

Quasi-solid-state nanocrystalline TiO₂ solar cells using gel network polymer electrolytes based on polysiloxanes

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Abstract A quasi-solid-state dye-sensitized nanocrystalline porous TiO₂ film solar cell was fabricated using a novel gel network polymer electrolyte based on polysiloxanes with both polyethylene oxide internal plasticized side chains and quaternary ammonium groups. The cell exhibited better photoelectrical conversion performance under 60 mW/cm² irradiation. The short photocurrent (I_{sc}) of 5.0 mA/cm² and open voltage (V_{oc}) of 0.68 V were achieved, and the energy conversion efficiency (η) and fill factor (ff) were 3.4% and 0.60, respectively.

Keywords: gel network polymer electrolytes, nanocrystalline porous TiO₂ film, dye-sensitized, solar cell.

Novel solar cells based on dye-sensitized nanocrystalline porous TiO₂ film have been attracted widespread attention and investigated intensively^[1–3]. These cells usually employ a liquid electrolyte containing an I⁻/I₃⁻ redox couple in organic solvents. However, the use of a liquid electrolyte results in the difficulty in cell sealing and the decrease in cell performance or life time during long-term operations due to evaporation or leakage of organic solvent. The approaches to solving these problems are solidification of electrolytes. Some attempts have been carried out to replace the liquid electrolytes with non-volatile or solid state materials, such as (1) ambient molten salts^[4], (2) p-type semiconductors^[5], (3) inorganic hole conductors^[6,7], (4) polymer electrolytes^[8,9] or (5) addition of low molecular weight gelators to the liquid electrolyte^[10,11]. The cells employing the former three electrolytes exhibit lower energy conversion efficiencies. The gelation of the liquid electrolyte by using low molecular weight gelators has yielded quasi-solid-state solar cells with comparable energy conversion efficiency to those with liquid electrolytes. But the sealing and stability of cells still remain the problems in these cells. The employment of polymer electrolytes is favorable to overcoming these problems. Therefore, they have been attracted intensive attention and have made significant progress^[12–15]. In comparison with linear polymers, chemi-

cally crosslinked gel network electrolytes have higher ability of retaining solvent and better physical stability. Yanagida et al.^[12] reported that solid-state cells were fabricated using the polymer electrolyte prepared by the *in-situ* polymerization of α -methacryloyl- ω -methoxyocta(oxyethylene) (MMO) with the crosslinking agent. These cells exhibited higher efficiency of 2.62%. But this polymerization cannot perform in the presence of iodide ions and therefore makes the fabrication of cells more complicated. We have succeeded in preparing a new type gel network polymer electrolyte based on polysiloxane with polyethylene oxide (PEO) internal plasticized chains by direct crosslinking reaction in the presence of iodide ions and constructing dye-sensitized solar cells^[16]. To increase ionic conductivity of polymer electrolytes and promote the interaction between the polymer and inorganic iodide in the electrolytes, the quaternary ammonium groups are further introduced on the main chains of the polymer. In this paper, we report the successful application of novel polysiloxane gel network electrolytes with both PEO internal plasticized side chains and quaternary ammonium groups to dye-sensitized nanocrystalline porous TiO₂ film solar cell.

1 Experimental

Preparation of dye-sensitized nanocrystalline porous TiO₂ electrodes is as follows. A colloidal TiO₂ suspension was prepared by hydrolysis of titanium isopropoxide (Aldrich, 97%) precursor in the pH=1 aqueous solution under vigorous stirring at 80 °C. The suspension was then autoclaved at 250 °C and evaporated in a rotary evaporator followed by adding carbowax (M-20,000) and ultrasonic dispersion to give a viscous TiO₂ paste. The nanocrystalline TiO₂ electrode was obtained by spreading the TiO₂ paste on the F-doped SnO₂ conducting glass (30 ohm square⁻¹) and then sintering at 450 °C for 30 min in air. After cooling to about 80 °C, the TiO₂ electrode was immersed in 5 × 10⁻⁴ mol/L dye solution of *cis*-di(thiocyanato)-N,N'-bis(2,2'-bipyridyl-4,4'-dicarboxylic acid) ruthenium (II) complex ([RuL₂(NCS)₂]) in absolute ethanol, and kept for 36 h.

Platinized counter electrodes were prepared by rotating spread of 1.5 × 10⁻² mol/L H₂PtCl₆ solution in isopropanol on the F-doped SnO₂ conducting glass and then sintering at 390 °C for about 13 min after air-drying.

Fabrication of quasi-solid-state dye-sensitized nanocrystalline TiO₂ solar cell is as follows. The polymer precursor was mixed with KI, I₂ and ethylene carbonate (EC)/propylene carbonate (PC) (8 : 2 V/V) according to a preset ratio. Then self-made crosslinker TMP-TDI was added and the mixture was heated at 80 °C for 1 h. After that, the mixture was applied on the nanocrystalline porous TiO₂ electrode. The platinized counter electrode was clipped on the top of the TiO₂ working electrode and heat-

ed continuously at 80 °C to complete the polymerization. Thus a quasi-solid-state solar cell was obtained.

Photoelectrical properties of the cell were recorded with a PAR potentiostat (model 273) and a type 3036 x-y recorder under 60 mW/cm² incident light intensity at room temperature. A 250 W tungsten halogen lamp was used as a light source and the active cell area was 0.20 cm².

2 Results and discussion

(i) Structure and conductivity of gel network polymer electrolytes. Fig. 1 shows the structure of prepolymers and gel network polymers. Fig. 1(a) exhibits the structure of polysiloxane only with internal plasticized PEO side chains^[17], while Fig. 1(b) is one with both PEO side chains and quaternary ammonium groups^[1], Fig. 1(c) gives the network structure crosslinked.

The optimum composition of gel network polymer electrolytes used in this paper is as follows. Electrolyte A was composed by mixing prepolymer (a) with 10 wt% KI, 200 wt% EC/PC solvent mixture, 5 × 10⁻² mol/L I₂ and crosslinker. Electrolyte B was formed by mixing prepolymer (b) with 23.5 wt% KI, 170 wt% EC/PC solvent mixture, 5 × 10⁻² mol/L I₂ and crosslinker.

The conductivity of the above gel network polymer electrolytes was measured using HIOKI LCR 3520 Hi TESTER at 1 KHz. The results are shown in Table 1. From the table it can be seen that the ion conductivity of both electrolyte A and B close to the magnitude order of 10⁻³, which is substantially at the similar order with the one of commonly used liquid electrolytes such as 3 × 10⁻¹ mol/L LiI/3-methoxy propionitrile (4.44 × 10⁻³ S · cm⁻¹) and 3 × 10⁻¹ mol/L KI/EC/PC (8 : 2 V/V) (6.06 × 10⁻³ S · cm⁻¹). This indicates that the gel network polymer electrolytes used herein will not increase significantly the internal resistance of the cell and interfere with the charge transport between the two electrodes. It can be further found by comparing the two electrolytes that the incorporation of quaternary ammonium group increases the

conductivity of polymer electrolyte significantly, which implies that the quaternary ammonium groups have certain cooperation with inorganic iodide. This should be helpful to increasing the solubility of salts in the polymer and accelerate the ion mobility.

Table 1 Ambient ion conductivity of gel network polymer electrolytes

Electrolyte	Ion conductivity (25 °C)/S · cm ⁻¹
A	0.85 × 10 ⁻³
B	1.51 × 10 ⁻³

(ii) Photoelectrical performance of quasi-solid-state nanocrystalline porous TiO₂ cells with gel network polymer electrolytes. Quasi-solid-state nanocrystalline porous TiO₂ solar cells were assembled with the above two novel gel network polymer electrolytes. Fig. 2 gives the photocurrent-photovoltage curves of the two cells. Their photoelectrical data are listed in Table 2. From Fig. 2 and Table 2, it can be seen that the two cells have different photocurrent-photovoltage characteristics. The cell with electrolyte A shows lower *I*_{sc}, *h*, *ff* and higher *V*_{oc}, while for the cell with electrolyte B, *I*_{sc}, *h* and *ff* are much higher than ones of the former, but with lower *V*_{oc}. These demonstrate that, compared with the former, a better interface contact between nanocrystalline TiO₂ electrode and electrolyte was formed in the latter, which accelerate greatly the reduction reaction of the oxidized dye cations by iodide in the electrolyte (2D⁺+3I⁻ → 2D+I₃⁻) (significant enhancement of *I*_{sc}) and increase slightly the recombination between the electrons injected into the TiO₂ conduct band from dye molecules and triiodide in the electrolyte (I₃⁻ + 2e_{cb} → 3I⁻) (slight decrease of *V*_{oc}). Furthermore, a preliminary stability experiment was performed by keeping the cell with electrolyte B unsealed. After 40 h, the *I*_{sc}, *V*_{oc}, *h* and *ff* of the cell were 5.25 mA/cm², 0.62 V, 3% and 0.55, respectively. Compared with original values, the maximum fluctuation of these data is less than 12%, showing that the novel gel network polymer electrolyte used in this paper has good physical stability.

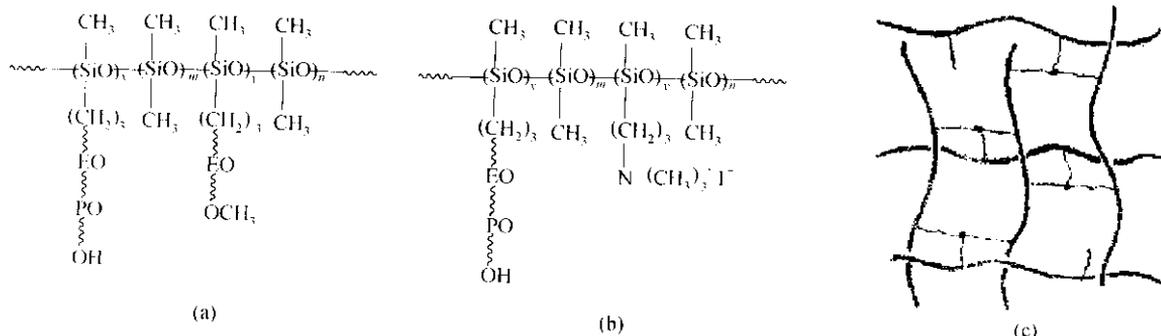


Fig. 1. Structure schemes of prepolymers and gel network polymers, wherein $(x + y) : (m + n) = 9 : 1$.

1) Kang, J. J., Fang, S. B., Synthesis and ionic conductivity of comb-like polysiloxanes with pendant oligo (ox > yethylene) side chains and quaternary ammonium groups, Polymer Bulletin, in press.

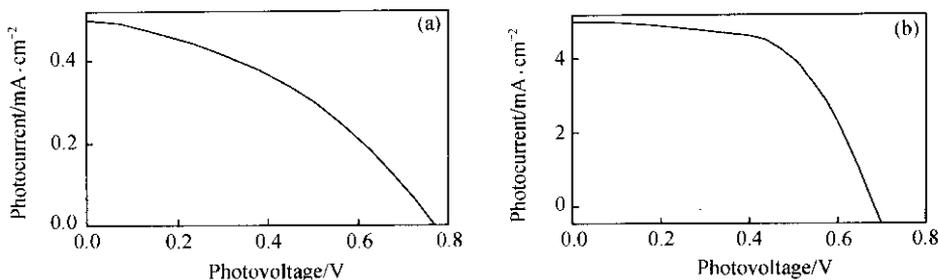


Fig. 2. Photocurrent-photovoltage curves of quasi-solid-state solar cells with the novel gel network polymer electrolytes. (a) Electrolyte A; (b) electrolyte B.

Table 2 Photoenergy conversion performance of cells assembled with the two electrolytes

Electrolyte	Short current $I_{sc}/\text{mA cm}^{-2}$	Open voltage V_{oc}/V	Fill factor (ff)	Photoenergy conversion efficiency η (%)
A	0.50	0.77	0.34	0.13
B	5.0	0.68	0.60	3.4

The incorporation of quaternary ammonium groups into the network backbone of polysiloxane with internal plasticized PEO side chains increased greatly the ion conductivity of the novel gel network polymer electrolyte. We applied this electrolyte successfully in dye-sensitized nanocrystalline porous TiO₂ film solar cell. The performance of the quasi-solid-state cell will be further improved by optimizing the composition of the gel network electrolyte and the interface between nanocrystalline TiO₂ electrode and the electrolyte.

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