



Robust conducting gel electrolytes for efficient quasi-solid-state dye-sensitized solar cells



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ABSTRACT

The incorporation of polyaniline (PANI) with three-dimensional (3D) gel matrix is versatile in expanding reduction reaction (triiodide → iodide) area from Pt counter electrode/electrolyte interface to 3D framework of the conducting gel electrolyte and elevating electrocatalytic activity. In the current work, four methods have been applied to fabricate PANi incorporated poly(acrylic acid)-poly(ethylene glycol) (PAA-PEG) conducting gel electrolytes with an aim of enhancing PANi dosage and therefore charge-transfer ability. The electrical and electrochemical performances of the resultant conducting gel electrolytes are thoroughly characterized. An impressive light-to-electric power conversion efficiency of 7.36% is determined from B2 gel electrolyte based dye-sensitized solar cell.

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1. Introduction

Dye-sensitized solar cells (DSSCs) are attracting growing academic and industrial interests because of their potential in resolving energy and environmental problems [1–3]. A typical DSSC is an electrochemical device converting solar energy into electricity with no pollution emission. It comprises a dye-sensitized TiO₂ anode, a Pt counter electrode (CE), and iodide/triiodide (I⁻/I₃⁻) redox couples in organic solvent [4]. The working principle of a DSSC is the transition of organic dyes from ground state to their excited state under irradiation of incident light, electrons are released from excited dye molecules and injected into conduction band of TiO₂ nanocrystalline along the conducting channels. The excited dyes will be subsequently recovered by I⁻/I₃⁻ redox species, which are finally reduced by a Pt CE under participation of reflux electrons (the electrons from external circuit to Pt CE) [5]. Generally, the I⁻/I₃⁻ redox couples are dissolved in organic solvent such as acetonitrile to prepare liquid electrolyte because of the rapid charge transfer. To date, an impressive power conversion efficiency of 12.3% has been recorded using liquid electrolyte [6]. A remaining problem is the leakage of liquid electrolyte and volatilization of organic solvent, which result in the attenuation of long-term photovoltaic performances of DSSCs [7,8]. This is also one of the critical restrictions for the commercialization of DSSCs. By

addressing this issue, full-solid-state electrolytes without organic solvent are preferred candidates [9–11]. However, the known solid-state electrolytes with vibration of molecular chains or segments can generate relatively low charge transfer kinetics in comparison with the facile migration of I⁻/I₃⁻ couples in organic solvents. Therefore, the photovoltaic performances of the DSSCs from solid-state electrolytes are unsatisfactory.

A compromise method is to integrate the rapid charge transfer ability of liquid electrolytes with chemical stability of solid-state electrolytes [12–14]. Considering the extraordinary absorption performance and retention of hydrophilic hydrogel to aqueous solution, an amphiphilic gel matrix can be designed by modifying the hydrophilic frameworks. Previous works on this field mainly focus on the imbibition of liquid electrolyte in various gel matrices [15–17]. Wu *et al.* have reported the incorporation of I⁻/I₃⁻ species in organic solvent with amphiphilic gel matrices, giving power conversion efficiencies of approximately ~ 6.0% [18,19]. Although strenuous efforts have been made in recent years, the enhancement of conversion efficiency is still slowpased. PANi has become one of the most important conducting polymers and been intensively studied in last two decades because of its organic semiconductor nature and interesting redox properties [20,21]. There are three states for typical PANi: protonated emeraldine, protonated pernigraniline, and leucoemeraldine [22]. The redox reactions among them are accompanied by electron migration, therefore, PANi nanostructures have been widely employed as CE materials in efficient DSSC devices [23,24]. With an assumption of introducing PANi into three-dimensional (3D) matrix to

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form a conducting hydrogel, in our early research [25–28], we have systematically the fabrication of conducting hydrogels. The results show that the PANi molecular chains have been homogeneously attached onto the inner surface of hydrogel matrices. Except PANi, graphite [29,30] and Cu [31] can also be incorporated into hydrogel matrices to design conducting hydrogels. It is expected that the PANi molecular chains can conduct electrons into whole conducting hydrogel framework. Supposing that such conducting hydrogels are employed as gel electrolytes in quasi-solid-state DSSCs, the reflux electrons (from external circuit to Pt CE) can be conducted from Pt layer to 3D framework of PANi incorporated conducting gel electrolyte. This presupposition has been consolidated validated by our recent research [32–35]. In our recent works [32–35], we have investigated the acceleration effect of conducting polymers [such as PANi and polypyrrole] or carbon materials (such as graphene, graphene oxide, or nanographite) on liquid electrolyte loading and electrocatalytic activity of conducting gel electrolytes for I^-/I_3^- redox species. We find that the manner of introducing conducting substances such as PANi has significant effect on photovoltaic performances of the resultant DSSC devices.

In the current work, we systematically investigate the dependence of electrical and electrochemical behaviors as well as photovoltaic performances of the resultant DSSCs on incorporation manner of PANi with polyacrylate-poly(ethylene glycol) (PAA-PEG) matrix. The resultant gel electrolytes are thoroughly evaluated by swelling kinetics, and electrical and electrochemical characterizations. The manner of incorporating PANi is optimized, giving an efficiency of 7.36% for its DSSC device.

2. Experimental

2.1. Synthesis of PAA-PEG membrane

The PAA-PEG membrane was synthesized according to the following procedures [36,37]: In detail, a solution mixture consisting of acrylic acid monomer (7.2 ml, AA, analytical reagent) and PEG (2.2 g, $M_w = 20,000$, analytical reagent) was made by agitating in deionized water (10 ml) in a water-bath at 80 °C. Under vigorous agitation, crosslinker *N,N'*-(methylene)bisacrylamide (NMBA, 0.015 g) and initiator ammonium persulfate (APS, 0.1 g) were subsequently added to the above mixture. With the proceeding of polymerization, the viscosity increased gradually. When the viscosity of the PAA-PEG reached around 180 mPa s⁻¹, the reagent was poured into a Petri dish and cooled to room temperature with the formation of an elastic transparent gel. The PAA-PEG membranes were then molded into ϕ 2.5 cm die. After rinsing with deionized water, the membranes were dried under vacuum at 50 °C for 24 h.

2.2. Preparation of PANi

0.592 ml of aniline was dissolved in 20 ml of 1 M HCl aqueous solution to obtain a homogeneous mixture. 20 ml of 0.125 M APS aqueous solution was dipped in the above mixture within 30 min. The polymerization reaction was carried out at 0 °C. After 3 h, the resultant reactant was rinsed by 1 M HCl aqueous solution, filtrated, and finally vacuum dried at 60 °C for 24 h.

2.3. Preparation of conducting gel electrolytes

The conducting gel electrolytes from PAA-PEG matrices were prepared by four manners, as was shown in Fig. 1. A redox liquid electrolyte consisted of 100 mM of tetraethylammonium iodide, 100 mM of tetramethylammonium iodide, 100 mM of tetrabutylammonium iodide, 100 mM of NaI, 100 mM of KI, 100 mM of LiI, 50 mM of I₂, and 500 mM of 4-tert-butyl-pyridine in 50 ml

acetonitrile. The resultant gel electrolytes were nominated A1, A2, B1, and B2, respectively.

2.4. Assembly of quasi-solid-state DSSCs

A layer of TiO₂ nanocrystal anode film with a thickness of 10 μ m and active area of 0.25 cm² was prepared by coating the TiO₂ colloid using a screen printing technique, followed by sintering in air at 450 °C for 30 min. Subsequently, the TiO₂ film was soaked in a 0.5 mM N719 [cis-di(thiocyanato)-*N,N'*-bis(2,2'-bipyridyl)-4-carboxylic acid-4-tetrabutylammonium carboxylate, purchased from Dyesol LTD, Australia] ethanol solution for 24 h to uptake N719 dye for the fabrication of dye-sensitized TiO₂ photoanode. The quasi-solid-state DSSCs from four gel electrolytes were fabricated by sandwiching a slice of gel electrolyte with a thickness of around 1 mm between dye-sensitized TiO₂ anode and a Pt counter electrode (300–400 μ m in thickness, purchased from Dalian HepatChroma SolarTech Co., Ltd).

2.5. Photovoltaic measurements

The photocurrent-voltage (*J-V*) curves of the assembled quasi-solid-state DSSCs were recorded on an electrochemical workstation (CHI600E) under irradiation of a simulated solar light from a 100 W xenon arc lamp in ambient atmosphere. The incident light intensity was calibrated using a FZ-A type radiometer from Beijing Normal University Photoelectric Instrument Factory to control it at 100 mW cm⁻² (AM 1.5). Each DSSC device was measured at least five times to eliminate experimental error and a compromise *J-V* curve was employed.

2.6. Characterizations

The ionic conductivities of the conducting gel electrolytes were measured by using a pocket conductivity meter (DSSJ-308A, LeiCi Instruments). The instrument was calibrated with 0.01 M KCl aqueous solution prior to experiments. Tafel-polarization curves of the symmetrical cells fabricated of samples were measured by CHI660E electrochemical workstation. The symmetrical dummy cells were fabricated by sandwiching a slice of gel electrolyte with thickness of around 1 mm between two identical Pt electrodes (Pt electrode/conducting gel electrolyte/Pt electrode). The electrochemical impedance spectroscopy (EIS) was carried out using a CHI660E electrochemical workstation at a constant temperature of 20 °C with an ac amplitude of 20 mV in the frequency range from 0.1 to 10⁵ Hz in the dark. The cyclic voltammetry was also carried out on a CHI660E electrochemical workstation in a N₂-purged PANi-free liquid electrolyte: a conducting gel electrolyte sandwiched by two symmetrical Cu electrodes was used as a working electrode, Pt foil as the counter electrode, and an Ag/AgCl electrode as reference electrode, the supporting electrolyte was 0.1 M LiClO₄, whereas the redox couple was 10 mM LiI and 1 mM I₂. The piercing depth of the Pt wire into gel electrolyte was controlled at 1 cm.

3. Results and discussion

The PAA-PEG matrix is a crosslinked 3D network structure of amphiphilic polymer with an ability to imbibe and retain aqueous or organic solutions. The imbibition nature of the matrix is due to the presence of functional groups (-COOH, -OH, and alkyl segments) in the crosslinked polymer network [38]. The presence of these functional groups results in a high osmotic pressure difference between the polymer matrix and surrounding medium, causing the inflow of a large amount of external solution and swelling of polymer network. The extremely high liquid adsorption and retention properties of the PAA-PEG matrix make it suitable for

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