Electrochimica Acta 94 (2013) 1–6

Contents lists available at SciVerse ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Optimization of plastic crystal ionic liquid electrolyte for solid-state dye-sensitized solar cell

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ARTICLE INFO

Article history:
Received 31 October 2012
Received in revised form 24 January 2013
Accepted 27 January 2013
Available online 1 February 2013

Keywords:
Dye-sensitized solar cell
Plastic crystal electrolyte
Ionic liquid
Succinonitrile
Lithium perchlorate

ABSTRACT

An efficient plastic crystal-based electrolyte is prepared by employing succinonitrile as solid solvent and binary ionic liquids as charge transfer mediators for dye-sensitized solar cells (DSSCs). It was found that combining succinonitrile with ionic liquids could improve the mechanical property of electrolyte and avoid the fluidity of ionic liquid, and the fabricated solid-state solar cell shows an overall conversion efficiency of 2.14%, which can be further improved to 5.50% after optimizing the addition amount of lithium perchlorate ($LiClO_4$) as charge transfer promoter into the plastic crystal electrolyte, and the role of $LiClO_4$ in the plastic crystal ionic liquid electrolyte is evaluated through electrochemical and photoelectrochemical measurements. The knowledge obtained from this plastic crystal-based electrolyte exhibits new eyeshot to find solid-state electrolyte for DSSCs with high performance.

1. Introduction

Dye-sensitized solar cells (DSSCs) have been attracting considerable scientific and industrial research attention since it was first invented by Grätzal and his co-workers in 1991 [1]. As a clean, low-cost and highly efficient alternative to traditional silicon solar cells, such type of inorganic–organic hybrid device composed of dye-sensitized nanocrystalline porous TiO_2 film, Pt counter-electrode and volatile liquid state electrolyte, has exceeded energy conversion efficiency of 11% [2–4]. However, with the conventional organic liquid electrolyte contained in DSSCs, leakage and volatility easily cause the long-term stability problem and hinder the progress of actual application. Thus further improvements in photoelectric conversion efficiency and stability are explored by designing more efficient electron mediators or solid-state electrolytes to replace the volatile organic solvent that normally used in the highly efficient DSSCs. Therefore, p-type inorganic semiconductors [5–8], organic hole-transport materials [9,10], polymer gel electrolytes [11–16], and solvent-free ionic liquid electrolytes [17–19], were investigated for the solid-state dye-sensitized solar cells to solve the long-term stability problems and promote the commercial prospect of DSSCs.

Succinonitrile, as a molecular plastic crystal, has been reported as a versatile matrix for solid-state ionic conductors [20]. It appears a monoclinic structure at low temperature, and then undergoes a first-order transition to a plastic phase at −40 °C, after which the plastic phase of succinonitrile then occupies a body-centered cubic structure until it melts at 58 °C. In this phase, the molecules exist in three isomeric conformations (two gauche isomers and one trans isomer), which are interrelated by a 120° rotation around the central C—C bond [21]. The high polarity of succinonitrile ensures its ability to dissolve various salts, and showing ionic conductivity that originates solely from the doping salt in non-ionic matrix. Therefore, considerable interest in plastic crystal (such as succinonitrile) has been developed after the recognition of their potential function as a new type of solid-state electrolyte in lithium battery since years ago [22–24].

Recently, succinonitrile plastic crystal with good mechanical flexibility was also employed as electrolyte matrix for all solid-state DSSCs, and satisfying results were obtained [25–27]. Herein, we report a plastic crystal-based electrolyte by employing succinonitrile as solid solvent, binary ionic liquids as iodide sources without addition of iodine for fabricating solid-state DSSCs. Combining succinonitrile with ionic liquid was to improve the mechanical properties of electrolyte and avoid fluidity of ionic liquid. Reducing I_2 (or I_3^-) content in the electrolyte was intended to avoid its high light absorption and volatility, which easily cause the enhanced dark current and reduced ionic conductivity of the electrolyte, and then the decrease of the cell performances. Moreover, it was found that incorporating lithium perchlorate ($LiClO_4$) as charge transfer promoter into the electrolyte can efficiently enhance the ionic conductivity of the plastic crystal ionic liquid electrolyte. The present novel plastic crystal-based electrolyte will broaden our eyeshot to find a series of new solid-state electrolyte materials with

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http://dx.doi.org/10.1016/j.electacta.2013.01.130

potential high photoelectrochemical characteristics in the application of DSSCs.

2. Experimental

2.1. Materials

Two kinds of ionic liquids, 1-methyl-3-propylimidazolium iodide (PMII) and 1-methyl-3-butylimidazolium iodide (BMII) were purchased from Wuhan Geao Company, China, and used as procured. Succinonitrile was supplied by Aladdin Chemistry Co. Ltd and used without further purification. Dye (N719, $Ru(dcbpy)_2(NCS)_2$) was obtained from Solaronix S.A. (Switzerland). 200 nm light-scattering anatase TiO_2 particles were provided by Dalian HeptaChroma Co., Ltd. Fluorine doped tin oxide (FTO) conductive glass with a sheet resistance of about 15 $\Omega\,sq^{-1}$ was used as substrate for supporting the porous TiO_2 films, which were cut into 1.8 cm × 1.2 cm sheets, and ultrasonically cleaned in detergent water, acetone and ethanol in turns before use.

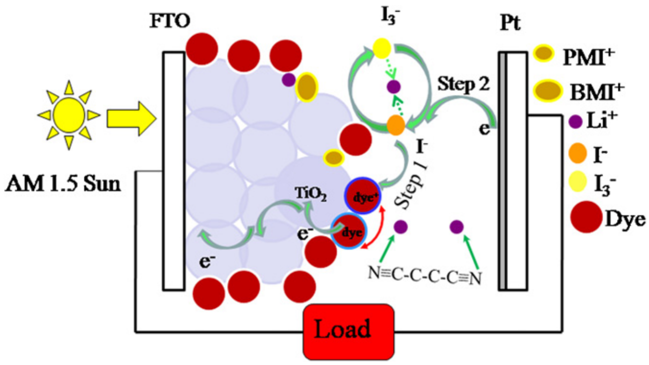
2.2. Preparation of paste and plastic crystal electrolyte

Homemade colloidal anatase TiO_2 paste was synthesized as follows. TiO_2 nanoparticles were synthesized from hydrolysis of 12.5 ml tetraisopropyl titanate in 75 ml of 0.1 M HNO_3, followed by autoclaving at 200 °C for 12 h. And then the TiO_2 nanoparticles were collected and mixed with ethanol, acetic acid and terpinol ethylcellulose, finally the mixture was ball-milling for 12 h to obtain the homogeneous TiO_2 paste.

The plastic crystal electrolyte was made by mixing PMII and BMII in succinonitrile with a mole ratio of 2:1:125, and then lithium perchlorate ($LiClO_4$) with different contents (0–7 wt%) was added to the mixture. Afterwards, it was stirred at 60 °C sufficiently to obtain the homogeneous electrolyte, which was preheated at 70 °C before spreading onto the dye-sensitized TiO_2 film by using doctor-blade method. The proposed charge transport mechanism in the present solid-state DSSC fabricated with plastic crystal ionic liquid electrolyte is shown in Scheme 1.

2.3. Assembly of dye-sensitized solar cell

Dye-sensitized solar cell was assembled by the routine method. A 10 μm-thick film of TiO_2 particles was prepared by spreading homemade colloidal anatase TiO_2 paste on the conducting glass with doctor-blade method followed by sintering at 500 °C for 30 min, and then a 4 μm thick second layer of 200 nm light-scattering anatase TiO_2 particles was coated onto it with another calcination process. Afterwards, the film electrode was heat treated in 50 mM $TiCl_4$ aqueous solution at 70 °C for 30 min and then sintered at 500 °C again. Subsequently, the TiO_2 electrode was immersed into 0.3 mM N719 ethanol solution overnight at room temperature for sufficient sensitization. The plastic crystal electrolyte was spread onto the TiO_2 electrode, and then a Pt counter electrode was covered to construct a sandwich solar cell device.



Scheme 1. Schematic diagram of the charge transport mechanism in the solid-state DSSC fabricated with plastic crystal-based electrolyte.

2.4. Characterization of plastic crystal electrolyte

Differential scanning calorimetry (DSC) curves of electrolytes were measured by using Thermal Analyzer (Laici STA 49 C) with a nitrogen flow rate of 50 mL min^{-1} and according to the following procedure: (1) heating from room temperature to 100 °C at 10 °C min^{-1}; (2) cooling to −80 °C at 20 °C min^{-1}; (3) second heating to 100 °C at a heating rate of 10 °C min^{-1}. The results presented here are based on the second heating step.

The ionic conductivity of electrolyte was surveyed through a conductivity meter (DDSJ-308A, Leici, Shanghai) equipped with a platinum black electrode. The redox behavior of I^-/I_3^- in the plastic crystal ionic liquid electrolyte was examined by cyclic voltammetry (CV) by using a Pt ultra-microelectrode as working electrode and Pt foil as counter electrode, Ag/AgCl electrode as reference electrode. Steady-state voltammetry was detected in a photoelectrochemical cell equipped with Pt ultra-microelectrode (~30 μm in diameter) work electrode, platinum foil counter electrode, and Ag/AgCl reference electrode.

2.5. Photoelectrochemical measurement of dye-sensitized solar cell

The electrochemical behavior and current density–voltage (*J–V*) characteristic for the fabricated DSSC were collected by using CHI618 electrochemical station (CH Instruments). The DSSC was illuminated by light with energy of a 100 mW cm^{-2} from 300 W AM 1.5G simulated sunlight (2 × 2 beam, w/6258 lamp, Newport, USA). The light intensity was determined using a SRC-1000-TC-QZ-N reference monocrystalline silicon cell system (Oriel, USA), which was calibrated by National Renewable Energy Laboratory, A2LA accreditation certificate 2236.01.

The electrochemical impedance spectra (EIS) measurement was carried out with applying bias of the open circuit voltage (V_{oc}) under the illumination conditions and recorded over a frequency range from 0.05 Hz to 10^5 Hz with ac amplitude of 10 mV. All of the measurements mentioned above were taken under ambient conditions.

3. Results and discussion

3.1. Physical characterization

Fig. 1 depicts the differential scanning calorimetry (DSC) curves of the bare succinonitrile and plastic crystal ionic liquid electrolytes. As can be seen, the plastic crystal phase of the bare succinonitrile can be observed in the temperatures ranging from −40 to 60 °C. Blending succinonitrile with binary ionic liquids decreased the melting temperature (T_m) from 60 to 50 °C, while the transition endothermic temperature (T_{pc}) remained constant. Adding $LiClO_4$ into the above mixture can further decrease the T_m while no obvious effect on the T_{pc} can be observed, suggesting that Li^+–succinonitrile matrix may have developed in the plastic crystal electrolyte due to the high polarity of succinonitrile, which could easily dissolve various salts. By considering the very low residual energy for the plastic crystal phase transformation into a more disordered state, it is likely that the salt-containing domains are disordered and highly dispersed in the plastic crystal phase [20]. With enhancing the $LiClO_4$ content up to 5 wt%, the T_m decreased to 35.5 °C, indicating an enlarged disordered salt-containing domain