Environmentally friendly LiI/ethanol based gel electrolyte for dye-sensitized solar cells

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Abstract

An environmentally friendly LiI/ethanol/SiO 2 based gel electrolyte was synthesized by adding SiO 2 nanoparticles into optimized LiI/ethanol based liquid electrolyte and used in quasi-solid-state dye-sensitized solar cells (DSSC), an energy conversion efficiency of 6.1% has been achieved at AM 1.5 simulated sunlight (91.3 mW cm -2 ). It was revealed that this gel electrolyte afforded almost identical energy conversion efficiency of DSSC to the corresponding liquid electrolyte. This promising gel electrolyte will enable the fabrication of environmentally friendly quasi-solid-state DSSC free of solvent evaporation and leakage.

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1. Introduction

Dye-sensitized solar cells (DSSC) have received considerable attentions over the past decade for their high light-to-electricity conversion efficiencies, relatively easy fabrication procedures and low production cost [1–3]. The DSSC consists of a nanocrystalline mesoporous semiconductor (typically TiO 2 ) electrode coated with a monolayer of dye molecules, an electrolyte containing I 3 /I - redox couple and a platinum electrode [4]. The electrolyte, which is one of the key components in the design of such solar cells, can be divided into several kinds, such as conventional organic solvent-based liquid electrolytes [5], solid-state p-type inorganic semiconductors [6,7], conductive organic materials [8], gel electrolytes [9,10], room-temperature ionic liquids [11], and so forth. As we know, liquid electrolytes were widely used in DSSC because of its high energy conversion efficiency in contrast to other kinds of electrolytes. However, solvent evaporation and leakage of liquid electrolytes as well as the sealing problem significantly limit their practical application [12]. Moreover, the toxic organic solvents in this electrolytes, for example, acetonitrile, methoxyacetonitrile or methoxypropionitrile, may be disadvantageous to DSSC’s preparation and operation, and even to the environment.

Recently, it has been reported that a non-toxic and ionic liquid based electrolyte LiI(C 2 H 5 OH) 4 – I 2 was used to fabricate dye-sensitized solar cells with energy conversion efficiency of 4.9% under AM 1.5 (100 mW cm -2 ) irradiation [13]. Compare with other organic solvents such as acetonitrile, methoxyacetonitrile, 3-methoxypropionitrile, etc., ethanol lays great advantages of non-toxicity and environmental safety. To further investigate the environmentally benign electrolyte and to increase the overall energy conversion efficiency of DSSC, herein LiI/ethanol based liquid electrolytes have been further prepared. The effect of LiI
content of electrolytes on the performance of DSSC and on the ionic conductivities of electrolytes has also been investigated detailedly. With the successful substitution of toxic organic solvent, highly efficient DSSC with LiI/ethanol based liquid electrolyte has been achieved.

Additionally, it is found that the nanoparticles can be dispersed into liquid electrolytes to form stable gels [14], and the addition of ceramic oxides particles can improve the performance of electrolyte [15,16]. These significant findings inspired us to optimize the LiI/ethanol based gel electrolyte. In this letter, we selected SiO2 nanoparticles as gelator to solidify the LiI/ethanol based liquid electrolyte and obtained the quasi-solid-state electrolyte. Fortunately DSSC with this gel electrolyte renders a high energy conversion efficiency which is almost identical to that of DSSC with LiI/ethanol based liquid electrolyte.

2. Experimental

Lithium iodide (99.9%) was purchased from Aldrich Chemical Co. and used as received, ethanol was chromatographic grade (Concord Tech Co., Tianjin, China) and distilled from CaH2 to further reduce the content of water before use. Indeed it is impossible to remove water completely. Luckily the presence of residual water does not have obvious influence on the electrolyte. LiI/ethanol based liquid electrolyte was prepared by adding C2H5OH into LiI powder with vigorous stirring in an argon-filled glove box (M. Braun, water content <0.5 ppm). Ionic conductivity measurements of these liquid electrolytes were carried out by an electrochemical cell of Pt electrodes assembled in the glove box. The cell constant was determined with 0.01 mol L⁻¹ KCl solution at 25 °C. The ionic conductivities of electrolytes were determined by an AC impedance technique using an HP 4192A impedance analyzer from 5 Hz to 13 MHz. The AC voltage was fixed at 0.005 V.

The TiO2 (P25, Degussa AG, Germany, average particle size 21 nm) porous films were deposited on F-doped tin oxide (FTO) conducting glass (12 Ω sq⁻¹) by a screen-printing technique. The thickness of the TiO2 film was about 12 μm. Dye (RuL₂(NCS)₂·2H₂O, L = 2,2'-bipyridyl-4,4'-dicarboxylic acid, Solaronix) adsorption was carried out by soaking the TiO2 films in the dye solution (3 × 10⁻⁴ mol L⁻¹) for about 8 h. For comparison, an organic solvent-based liquid electrolyte was also prepared, which consists of 0.6 mol L⁻¹ dimethylpropylimidazolium iodide, 0.1 mol L⁻¹ of iodine (YiLi Fine Chemicals, Beijing, China), 0.5 mol L⁻¹ tert-butyl-pyridine and 0.1 mol L⁻¹ of lithium iodide in methoxyacetonitrile [17]. The electrolytes were dropped on the dye-anchored TiO2 film and then a platinum-sputtered conducting glass plate was firmly clipped with it, and a mask with a window of 0.15 cm² was also clipped on the TiO2 side to define the active area of the cell. The cells were illuminated by an Oriel solar simulator (91192) under AM 1.5 (91.3 mW cm⁻²) irradiation. The incident light intensity was measured by a radiant power/energy meter (Oriel 70260). The characteristics of the photocurrent density–photovoltage of the cells under this condition were recorded on a potentiostat/galvanostat (Princeton Applied Research, Model 263A).

In order to study the effect of the amount of LiI on electrolytes, we prepared LiI/ethanol solutions of different LiI content. After the LiI was completely dissolved in ethanol, I2 (LiI:I2 = 100:1, in molar ratio), 1.0 mol L⁻¹ 4-tert-butyl-pyridine (Aldrich Chemical Co.) were added into each solution, respectively.

3. Results and discussion

Table 1 displays the effect of LiI concentration (mol L⁻¹) on the photoelectrochemical performance parameters such as short circuit current (Isc), open circuit voltage (Voc), fill factor (FF) and efficiency (η) of DSSC with different LiI content (mol L⁻¹) electrolytes as well as room-temperature conductivities. From Table 1 we can see that the room-temperature ionic conductivity of the electrolyte initially increases with the increasing of LiI concentration, then reaches a maximum conductivity of 11.1 × 10⁻³ S cm⁻¹ at 1.70 mol L⁻¹, then decreases as the LiI is further added. The similar phenomena can also be observed in photocurrent density and energy conversion efficiency. Therefore, we can draw the conclusion that the LiI concentration of electrolyte has great influence on DSSC performance. When the LiI concentration in ethanol solution is 1.70 mol L⁻¹ (LiI:C2H5OH = 1:10, in molar ratio), DSSC with this LiI/ethanol based liquid electrolyte has its best performance, the open circuit voltage, short circuit current, fill factor and efficiency are 623 mV, 16.5 mA cm⁻², 56.3%, 6.3%, respectively.

With the purpose of optimizing the 1.70 mol L⁻¹ LiI/ethanol based liquid electrolyte, 5 wt% SiO2 nanoparticles (Degussa, A150, particle diameter 14 nm, supplied by Beijing Entrepreneur Science & Trading Co. Ltd. as a gift) were added with stirring and then sonicated to form a stable gel. Although the viscosity of LiI/ethanol/SiO2 based gel electrolyte is much higher than that of LiI/ethanol based liquid electrolyte, the ionic conductivity of 9.3 × 10⁻³ S cm⁻¹ does not change substantially, which is only 16%
lower than that of corresponding liquid electrolyte. The performance of DSSC with this gel electrolyte also scarcely changed, the open circuit voltage, short circuit current, fill factor and efficiency are 619 mV, 16.5 mA cm\(^{-2}\), 54.7%, 6.1%, respectively. Fig. 1 presents the photocurrent density–photovoltage curves of DSSC with LiI/ethanol based liquid electrolyte and LiI/ethanol/SiO\(_2\) based gel electrolyte at AM 1.5 illumination. Those two curves are almost identical, suggesting that the gel electrolyte is as efficient as corresponding liquid electrolyte. The possible reason for this phenomena is SiO\(_2\) nanoparticles we used are smaller than the pores of TiO\(_2\), so that the gel electrolytes can penetrate into the mesoporous TiO\(_2\) film easily to make a good contact with nanocrystalline TiO\(_2\). Additionally, triiodide and iodide can freely transfer in the open channels of silica nanoparticle network [14]. This quasi-solid-state DSSC maintains the advantages of non-toxicity and environmental safety, at the same time, it overcomes some drawbacks of the corresponding liquid DSSC, such as evaporation and leakage, and the most important, it maintains a high overall energy conversion efficiency.

The methoxyacetonitrile based liquid electrolyte mentioned above was also investigated in order to make a comparison, the highest energy conversion efficiency of DSSC with this electrolyte in our lab was 7.3% which was lower than 10.4% mentioned in Ref. [17]. So we can see that the DSSC with LiI/ethanol based electrolyte still has large space for further improvement by optimizing the TiO\(_2\) film, dyes and other assembling processes, moreover it is nontoxic and environmentally friendly, and will be promising for further practical applications.

4. Conclusion

Environmentally friendly LiI/ethanol/SiO\(_2\) based gel electrolyte has been synthesized and used in quasi-solid-state dye-sensitized solar cells. First, 1.70 mol L\(^{-1}\) LiI/ethanol based liquid electrolyte was synthesized, DSSC with this electrolyte exhibits the best performance compared with DSSC with other LiI concentration liquid electrolytes. Then, the LiI/ethanol/SiO\(_2\) based gel composite electrolyte was obtained by adding 5 wt% SiO\(_2\) nanoparticles into 1.70 mol L\(^{-1}\) LiI/ethanol based liquid electrolyte. The energy conversion efficiency of DSSC with this gel electrolyte is 6.1% under illumination of AM 1.5 simulated sunlight (91.3 mW cm\(^{-2}\)). This quasi-solid-state electrolyte alleviates the problems of solvent evaporation and leakage of DSSC, moreover, it is nontoxic and environmentally friendly. Thus, LiI/ethanol/SiO\(_2\) based quasi-solid-state electrolyte holds great potential for practical applications in dye-sensitized solar cells.

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