices based on chemically deposited Pt/FTO glass, achieving a photovoltaic conversion efficiency of 4.43%. The results provides useful information in investigation and development of stable, low-cost, simple-design, flexible and lightweight DSCs.

Keywords: Polyvinylidene fluoride; Counter electrode; Flexible; Dye-sensitized solar cell

Citation: Xiaodong Li, Dingwen Zhang, Si Chen, Heng Zhang, Zhuo Sun, Sumei Huang and Xijiang Yin, "Dye-sensitized Solar Cells with Higher J_{sc} by Using Polyvinylidene Fluoride Membrane Counter Electrodes", Nano-Micro Lett. 3 (3), 195-199 (2011). http://dx.doi.org/10.3786/nml.v3i3.p195-199

Introduction

Dye-sensitized solar cells (DSCs) have been regarded as one of the most promising third generation photovoltaic devices due to their easy production, possibility of low-cost manufacture process and relatively high efficiency to convert solar energy into electricity [1-5]. DSCs have been proved to achieve a record photoelectric conversion efficiency rate of 12.3% under global air mass (AM) 1.5 (100 mW/cm^2) [2] and long term stability under heat treatment [6-8]. Nevertheless, searching for better TiO_2 mesoporous electrodes [9], inversed opal nanostructures [10], hierarchical brush micro/nano structures [11], better sensitizers [12], better catalytic material [13] and more reliable sealing technology [14] to achieve high photovoltaic performance, good durability as well as low cost is a never-end work. Typically, a DSC comprises a dye-sensitized nanocrystalline titanium dioxide (TiO_2) electrode, electrolyte solution usually with a dissolved iodide/triiodide redox couple between the electrodes, and a counter electrode (CE). The function of the CE is to transfer electrons arriving from the external circuit back to the redox electrolyte and to catalyze the reduction of the triiodide ion [1,5]. Pt is used as the catalytic material and two pieces of transparent fluorine-doped tin oxide (FTO) coated glass as substrates for both counter and working electrodes. The relatively high sheet resistance of FTO glass imposes performance limitation, especially in large area devices [15]. FTO glass also has the problem of high cost. Conductive glass substrates account for over 30% of the total material cost of the DSC [16]. In addition, the shape limitation and fragile feature will bring transport problem for the FTO glass based DSCs. Future large solar electric conversion systems will prefer materials abundantly available and easily handled. Therefore, it is necessary to develop cheap and flexible materials for CEs which also exhibit high electrical

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conductivity, good chemical stability and good catalytic activity to the reduction of triiodide ions.

Inexpensive carbonaceous materials, such as graphite, carbon black, activated carbon, hard carbon sphere, various carbon nanotube, fullerene and graphene, have been widely investigated as the catalytic materials on FTO or ITO (indium tin oxide) glass for the CEs [17-20]. For example, monolithic DSCs have been developed using carbon as a back contact to cut the material cost [19,20], offering a prospect of low cost fabrication and simple manufacturing process [21]. Meanwhile, novel substrates such as plastic foils have been used to fabricate flexible CEs to achieve the requirement for portable electricity and high-throughput industrial roll-to-roll production [22,23]. However, the efficiency of the DSCs with these substrates is not high enough. Their long time stability is also needed to be improved for future applications.

Here, we present the feasibility of Pt coated membrane without using transparent conductive oxide glass substrate as the flexible CE for DSCs. In this CE a flexible and porous polyvinylidene fluoride (PVDF) membrane is used as support media for a Pt catalyst. The Pt metal was sputtered onto the membrane surface as the catalytic material. Non-conventional structure DSCs were developed using the fabricated CEs. Photovoltaic parameters were evaluated for the formed cells. The formed DSC with porous and flexible membrane CE shows higher photocurrent density than chemically deposited Pt/FTO glass based devices, achieving a photovoltaic conversion efficiency of 4.43%. Furthermore, the density of the flexible membrane is very low. Its mass per unit area is only 0.5% of that for the FTO glass with a thickness of 2.2 mm. This will benefit for lowering the transportation cost for large scale production. Another promising advantage is that the membrane CE provides cylindrical pores to hold the liquid electrolyte, which could retard liquid electrolyte leakage and improve the stability of DSC.

Experimental

Preparation of photo- and counter-electrodes

A design for a DSC with a membrane CE is schematically shown in Fig. 1. A FTO (Nippon) glass was first treated with 40 mM TiCl$_4$ aqueous solution at 70°C for 30 min, in order to make a good mechanical contact between the following printed TiO$_2$ layer and the conducting glass matrix. Next, a nanocrystalline TiO$_2$ film was fabricated on the FTO glass by screen-printing a TiO$_2$ (Degussa P25) paste [24]. The thickness of the nanocrystalline TiO$_2$ film was $12\sim14\,\mu$m. Then, a second $4\sim5\,\mu$m thick scattering layer of 300 nm sized TiO$_2$ particles (Sinopharm) was superimposed onto the nanocrystalline TiO$_2$ film by screen-printing. The screen-printed layers were gradually heated in air at 450°C for 15 min and 500°C for 15 min, respectively, to remove all organic components and establish sufficient inter-contacts between particles. After treated with 40 mM TiCl$_4$ solution [3], the TiO$_2$ electrode was sintered again at 500°C for 30 min in air, and then dye-coated in a 0.5 mM solution of dye N719 (Solaronix) in acetonitrile and tert-butyl alcohol (Volume ratio of 1:1) at room temperature for 20-24 h. The membrane CE was prepared by depositing Pt metal onto one surface of a micro-porous membrane with nominal pore size of 0.45 µm (PVDF, Membrane solutions) using radio frequency (RF) magnetron sputtering technique. Pt deposition was carried out for 40 s at a working pressure of 1.0 Pa of argon with a RF power of 80 W. The thickness of the deposited Pt layer was about 150 nm.

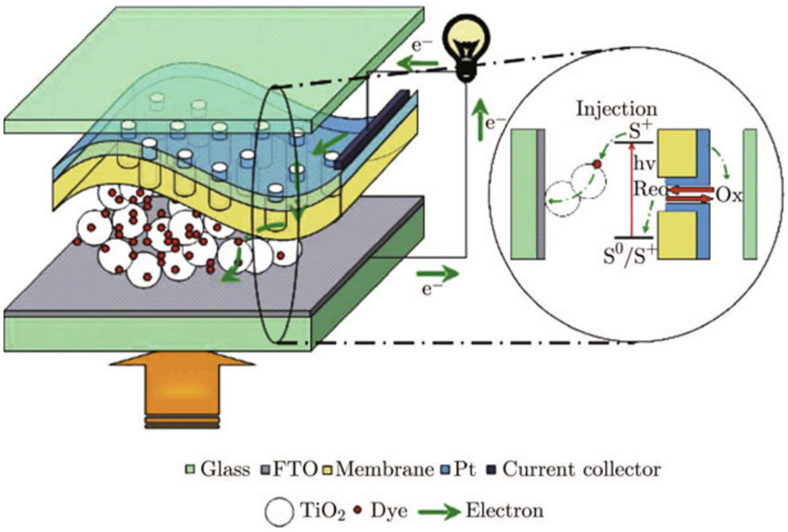

Fig. 1 The schematic of DSC with membrane counter electrode

Assembly of DSCs

Non-conventional structure DSCs were assembled using the fabricated working electrodes and PVDF CEs as shown in Fig. 1. The membrane CE was placed on the top of the TiO_2 electrode. The PVDF membrane surface without Pt coating was directly attached to the TiO_2 electrode. A thin cover glass sheet was then placed on the top of the membrane CE to assemble a sandwich-type cell. A drop of electrolyte solution (1 M 1-methyl-3-propylimidazolium iodide (MPII), 0.03 M I_2, 0.1 M Guanidine Thiocyanate (GuSCN) and 0.5 M tert-buthylpyridine in acetonitrile) was introduced into the cell by capillarity. The redox pairs within the electrolyte were allowed to pass the membrane though micro pores, as shown in the enlargement of Fig. 1.

Measurements of DSCs performance

Photocurrent–voltage (I-V) measurements were performed using an AM 1.5 solar simulator equipped with a 1000 W Xenon lamp (Model No. 91192, Oriel, USA). The solar simulator was calibrated by using a standard Silicon cell (Newport, USA). The light intensity was 100 mW/cm^2 on the surface of the test cell. I-V curves were measured using a computer-controlled digital source meter (Keithley 2440). The area of the solar cells is 0.196 cm^2.

Results and discussion

Morphology and structure characterization of membranes

Figure 2 shows a typical digital photograph of PVDF membrane surface before and after Pt coating. Pt deposition gave rise to a shinier surface, which can be expected to function as a back reflector to confine light and enhance the light absorption in the cell. The PVDF membranes both before and after Pt deposition showed so excellent flexibility that they can be attached on the surface of the TiO_2 electrode directly and firmly. The pore size and morphology of the original micro-porous membrane and the formed membrane CE was examined using scanning electron microscope (SEM). The original membrane showed a circular pore morphology in Fig. 3(a). The mean pore size was estimated to be about 0.45 µm. The thickness of the membrane was about 80 µm. The surface morphology of the Pt-coated membrane was shown in Fig. 3(b). The pore size of the Pt-coated membrane decreased to 0.1–0.2 µm approximately. The pores of the original and Pt-coated membranes were perpendicular to the membrane surface and exhibited cylindrical geometry. This vertical and unbending path is beneficial for ion transport. The porosity (the void fraction per unit volume of the porous film) was calculated from the total pore cross-sectional area within the scanned area. From the cross-section SEM analysis, the porosity value was high up to 25%, which helps the ionic diffusion in the electrolyte. Furthermore, PVDF, with the presence of fluorine which has the smallest ionic radius and the

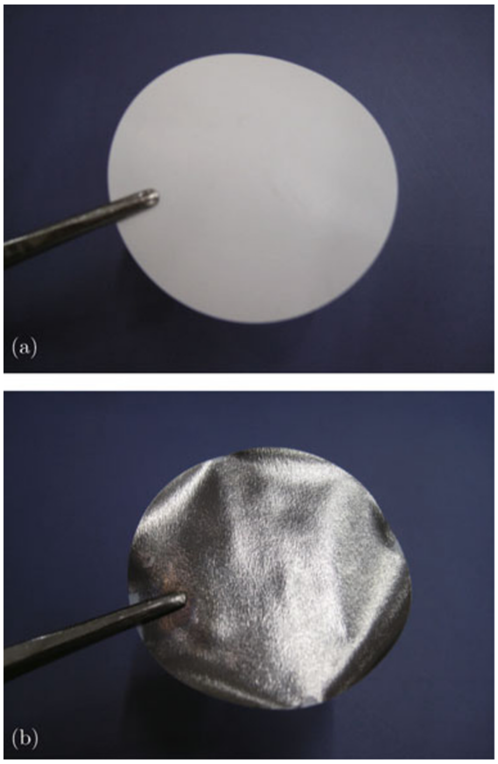

Fig. 2 Digital photograph of membrane (a) before and (b) after Pt coating

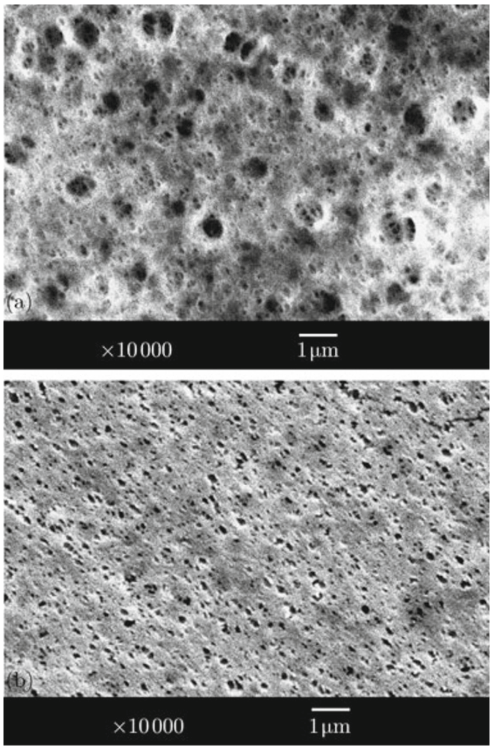

Fig. 3 SEM images of surface morphology of (a) membrane, (b) Pt-coated membrane CE

largest electronegativity, is expected to improve the ionic transport and reduce the recombination rate at TiO_2/electrolyte interface. It is reported that the solid electrolyte based on PVDF and poly (ethylene oxide) (PEO) showed good miscibility and improved ionic conductivity and achieved a high photo-to-current conversion efficiency, comparing to that of pure PEO polymer electrolyte [25].

Photovoltaic performance of devised DSCs

Figure 4 shows the photocurrent density-voltage characteristics of DSCs with Pt coated membrane and chemically deposited Pt/FTO as CEs, respectively, under air mass AM 1.5 simulated solar illumination at $100\,\mathrm{mW/cm^2}$. The detailed photovoltaic performance parameters are listed in Table 1. It can be seen that DSCs with the conventional CE exhibited a short-circuit current density (J_{sc}) of $14.04\,\mathrm{mA/cm^2}$, open-circuit voltage (V_{oc}) of 0.798 V, fill factor (FF) of 72.3% and conversion efficiency (η) of 8.10%. DSCs with the PVDF membrane CE displayed a lower V_{oc} of 0.724 V, a lower *FF* of 41.9%, but a higher J_{sc} of $14.62\,\mathrm{mA/cm^2}$. As a consequence, a η of 4.43% is achieved for DSCs with the flexible membrane CE.

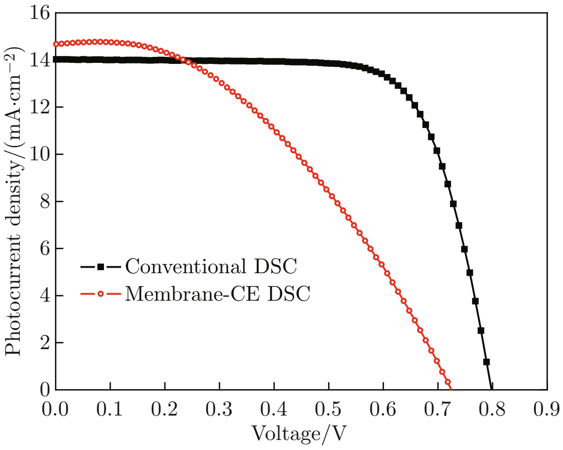

Fig. 4 Photocurrent density-Voltage characteristics of DSC with conventional (square) and membrane (circle) counter electrode

Table 1 Characteristics of photovoltaic performance of conventional and membrane-CE cells

Cells	J_{sc} (mA·cm^{-2})	V_{oc} (V)	*FF*	η (%)
Conventional DSC	14.04	0.798	0.723	8.10
Membrane-CE DSC	14.62	0.724	0.419	4.43

The higher J_{sc} value of DSCs with the PVDF membrane CE can be attributed to the circular and vertical pore morphology as well as the shiny surface of Pt coated membrane, which worked more efficiently as a back reflector to confine light and enhance the light absorption in the cell. In the case of the conventional sandwiched DSC based on chemically deposited Pt/FTO, the light passing through the photoanode and the electrolyte could also be reflected back by the Pt CE. However, since the residual photons need to pass through the dark color electrolyte twice and go back the TiO_2 layer, double absorption of the dark electrolyte weakens the residual light reflected back onto the photoanode. In the case of DSC with membrane CE, the light reflection can take place on both sides of the membrane, and the liquid electrolyte is only trapped in the pores of the membrane CE. As a result, the light absorption in the photoanode is enhanced, leading to a higher J_{sc} in DSC with the membrane CE.

Compared with the performance of the DSCs with CEs based on chemically deposited Pt/FTO, the most pronounced change of DSCs with the membrane CE is *FF*, which decreases from 72.3% to 41.9%. The lower *FF* value in the DSC with the membrane CE may originate from its lower rate to supply I_3^- ions to the Pt CE after membrane incorporation. The membrane film had a porosity of 25%, indicating that only 25% of the space was opened for the electrolyte transporting. Moreover, the photoanode and the Pt catalytic layer were separated by a Surlyn spacer (25 µm thick) in the conventional DSC. However, the thickness of the used membrane is up to 80 µm which is about three times thicker than the electrode gap of the conventional DSC. The increase of the electrode gap in the DSC results in the rise of the resistance of the electrolyte diffusion. This might have caused I_3^- depletion and retarded the dye regeneration kinetics [26], reducing the *FF* of the DSC with the membrane CE. Ito et al. found that significant performance increases can be achieved if the width of the spacer between the two electrodes in the conventional DSC is reduced [27]. Thus, higher efficiency can be expected for DSC based on the membrane CE by decreasing the thickness of the membrane.

The initially developed membrane CEs have shown high catalytic properties, good flexibility, capability of retarding liquid electrolyte leakage and good adhesion to TiO_2 electrodes, thus permitting good adhesion of TiO_2 electrode layer with flexible substrate and allowing the fabrication of stable, flexible, and cost-effective dye-sensitized solar cells. We are investigating the properties of the membrane CE by changing membrane geometry, thickness and Pt content in order to improve electrical conductivity and catalytic activity to the reduction of triiodide ions, which should significantly increase the *FF*, and thus raise the photovoltaic conversion efficiency. We believe that resolving this issue will allow us to produce solar cells with much higher efficiencies.

Conclusions

We have investigated the feasibility of a non-conventional structure dye-sensitized solar cell. A flexible counter electrode (CE) has been developed and tested for DSCs using a micro-porous PVDF membrane as support media for catalysts. The Pt metal was sputtered onto one surface of the membrane as the catalytic material. Non-conventional DSCs were fabricated by positioning the membrane CE onto the top of the TiO_2 electrode with the membrane surface without Pt coating being adjacent to the TiO_2 layer. The fabricated DSC with the flexible membrane CE shows higher photocurrent density than the conventional devices based on chemically deposited Pt/FTO glass, achieving a photovoltaic conversion efficiency of 4.43%. Improvements in device performance are expected with further studies as more of the material and morphological properties of membrane CEs are understood. Moreover, the method can be developed as a technology to fabricate flexible DSCs for portable electricity and large scale roll-to-roll production.

Acknowledgements

This work was supported by National Natural Science Foundation of China (No. 10774046), Shanghai Municipal Science & Technology Committee (No. 09JC1404600, No. 0852nm06100 and No. 08230705400) and Singapore Ministry of Education innovation fund (MOE IF Funding MOE2008-IF-1-016).

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