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RAPID COMMUNICATION

Nanocellulose aerogel membranes for optimal electrolyte filling in dye solar cells

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Abstract
A new method for depositing electrolyte in dye solar cells (DSCs) is introduced: a nanocellulose hydrogel membrane is screen printed on the counter electrode and further freeze-dried to form a highly porous nanocellulose aerogel, which acts as an absorbing sponge for the liquid electrolyte. When the nanoporous dye-sensitized TiO_2 photoelectrode film is pressed against the wetted aerogel, it becomes filled with the electrolyte. The electrolyte flows inside the TiO_2 film only about ten micrometers (i.e. the TiO_2 film thickness) whereas in the conventional filling method, where the electrolyte is pumped through the cell, it flows about 1000-times longer distance, which is known to cause uneven distribution of the electrolyte components due to a molecular filtering effect. Furthermore, with the new method there is no need for electrolyte filling holes which simplifies significantly the sealing of the cells and eliminates one common pathway for leakage. Photovoltaic analysis showed that addition of the nanocellulose aerogel membrane did not have a statistically significant effect on cell efficiency, diffusion in the electrolyte or charge transfer at the counter electrode. There was, however, a clear difference in the short circuit current density and open circuit voltage between the cells filled with the aerogel method and in the reference cells filled with the conventional method, which appeared to be caused by the differences in the electrolyte filling instead of the nanocellulose itself. Moreover, accelerated aging tests at 1 Sun 40 °C for 1000 h showed that the nanocellulose cells were as stable as the conventional DSCs. The nanocellulose aerogel membranes thus appear

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inert with respect to both performance and stability of the cells, which is an important criterion for any electrolyte solidifying filler material.

Introduction

Dye-sensitized solar cells, also known as dye solar cells (DSC), are based on cheap materials and easy preparation methods. Scaling up towards mass production roll-to-roll processes may offer an additional way to keep the manufacturing costs low [1,2]. Printing a dye solar cell involves several steps, but so far finding a printable electrolyte has been one of the bottlenecks [2]. Normally, the electrolyte is in liquid form which causes difficulties in the assembly and handling of the cell. When employing conventional filling methods, the electrolyte is pumped through the cell which is inconvenient for mass production purposes. Also, the porous dyed TiO_2 layer acts as a filter adsorbing some of the electrolyte additives, leading to an uneven distribution of the electrolyte components in the cell. Hence, significant spatial variations in the performance may result [3-6]. The efficiency losses due to this spatial effect have been as high as 35% [4]. The effects can be reduced to some extent by changing, e.g. the electrolyte composition [4-6]. Optimally, the electrolyte filling method should intrinsically result in an even spatial distribution.

For a printed electrolyte one would prefer a low cost and a high performance. The practical issue is to form an electrolyte which would not spill under the edge sealant, but would still pass easily through the porous TiO_2 layer. Semi-solid electrolytes are an attractive, although to date largely unexplored, solution to these problems: mixing the normal liquid electrolyte either with polymers and/or with nanoparticles has been proposed. Among those there are no recipes for printed electrolytes for DSCs. Another way to make a semi-solid electrolyte is to fill a porous polymer membrane with a liquid electrolyte [7,8]. To avoid any interference between such a membrane and the operation of the cell, the membrane should be thin to avoid a thick cell structure, and highly porous to enable a high charge transfer in the cell. In practice, fulfilling both requirements simultaneously and having a membrane that can be handled without breaking is problematic [7,8].

Here we propose using a nanocellulose aerogel membrane, which can be prepared by freeze-drying the nanocellulose hydrogel printed directly on the counter electrode. The nanocellulose aerogel serves as an absorbent for the electrolyte withholding it from spreading on the substrate and since the aerogel is supported by the counter electrode, the membrane can be made both highly porous and very thin. The nano-cellulose “sponge” is wetted with the electrolyte prior to the assembly of the cell. When the cell is encapsulated, the electrolyte sponge wets also the photoelectrode side of the cell. In this way the electrolyte comes into contact with the dyed TiO_2 film spatially, and it is not pushed laterally through the cell, which is important to achieve an even distribution of electrolyte components (Figure 1). Additionally, holes for filling the electrolyte are unnecessary, improving the reliability of the encapsulation. Nanocellulose is an interesting material for many practical applications, since it has multiple benefits; it derives from economic, abundant and renewable resources. In addition, being a non-toxic and sustainable biopolymer, it can be regarded as environmentally friendly. Relatively similar absorbing nanocellulose sponges, which herein are used to support the solar cell electrolyte, have been suggested as a solution to other environmental problems, such as cleaning the oil spills in marine environments [9].

Material and methods

Cell preparation

Fluorine-doped tin oxide (FTO) glass (TEC-15, Pilkington) was used as substrates for all of the prepared DSCs. Using glass substrates, we can avoid any questions related to the stability of the substrate which simplifies the stability analysis. The catalyst for the counter electrode was made by spreading 4 μl of 5 mM H_2PtCl_6 in 2-propanol on a clean substrate and then it was heated at 390 °C for 15 min. After the Pt catalyst layer was prepared, the nanocellulose hydrogel was screen printed on top of the counter electrodes by a screen printer (AT-60PD, ATMA) equipped with a mesh (NBC, 43-080 22.5°). Cellulose nanofibers were made of never-dried bleached birch kraft pulp and pre-treated as described elsewhere [10,11]. The gel was prepared by feeding the modified fiber suspension into a Microfluidizer M-7115-30. The fluidizer was equipped with a pair of ceramic (500 μm) and diamond (200 μm) chambers. The slurry had dry content of 1.0 wt% and it passed once through the chambers at the operating pressure of 1500 bar. After the printing, the layers were instantly frozen in liquid nitrogen, followed by vacuum freeze-drying to give nanocellulose aerogels with over 98% porosity, as reported previously [12]. The resulting membranes were on average about 10 μm thick. Since the nanocellulose hydrogel was not customized for screen printing the mesh left its mark as height variation in the film. Since the nanocellulose has only the purpose of restraining the electrolyte, the variation in height did not affect this main feature as Figure 2 indicates. We have also tested that this aerogel membrane preparation method works with flexible ITO-coated PET plastic substrates.

The photoelectrodes were made on FTO glass to simplify the analysis. A $TiCl_4$ treatment was given to the photoelectrode substrate before adding the TiO_2 layers: the substrates were placed in a solution of titanium (IV) chloride tetrahydrofuran complex (1 wt%) in distilled water and then heated in 70 °C for 30 min [13]. Three layers of TiO_2 were screen printed: the first two using a paste with small TiO_2 particles (Dyesol, 18NR-T) and the last layer using TiO_2

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