A 7.72% efficient dye sensitized solar cell based on novel necklace-like polymer gel electrolyte containing latent chemically cross-linked gel electrolyte precursors

Li Wang, Shibi Fang,* Yuan Lin, Xiaowen Zhou and Miyu Li

Received (in Cambridge, UK) 21st July 2005, Accepted 19th September 2005
First published as an Advance Article on the web 19th October 2005
DOI: 10.1039/b510335e

Novel necklace-like polymer gel electrolytes containing latent chemically cross-linked gel electrolyte precursors were prepared for quasi-solid dye sensitized solar cells with a highest efficiency of 7.72% and an active area of 0.25 cm^2 under AM1.5 condition at 100 mW cm^{-2} irradiation.

In recent years, dye sensitized solar cells (DSC) based on nanocrystalline porous TiO_2 films have attracted much attention because of their relatively higher efficiency and low cost compared with conventional inorganic photovoltaic devices.[1,2] This type of solar cell has achieved an impressive photo-to-energy conversion efficiency of over 10% where the electrolyte is organic liquid solvents containing I^-/I_3^- as redox couple. Because of high volatility, solvent losses occur during long-term operations, resulting in lower DSC performances. Additionally, leakage of liquid electrolyte also limits the durability of DSC. Several attempts have been made to replace the organic liquid electrolytes by p-type semiconductor,[3] hole-transporting materials,[4] polymer electrolytes,[5–7] solidification of liquid electrolytes with physically cross-linked gelators[8–15] and polymer gel electrolytes.[16,17] However, the cells fabricated with p-type semiconductor, hole-transporting materials and polymer electrolytes as electrolytes still show lower conversion efficiencies. The gel electrolytes made from physically cross-linked gelators are not stable. Therefore, polymer gel electrolytes are promising electrolytes for DSC.

As is well known, quasi-solid electrolytes have difficulty permeating into the pores of TiO_2 electrodes because of high viscosity. However, this problem can be solved by thermal polymerization after permeation of the monomer and electrolyte into the pores of the TiO_2 electrode. Furthermore, vinyl monomers are difficult to polymerize in DSC electrolyte because radical intermediates are deactivated by iodine.[9] However, in our study, the quaternization reaction of two constituents of latent chemically cross-linked gel electrolyte precursors was not inhibited by iodine because the reaction proceeds with the formation of quaternary ammonium salt. The latent chemically cross-linked gel electrolyte precursors are suitable for *in situ* polymerization of DSC electrolytes because the quaternization reaction occurs at high temperatures even if the solution contains iodine.[18]

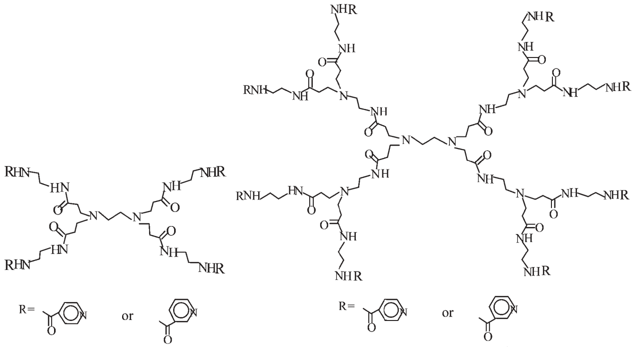
The Hayase group have reported several papers on polymer gel electrolytes containg chemically cross-linked gelators.[19–24] However, the gelators in most of their work contain one high molecular-weight constituent with high viscosity, as a result of which the constituent finds difficultly to permeate into the pores of TiO_2. Only one paper of their group has reported on 'latent chemically cross-linked gel electrolyte precursors'.[20] The Yanagida group have investigated imidazole ionic polymer electrolytes containing chemically cross-linked gelators by *in situ* polymerization.[18] Their gelators can also be denoted as 'latent chemically cross-linked gel electrolyte precursors'. However, the cell efficiency of the systems reported by these two groups is not high and they have not investigated the structure of polymer gel electrolytes.

Here, we provide another novel type of latent chemically cross-linked gel electrolyte precursors and focus our attention on the easy cell fabrication with the novel precursors, the structure of novel polymer gel electrolytes and their ability to retain the liquid electrolyte performances. The viscosity of the precursors is low at first and does not increase during the storage at room temperature. However, when the precursors are heated at 80 °C, they solidify the electrolytes immediately. The polymer gel electrolytes have three features: (1) they have good contact with the TiO_2 electrodes because the latent chemically cross-linked gel electrolyte precursors in liquid electrolyte can permeate easily into pores of TiO_2 electrodes, and then form the polymer gel electrolytes through quaternization reaction *in situ* when heated; (2) they have the ability to show >90% of the conversion efficiency of the liquid electrolytes; (3) they have a crosslinking necklace-like structure which was verified by atomic force microscopy (AFM). The novel polymer gel electrolytes consisted of iodine, *N*-methylbenzimidazole (NMBI) or *tert*-butylpyridine (TBP), inorganic salts (KI or LiI) and two constituents of latent chemically cross-linked gel electrolyte precursors in ionic liquid or other organic solvents. The first constituent of latent chemically cross-linked gel electrolyte precursor as shown in Scheme 1 are polypyridyl-pendant poly(amidoamine) (PAMAM) dendritic derivatives (PPDD) while the second constituent is a difunctional halogen derivative (DHD) of poly(ethylene oxide) (PEO) having iodide groups on the chain ends ($I(CH_2CH_2O)_nCH_2CH_2I$, $M_n = 370$). Photoelectrochemical characteristics of dye sensitized solar cells with the polymer gel electrolytes is investigated and discussed.

Dendrimers have highly branched, monodisperse structure and globular, void-containing shapes, which make them interesting and important precursor building blocks in synthesis. The noncrystalline nature of the dendrimers makes them attractive as the host for electrolytes in order to overcome the crystallization of inorganic salts.[9] Additionally, these branched polymer electrolytes contain a large number of chain ends which should result in a high free volume and low glass transition temperature, which can improve the conductivity and DSC performances. In consideration of

---

Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China. E-mail: fangsb@iccas.ac.cn; Fax: 86-10-62559373; Tel: 86-10-62613252



1 2 3 4

Scheme 1 Structure of PPDD

special structure and function of dendrimers, the first constituent of the latent chemically cross-linked gel electrolyte precursors with PAMAM dendritic structure was designed.

The difunctional halogen derivative was synthesized in consideration of the interaction between TiO_2 and ethylene oxide and the polarity effect of ethylene oxide chain group, which can improve the ion-dissociation and, consequently, provide excellent redox charge–transport properties.[25,26] The ethylene oxide chains can provide very high free volume resulting in good segmental mobility while maintaining good mechanical properties.

PAMAM dendrimers (G1.0 and G2.0) were prepared according to the literature.[27] PPDD† were synthesized by the reaction between PAMAM dendrimers (G1.0 or G2.0) and nicotinic acid or isonicotinic acid with 1-hydroxybenzotriazole (HoBt) and *N*,*N*′-dicyclohexylcarbodiimide (DCC) as condensation reagents.

DHD (M_n = 370)† was synthesized through halogen exchange reaction from $Cl(CH_2CH_2O)_nCH_2CH_2Cl$ (M_n = 187) and anhydrous sodium iodide while $Cl(CH_2CH_2O)_nCH_2CH_2Cl$ (M_n = 187)† was prepared from the reaction between poly(ethylene glycol) (M_n = 150) and thionyl chloride with pyridine in dichloromethane.

The TiO_2 electrode (crystal phase of TiO_2 particles made in our lab: anatase, particle size is 13.5 ± 1 nm, film thickness: 8 μm, roughness factor: 1200, porosity: 40%) was obtained by spreading the TiO_2 paste on the conducting glass (fluorine-doped tin oxide glass, sheet resistance: 30 Ω square^{-1}) substrate using the 'doctor blade method' and then sintered at 450 °C for 30 min in air. After cooling to 80 °C, TiO_2 electrodes were dipped into 0.5 mM solutions of *cis*-di(thiocyanato)-*N*,*N*′-bis(2,2′-bipyridyl-4,4′-dicarboxylic acid)ruthenium(II) ($[RuL_2(NCS)_2]$) in absolute ethanol for 24 h at room temperature. Afterwards, the dye-sensitized TiO_2 electrode was rinsed with absolute ethanol and dried in air. A platinized electrode prepared by thermal decomposition of H_2PtCl_6 on the conducting glass substrate at 390 °C for 15 min was used as the counter electrode. The cells were illuminated by an Oriel solar simulator (91192) under AM1.5 (100 mW cm^{-2}) irradiation. Photoelectrochemical measurements were performed with a potentiostat/galvanostat (EG&G Princeton Applied Research, model 273) at room temperature. The active area was 0.25 cm^2.

Dye-sensitized solar cells with polymer gel electrolytes were fabricated as follows. First, 0.5 M iodide, 0–0.5 M inorganic salt, 0.5 M NMBI or TBP and the two constituents of latent chemically cross-linked gel electrolyte precursors (10wt%) were stirred and dissolved in ionic liquid or organic solvent at room temperature to obtain a homogeneous phase solution. Second, the dye-sensitized solar cells were fabricated by sandwiching the homogeneous phase solution between the TiO_2 electrode and the counter electrode with a clamp. Finally, the homogeneous phase solution became a chemically cross-linked polymer gel electrolyte when the cells were heated at 80 °C for 0.5 h and then cooled to room temperature. From the above process, it can be seen that the polymer gel electrolytes should have good contact with the TiO_2 electrode. Cells with liquid electrolyte (0.5 M iodide, 0–0.5 M inorganic salt and 0.5 M NMBI or TBP in ionic liquid or organic solvent) as reference electrolytes were also fabricated.

The polymer gel electrolytes containing compound **1** and DHD have almost the same ionic conductivity ($>10^{-3}$ S cm^{-1}) as those containing compounds **2–4** and DHD. So in this study, we only selected compound **1** with DHD to form chemically cross-linked polymer gel electrolytes. Further research on compounds **2–4** with DHD will be reported in due course in other papers.

The two constituents of latent chemically cross-linked gel electrolyte precursors contain different functional groups. When they reacted with each other, their mol ratio can be 1:1, 1:2 or 1:3, respectively. We found that 1:2 is the best ratio for the chemically cross-linked polymer gel electrolytes where the cells have higher efficiency and conductivity than those with other mol ratios. Therefore in our study, the 1:2 mol ratio for the two constituents of latent chemically cross-linked gel electrolyte precursors was fixed.

The 1:2 mol ratio of the two constituents of latent chemically cross-linked gel electrolyte precursors means 1:1 functional group mol ratio of the two precursors. The extent of cross-linking reaction is almost 100% according to the disappearance of the peaks in FTIR (C–I, 502 cm^{-1}) and ^1H NMR ($-CH_2I$, δ 3.2).

When the latent chemically cross-linked gel electrolyte precursors concentration is above 10 wt%, the chemically cross-linked polymer gel electrolytes can be formed. The conductivity is reduced when the latent chemically cross-linked gel electrolyte precursors concentration is above 20 wt%. Thus 10 wt% of latent chemically cross-linked gel electrolyte precursors was chosen for the polymer gel electrolytes.

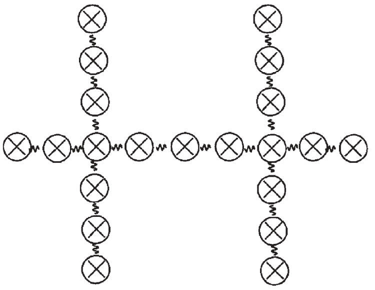
Table 1 shows photoelectrochemical performances of cells fabricated with polymer gel electrolytes (G1–G7) and the corresponding liquid electrolytes (L1–L7), respectively. The highest efficiency is 7.72% with J_{sc} = 17.1 mA cm^{-2}, V_{oc} = 700 mV and ff = 0.64 where the polymer gel electrolyte contains 0.1 M LiI, 0.1 M I_2, 0.5 M NMBI, 0.6 M 1-hexyl-3-methylimidazolium iodide (HMII) and 10 wt% latent chemically cross-linked gel electrolyte precursors in 3-methoxypropionitrile (MPN) under AM1.5 condition at 100 mW cm^{-2} irradiation. From Table 1 it can be seen that G1–G7 have good ability to retain over 90% of the conversion efficiency of L1–L7, respectively, which is attributed to the special structure and function of dendrimers, the interaction between TiO_2 and ethylene oxide and polarity effect of the ethylene oxide chain group. The efficiency of cells fabricated with polymer gel electrolytes changes little in several months while that of cells made with liquid electrolytes decreases substantially.

Scheme 2 is a crosslinking necklace-like structural representation of the polymer gel electrolytes where the bead on the necklace represents the dendrimer part while the chain between the beads is the DHD part because the dendrimers usually have global or elliptical structure[27] and DHD has chain structure. The

Table 1 Cell photoelectrochemical performances with G1–G7 and L1–L7 with active area of 0.25 cm^2 under AM1.5 condition at 100 mW cm^{-2} irradiation

Electrolyte	J_{sc}/mA cm^{-2}	V_{oc}/mV	ff	η (%)
G1	9.20	610	0.62	3.50
G2	14.00	744	0.66	6.87
G3	14.55	752	0.60	6.60
G4	13.40	750	0.64	6.40
G5	17.10	700	0.64	7.72
G6	13.70	721	0.65	6.42
G7	14.50	722	0.63	6.60
L1	13.20	570	0.60	4.50
L2	18.10	680	0.60	7.40
L3	16.20	656	0.65	6.90
L4	13.50	760	0.70	7.20
L5	18.80	690	0.61	7.90
L6	13.67	700	0.73	7.00
L7	17.10	670	0.65	7.45

[a] L1: 0.5 M LiI, 0.5 M I_2, 0.5 M NMBI in HMII; L2: 0.5 M KI, 0.05 M I_2, 0.5 M TBP, in ethylene carbonate (EC)–propylene carbonate (PC) (4:1, v:v); L3: 0.1 M KI, 0.1 M I_2, 0.5 M TBP, 0.6 M HMII in EC/PC (4:1, v:v); L4: 0.1 M LiI, 0.1 M I_2, 0.5 M NMBI, 0.6 M HMII in acetonitrile; L5: 0.1 M LiI, 0.1 M I_2, 0.5 M NMBI, 0.6 M HMII in MPN; L6: 0.1 M LiI, 0.5 M I_2, 0.5 M NMBI in HMII/MPN (13:7, v:v); L7: 0.5 M LiI, 0.05 M I_2, 0.6 M HMII in EC–butyrolactone (3:7, v:v); G1–G7 are the corresponding polymer gel electrolytes of L1–L7, respectively. The content of latent chemically cross-linked gel electrolyte precursors in the polymer gel electrolytes is fixed at 10 wt%. The mol ratio of PPDD:DHD is 1:2.



Scheme 2 Sketch map of the necklace-like polymer gel electrolytes.

crosslinking necklace-like nanostructure, which provides tunnels which help the diffusion and transport of iodide and triiodide, was verified by AFM as seen in Fig. 1.

In conclusion, novel chemically cross-linked polymer gel electrolytes were successfully employed for DSC with the highest efficiency of 7.72%. The crosslinking necklace-like nanostructure was verified by AFM. The cell performances show that the chemically cross-linked polymer gel electrolytes are promising electrolytes because of three advantages: (1) they have good contact with the TiO_2 electrodes because the latent chemically cross-linked gel electrolyte precursors in liquid electrolytes can permeate easily into pores of TiO_2 electrodes and form polymer gel electrolytes through quaternation reaction *in situ* when heated. (2) They retain >90% of the conversion efficiency of the liquid electrolytes. (3) The cells based on them have high efficiency.

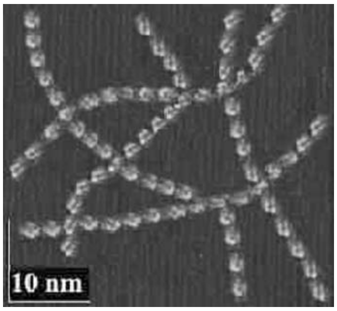


Fig. 1 AFM image of G3.

This work was supported by the high tech research and development (863) program (Grant No. 2002AA302403), National Basic Research Program (973) (Grant No. G2000028205) and National Natural Science Foundation of China (Grant No. 50473055).

Notes and references

† ^{1}H NMR (D_2O): **1**: δ 2.24 (m, 8H), 2.34 (m, 4H), 2.64 (m, 8H), 3.3–3.4 (m, 16H), 7.53 (m, 8H), 8.52 (m, 8H). **2**: δ 2.24 (m, 8H), 2.34 (m, 4H), 2.64 (m, 8H), 3.3–3.4 (m, 16H), 7.35 (m, 4H), 7.86 (m, 4H), 8.68 (m, 4H), 8.78 (m, 4H). **3**: δ 2.2–2.9 (m, 76H), 3.35 (m, 32H), 7.65 (m, 16H), 8.6 (m, 16H). **4**: 2.2–2.9 (m, 76H), 3.35 (m, 32H), 7.35 (m, 8H), 7.86 (m, 8H), 8.68 (m, 8H) ,8.78 (m, 8H). ^{1}H NMR ($CDCl_3$) for DHD: 3.7–3.9 (m, CH_2CH_2O), 4.2 (m, ICH_2); Anal. Calc. for DHD: C 19.46, H 3.24, O 8.65, I 68.65; found: C 19.50, H 3.32, O 8.62, I 68.56%

1 A. B. O'Regan and M. Gratzel, *Nature*, 1991, **353**, 737.
2 A. Hagfeldt and M. Gratzel, *Chem. Rev.*, 1995, **95**, 49.
3 B. O'Regan and D. T. Schwartz, *Chem. Mater.*, 1995, **7**, 1349.
4 U. Bach, D. Lupo, P. Comte, J. E. Moser, F. Weissortel, J. Salbeck, H. Spreitzer and M. Gratzel, *Nature*, 1998, **395**, 583.
5 A. F. Nogueira, M. A. D. Paoli, I. Montanari, R. Monkhouse, J. Nelson and J. R. Durrant, *J. Phys. Chem. B*, 2001, **105**, 7517.
6 J. H. Kim, M. S. Kang, Y. J. Kim, J. Won and Y. S. Kang, *Solid State Ionics*, 2005, **176**, 579.
7 T. Stergiopoulos, I. M. Arabatzis, G. Katsaros and P. Falaras, *Nano Lett.*, 2002, **2**, 1259.
8 W. Kubo, K. Murakoshi, T. Kitamura, Y. Wada and S. Yanagida, *Chem. Lett.*, 1998, 1241.
9 W. Kubo, K. Murakoshi, T. Kitamura, S. Yoshida, M. Haruki, K. Hanabusa, H. Shirai, Y. Wada and S. Yanagida, *J. Phys. Chem. B*, 2001, **105**, 12809.
10 F. Cao, G. Oskam and P. C. Searson, *J. Phys. Chem.*, 1995, **99**, 17071.
11 M. Matsumoto, H. Miyazaki, K. Matsuhiro, K. Yoshimasa and T. Yoichi, *Solid State Ionics*, 1996, **89**, 263.
12 P. Wang, S. M. Zakeeruddin, P. Comte, I. Exnar and M. Gratzel, *J. Am. Chem. Soc.*, 2003, **125**, 1825.
13 E. Stathatos, P. Lianos, S. M. Zakeeruddin, P. Liska and M. Gratzel, *Chem. Mater.*, 2003, **15**, 1825.
14 H. Usui, H. Matsui, N. Tanabe and S. Yanagida, *J. Photochem. Photobiol. A: Chem.*, 2004, **164**, 97.
15 J. H. Kim, M. S. Kang, Y. J. Kim, J. Won, N. G. Park and Y. S. Kang, *Chem. Commun.*, 2004, 1662.
16 T. Asano, T. Kubo and Y. Nishikitani, *J. Photochem. Photobiol. A: Chem.*, 2004, **164**, 111.
17 S. R. Scully, M. T. Lloyd, R. Herrera, E. P. Giannelis and G. G. Malliaras, *Synth. Met.*, 2004, **144**, 291.
18 K. Suzuki, M. Yamaguchi, S. Hotta, N. Tanabe and S. Yanagida, *J. Photochem. Photobiol. A: Chem.*, 2004, **164**, 81.
19 S. Murai, S. Mikoshiba, H. Sumino, T. Kato and S. Hayase, *Chem. Commun.*, 2003, 1534.
20 T. Kato, A. Okazaki and S. Hayase, *Chem. Commun.*, 2005, 363.
21 S. Murai, S. Mikoshiba, H. Sumino and S. Hayase, *J. Photochem. Photobiol. A: Chem.*, 2002, **148**, 33.
22 Y. Shibata, T. Kado, T. Kado, R. Shiratuchi, W. Takashima, K. Kaneto and S. Hayase, *Chem. Commun.*, 2003, 2730.
23 S. Sakaguchi, H. Ueki, T. Kato, T. Kado, R. Shiratuchi, W. Takashima, K. Kaneto and S. Hayase, *J. Photochem. Photobiol. A: Chem.*, 2004, **164**, 117.
24 S. Mikoshiba, S. Murai, H. Sumino, T. Kado, D. Kosugi and S. Hayase, *Curr. Appl. Phys.*, 2005, **5**, 152.
25 A. F. Nogueira, J. R. Durrant and M. A. De Paoli, *Adv. Mater.*, 2001, **13**, 826.
26 R. Kumar, A. K. Sharma, V. S. Parmar, A. C. Watterson, K. G. Chittibabu, J. Kumar and L. A. Samuelson, *Chem. Mater.*, 2004, **16**, 4841.
27 B. P. Devin and D. A. Tirrell, *Macromolecules*, 1986, **19**, 2466.