Supporting Information

A Quasi-Solid-State Solar Rechargeable Battery with Polyethylene Oxide Gel Electrolyte

Bao Lei, Guo-Ran Li, Peng Chen, Xue-Ping Gao*

Institute of New Energy Material Chemistry, School of Materials Science and Engineering, Nankai University, Tianjin 300350, China.

* E-mail: xpgao@nankai.edu.cn, Tel/Fax: +86-22-23500876.
Experimental section

1. Pre-treatment of Nafion membrane

Before experiments, the Nafion membrane was pretreated. Briefly, the Nafion 117 membrane was immersed in H₂O₂ (5 %) and H₂SO₄ solution (1 mol L⁻¹) and boiled for 1 h, respectively. After immersing in boiling de-ionized water for several times to remove the sulfuric acid, the cleaned membrane was treated in boiling water containing LiClO₄ (1 mol L⁻¹) till to the pH=7 to exchange H⁺. Followed by rinsed with absolute ethanol, the pretreated Nafion 117 membrane was stored in the mixed solution of propylene carbonate (PC) and ethylene carbonate (EC) with volume ratio of 1:1.

2. Preparation of the photo-anode and counter electrode

The N719 sensitized TiO₂ photo-anode film was prepared as following. A TiO₂ film was coated on FTO (F-doped SnO₂) conductive glass by a typical doctor-blade method, and then sintered in muffle furnace at 500 °C for 1 h with a heating rate of 10 °C min⁻¹. After cooling to room temperature naturally, the resulting TiO₂ film was immersed in N719 dye (ethanol solution, 40 mmol L⁻¹) for 12 h in the dark. When further rinsed with absolute ethanol and dried by a hair drier, the dye-sensitized TiO₂ photo-anode was finally obtained. The effective area of the TiO₂ photo-anode was 1 cm². The 9,10-anthraquinone (AQ) was mixed with multi-walled carbon nanotubes (MWCNTs), carboxymethyl cellulose sodium (CMC, 10 wt. %) aqueous solution with the mass ratio of 8:1:1. The mixture was ground to form a paste, which was coated on clean nickel foam by the doctor-blade method. After drying and pressing under 30 MPa, the bi-functional electrode was prepared as a counter electrode in DSSCs and an energy storage anode in secondary battery.
3. Preparation of gel electrolyte

LiClO$_4$(1.064 g) was added to the mixed solvent of EC (5 mL) and PC (5 mL). And then, PEO (average Mw=100000) was added to the solution to form a gel electrolyte, the obtained gel electrolyte was worked as anode electrolyte directly. The cathode electrolyte contained 4-tert-butylpyridine (TBP, 0.5 mol L$^{-1}$) in the as-prepared gel electrolyte.

4. Fabrication of the solar rechargeable battery

The solar rechargeable battery with sandwich construction was assembled by stacking the dye-sensitized TiO$_2$ photo-anode, LiI cathode, Nafion membrane separator and counter electrode/anode in order. The spaces between electrodes and separator were full of the as-prepared cathode and anode gel electrolytes with an injector.

5. Electrochemical measurements

In cyclic voltammograms (CVs) of LiI cathode, N179 dye and 9,10-anthraquinone (AQ) anode, a conventional three-electrode system with metal Pt counter electrode and Ag/Ag$^+$ reference electrode was carried out on a IM6ex (Zahner) electrochemical workstation. The CV test of LiI cathode with a scan rate of 50 mV s$^{-1}$ was conducted using a mirror-like Pt/FTO as working electrode in gel electrolyte containing LiI (0.1 mol L$^{-1}$). The CV measurement of N719 dye was performed using adsorbed N719 dye FTO conductive glass as working electrode with a scan rate of 100 mV s$^{-1}$. The CV test of AQ was operated in gel electrolyte with a scan rate of 50 mV s$^{-1}$. Electrochemical impedance spectra (EIS) were measured on a IM6ex (Zahner) electrochemical workstation using a symmetric cell with two identical FTO conductive glass electrodes from 100 kHz to 100 mHz with an amplitude voltage of 5 mV. The ion conductivity ($\sigma$) of the gel electrolyte was calculated from the EIS results. The photo-charge and electrochemical
constant-current discharge measurements of the solar rechargeable battery was checked on a LAND-CT2001A instrument with an assistant illumination by a sunlight simulator (Oriel Sol 2A, Newport) under 100 mW cm\(^{-2}\) irradiation in the photo-charge process.

![Photo of the as-prepared quasi-solid-state gel electrolyte.](image1)

Fig. S1. Photo of the as-prepared quasi-solid-state gel electrolyte.

![Typical charge-discharge curves in initial 3 cycles of the solar rechargeable battery with liquid and PEO gel electrolytes.](image2)

Fig. S2. Typical charge-discharge curves in initial 3 cycles of the solar rechargeable battery with liquid and PEO gel electrolytes.
Fig. S3. (a) Voltage profiles of the solar rechargeable battery with PEO gel electrolyte in different photo-charging time under 100 mW cm$^{-2}$ irradiation, and discharging at a discharge current density of 4 mA g$^{-1}$ in the dark. (b) Discharge capacity vs. cycle number during 10 cycles.

Fig. S4 Nyquist plots of the solar rechargeable battery photo-charged for 10 min in the frequency range from 100 kHz to 10 mHz.
Fig. S5 (a) J-V curves of the dye-sensitized solar cells with AQ and Pt counter electrodes under irradiation (100 mW cm\(^{-2}\)). (b) \(\eta_{\text{CE}}\), \(\eta_{\text{EC}}\) and \(\text{OECE}\) of the solar rechargeable battery with 7.5 wt % PEO gel electrolyte at the discharge current density of 4 mA g\(^{-1}\) in the dark after photo-charging for 10 min.

References

1. Li, L.; Drillet, J. F.; Dittmeyer, R.; Juttner, K. Formation and Characterization of PEDOT-Mofified Nafion 117 Membranes. J. Solid State Electrochem. 2006, 10, 708-713.