Journal of Photochemistry and Photobiology A: Chemistry 217 (2011) 308–312

Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

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

Quasi-solid electrolyte based on polyacrylonitrile for dye-sensitized solar cells

Oliver A. Ileperuma*, G.R. Asoka Kumara, Hong-Sheng Yang, Kenji Murakami

Research Institute of Electronics, Shizuoka University, Joho-ku, 432-8011 Hamamatsu, Japan

ARTICLE INFO

Article history:
Received 23 September 2010
Accepted 25 October 2010
Available online 3 November 2010

Keywords:
Dye sensitized solar cell
Polyacrylonitrile
Quasi-solid electrolyte

ABSTRACT

A quasi-solid gel–polymer electrolyte for dye-sensitized nanostructured TiO_2 sensitized by N719 ruthenium dye has been developed. The electrolyte comprises of polyacrylonitrile along with plasticizers, ethylene carbonate and propylene carbonate in the 15:35:50 ratio and the redox couple consists of tetrabutyl ammonium iodide and iodine along with tertiary butyl pyridine. The concentration of iodide:iodine was optimized and optimal activity was found when the molar ratio is 1.50:0.05. This gel electrolyte has a high electrical conductivity of 4.33 mS cm^{-1} and overall conversion efficiencies of over 7% were obtained for solar to electrical energy conversion which is higher than the values reported for other similar gel–polymer electrolytes. The reduction in efficiency compared to a solar cell employing a liquid electrolyte can be attributed to incomplete wetting of pores and due to mass transfer limitations of redox species through a more viscous medium.

1. Introduction

Dye sensitized solar cells (DSCs) based on mesoporous TiO_2 have attracted attention owing to their ease of production from relatively impure materials as low cost alternatives to silicon photovoltaics [1,2]. This type of solar cell comprises of a nanoporous TiO_2 electrode sensitized by a ruthenium bipyridine dye, a redox electrolyte and a platinum counter electrode. Photoexcited electrons on the dye are transferred to the conduction band of the TiO_2 and the oxidized dye cation is regenerated by the I^- in the redox couple and the I_2 so formed in turn gets reduced at the platinum secondary electrode, completing the cycle and generating a photocurrent. Optimization studies carried out world-wide have resulted [3,4] in the fabrication of cells with efficiencies exceeding 10% with the highest reported efficiencies of ~11.0% achieved using sub-micrometer size scattering particles either incorporated into the TiO_2 film [4] or as a topcoat over layer [5]. The use of a liquid electrolyte causes practical problems of leakages and its volatilization, desorption and photodegradation of the dye, corrosion of the platinum secondary electrode and ineffective sealing of cells for long term applications in solar panels. Some of the attempts to solve this problem include the use of polymer electrolytes [6–10], use of gelling agents [11,12] and the use of both organic [13] and inorganic [14] hole conductors. A common feature of all such alternatives is the notable reduction in efficiency of the resultant solar cells primarily due to the lower mobility of the iodide species through the solid or quasi-solid medium and imperfect wetting of pores with the electrolyte. The conversion efficiencies with the gel polymer electrolytes typically do not exceed 5%. However, even at these low efficiencies, these cells may become viable alternatives to the organic liquid containing Grätzel type cells due to improved stability and better sealing ability. The dyes are less liable to undergo photo-corrosion and desorption and the corrosion effects on the platinum counter electrode are lower.

Gel polymer electrolytes or plasticized polymer electrolytes offer the advantages of the cohesive properties of a solid along with the diffusive nature of liquids. They offer good contacting properties and pore filling between the two electrodes and also show high conductivity owing to the continuity of the trapped electrolytes. A gel is formed between the polymer backbone and the plasticizer ensuring the non-volatility of the electrolyte. Polyacrylonitrile (PAN) offers a homogeneous hybrid electrolyte film where the salts and the plasticizers are molecularly dispersed [15]. PAN host structure is inactive in ionic conduction but provides a matrix for structural stability. A typical polymer electrolyte composition of PAN (12%), ethylene carbonate (EC, 40%), propylene carbonate (PC, 40%) and $LiClO_4$ has a conductivity as high as 2×10^{-3} S cm^{-1} at room temperature and this type of polymer electrolyte has been employed in lithium–manganese batteries [16]. Cao et al. [17] reported the first example of a quasi-solid polymer electrolyte for a DSC based on PAN with acetonitrile and ethylene carbonate as plasticizers exhibiting an efficiency of 4.4%. Use of an acetonitrile free gel–polymer electrolyte comprising of comprises PAN, along with EC and PC as plasticizers for the N3-dye sensitized TiO_2 solar cells with 2.99% efficiency [7] has been reported. Here, these low molecular weight organic solvents decrease chain interactions

---

* Corresponding author. Present address: Department of Chemistry, University of Peradeniya, University Park, Peradeniya 24100, Sri Lanka. Tel.: +94 81 2394421; fax: +94 81 2388018.
E-mail address: oliveri@pdn.ac.lk (O.A. Ileperuma).

1010-6030/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.jphotochem.2010.10.024

in the polymer network and hence impart increased amorphous character to the resulting electrolyte. The ionic conductivities of such polymer electrolytes reach values in excess of 10^{-3} S cm^{-1} and comparable to the conductivities in the liquid state [8]. These quasi-solids keep a large percentage by mass of liquid electrolyte. The electrolyte compositions were selected based on the results connected to lithium batteries where the proportions of the plasticizers to the polymer have been optimized. Those showing the highest electrical conductivity were selected for the polymer electrolyte study. However, unlike in the case of batteries which depend on lithium ion conductivity, the solar cell functioning depends on the conduction of the triiodide ion. This is generally achieved by the use of larger cations such as tetraalkyl ammonium and other ionic liquids with long side chains which get immobilized owing to their adsorption to the polymer matrix.

In the above study with the PAN based electrolyte [7] an efficiency of 2.99% was obtained for a PAN based electrolyte when the PAN:PC:EC ratio was optimized for ionic conductivity while the I^-:I_2 molar ratio was maintained at a fixed value of 0.70:0.05. This ratio was selected on the basis of the ratio of I^-:I_2 generally employed in the organic liquid electrolyte used in DSCs. In polymer electrolytes, larger cations of a homologous series tend to interact more strongly with the polymer matrix due to viscous forces, thereby enhancing anionic conductivity [18]. Adsorbed cations have been shown to have an effect on the kinetics of the reduction of the oxidised dye by I^- during dye regeneration [19]. Adsorption of cations on the TiO_2 particles also controls the energy of the conduction band and affects the injection of photoelectrons from the photoexcited dye molecules. This is due to the screening effects of the different cations on the movement of electrons through the nanoparticle network.

On the basis of these arguments, there is scope to improve solar cell performance by varying the nature of the iodide source and the ratio of I^-:I_2 and such optimization studies giving relatively high efficiencies of over 7% for semi-solid polymer electrolytes are reported here.

2. Experimental

2.1. Preparation of electrodes

TiO_2 electrodes were prepared by a spray pyrolysis technique starting with a colloidal solution containing 6 nm particles in a 2.2% suspension (TKC-302 from Tayca, Japan) as previously described [20]. This colloidal TiO_2 solution (20 ml) was ultrasonically mixed with 5.5 ml of acetic acid, 3 drops of Triton X-100 and 0.2 g of P-25 TiO_2 powder (Nihon Aerosol, Japan). The mixture was sprayed onto FTO glass plates (Nippon Sheet Glass, Japan, 4 mm thickness, 10 Ω/□) maintained at a temperature of 150 °C. The plates were next heated at 500 °C for 30 min in air. The absorption of a 4×10^{-4} M N-719 dye, *cis*-di(thiocyanato)-N,N′-bis(2,2′-bipyridyl-4-carboxylicacid-4′-tetrabutylammonium carboxylate)ruthenium(II) dye (Peccell Inc., Japan) was carried out by soaking the TiO_2 plate pre heated at 80 °C in an acetonitrile/*tert*-butanol (1:1,v/v) solution. The area of the circular cells so fabricated was ca. 0.25 cm × 0.25 cm. Film morphology and film thicknesses were determined from scanning electron microscopy (SEM) measurements taken using a JEOL 6320F SEM machine.

2.2. Preparation of the electrolyte

Tetrabutyl ammonium iodide (n-Bu$_4$ N$^+$I$^-$), EC, PC and *tert*-butyl pyridine were purchased from Wako Pure Chemicals Ltd. PAN was purchased from Aldrich and all chemicals with purity >98% were used as received. The polymer electrolyte had the following composition: PAN (0.225 g), EC (0.525 g), PC (0.750 g). Varying concentrations of n-Bu$_4$ N$^+$I$^-$ and I_2, calculated on the basis of the volume of propylene carbonate used, were employed in order to optimize the composition of the redox species in the electrolyte medium. The contents were well mixed ultrasonically after the addition of each component. Resultant mixture was next heated with stirring to about 120 °C when a viscous gel is obtained which was pressed between two glass plates to give films of about 1 mm thickness. These films were stored in a desiccator until further used.

2.3. Conductivity measurements

The polymer electrolyte film was cut into small discs of diameter 12 mm and gently pressed between two stainless steel electrodes held in a sample holder. The ionic conductivity was measured by the complex impedance technique in the 20–60 °C temperature range using a Solatron 1240 model impedance analyzer. Measurements were done in the 1 Hz to 1 MHz frequency range.

2.4. Fabrication of the solar cell

A strip of polymer film about 0.40 cm × 0.40 cm area was placed covering the photo-electrode (area 0.25 cm × 0.25 cm) and heated to around 80 °C and the cell was completed by pressing a platinum mirror electrode placed over the polymer film. Film thicknesses were typically in the 0.3–0.4 mm range.

2.5. Photoelectrochemical measurements

I–V measurements were taken using a calibrated JASCO CEP-25 BX solar cell evaluation system. An external bias was applied to the cell and the photocurrent generated was measured with a Keithley model 2400 digital source meter. The solar simulator of this system was calibrated using an EKO-LS-100 spectroradiometer and a calibrated silicon photodiode. The voltage step was 20 mV and sweeping time was 25 mV/s.

3. Results and discussion

3.1. Electrode characterization

The titanium dioxide electrodes were prepared by using a combination of particles with an intimate admixture of 3–6 nm particles along with larger 25–30 nm particles where the mass percentages of the two types were 68 and 31, respectively. This optimum concentration was obtained by using various weight ratios of the two types of particles and testing their photovoltaic properties by using the standard acetonitrile based liquid electrolyte. The high efficiency of such TiO_2 films can be attributed to the highly porous nature of the TiO_2 film formed by the adherence of small particles around larger particles. Fig. 1 shows the scanning electron micrograph of the TiO_2 electrode which clearly shows the high porosity imposed on the structure by the use of two different particle sizes. All particles are intimately bonded together after the sintering process and this type of highly porous structure permits higher dye adsorption and also efficient wetting of the film by the electrolyte. Ito et al. [21] have used a “double-layer” film comprising of comprises a 12–14 μm thick layer of TiO_2 with 20 nm size particles and an over layer of a film about 4–5 μm thickness having comprises much larger 400 nm particles for obtaining efficiencies over 10% in a solar cell through photon trapping. The larger particles effectively scatter the light thereby extending the IPCE values extensively into the red region. While scattering of light by particles >100 nm in size has been suggested [22] on theoretical grounds, our films having

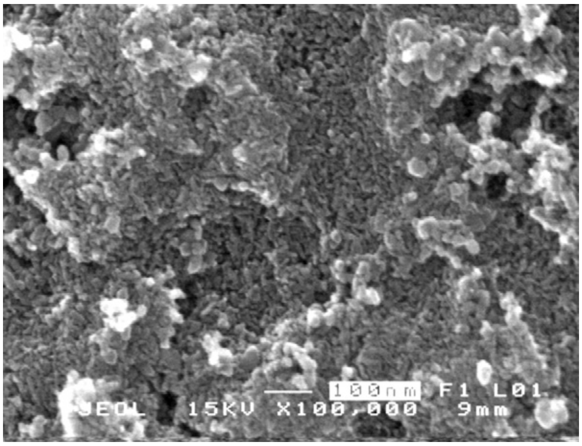

Fig. 1. SEM photograph of a TiO_2 film prepared by mixing 0.2 g of P-25 powder and 20 ml of colloidal suspension containing 6 nm particles (TiO_2 content 2.2%, w/w).

aggregates of 25 nm particles could also behave in a similar manner to those having much larger particles.

3.2. Electrolyte characterization

Based on previous work [7] we have employed the ratio of PAN (0.225 g):EC (0.525 g):PC (0.750 g) where the ratios were varied for optimal conductivity and solar energy conversion. There is evidence that increase in polymer concentration decreases ionic conductivity owing to the greater distances the ions have to travel through the tubular structure imposed by the polymer [23]. However, this previous study employed a fixed amount of tetra-*n*-propyl ammonium iodide and iodine and no attempts were made to optimize the iodide:iodine ratio for solar energy conversion efficiency. Here, a new iodide source, viz. tetrabutyl ammonium iodide was employed where both its amount and its ratio to iodine were varied in order to optimize solar cell performance.

Table 1 gives the electrolyte compositions and their room temperature ionic conductivities (298 K). The motion of ions essentially takes place in the liquid trapped within the polymer matrix and ionic conductivity primarily occurs in the amorphous regions of the polymer backbone. Polyblend electrolytes containing alkali metal iodides show Arrhenius type of conductivity–temperature behavior which can be attributed mechanistically to ionic transport involving intermolecular ion hopping. For ionic species such as tetrabutyl ammonium iodide where the cation is very large, such hopping is unlikely and the conductivity–temperature variation in general shows curvature. The temperature dependence of the conductivity of polymer electrolytes involving large cations and where the ion-transport is dominated by the mobility of solvent molecules, is best described by the Vogel–Tamman–Fulcher (VTF) equation [18].

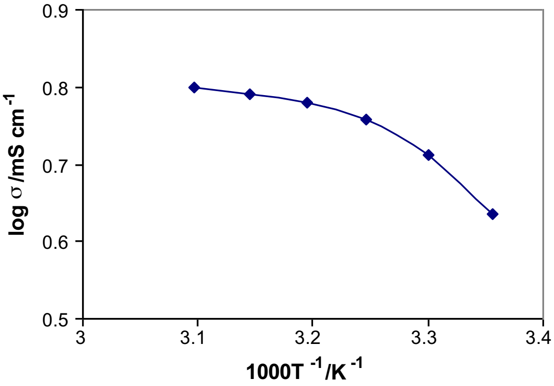

Fig. 2. Variation of ionic conductivity with temperature for the PAN electrolyte for composition *f* having the highest ionic conductivity.

$$\sigma = AT^{-1/2}\exp\left[\frac{-B}{T-T_0}\right]$$

Here, σ is the conductivity, A is a constant which is proportional to the number of carrier ions, B is a constant and T_0 is the temperature at which configurational entropy of the polymer becomes zero and is practically taken as the glass transition temperature (T_g). Generally this equation fits conductivity rather well over a temperature range from T_g to $T_g + 100\,^\circ C$. The temperature dependence of the conductivities in the temperature range of 25–50 °C is given in Fig. 2 showing excellent VTF-type dependence. The general applicability of this equation to ionic conductivity implies that ionic conductivity in the polymer is coupled to the flow behavior of the plasticizers in the polymer matrix. Such high ionic conductivities are obtained for polymers having flexible backbones and low glass transition temperatures. They should also impart little or no crystallinity in order to be highly conducting. In the case of lithium ion batteries which work on Li ion conductivity, this is achieved by having large anions. Similarly where iodide ion conductivity is desired, larger cations exhibit higher ionic conductivity and hence higher efficiencies in solar cells.

In general high permittivity solvents such as PC and EC or their mixtures bring about high conductivities of the order of $10^{-3}\,S\,cm^{-1}$ even at temperatures as low as −10 °C. The maximum ionic conductivity was observed for the electrolyte *f* where the molar ratio of $I^-/I_2 = 1.50{:}0.05$. There was no evidence of any separation of salts at concentrations as high as 1.5 M and no liquids exuded after the photocurrent measurements indicating that the electrolyte is well encapsulated in the polymer matrix. As such, these polymer membranes act as self sealants and will not have leakage problems normally encountered with organic liquid electrolytes.

Table 1
Electrolyte compositions and room temperature (298 K) ionic conductivities for polymer composition, PAN (15%), PC (50%), EC (35%).

Electrolyte	Iodide (g)	Iodine (g)	I/I_2 molar ratio	σ_{RT} (mS cm^{-1})
a	0.115	0.016	0.50:0.10	3.36
b	0.136	0.019	0.60:0.12	3.84
c	0.161	0.022	0.70:0.14	3.96
d	0.230	0.032	1.00:0.20	4.14
e	0.115	0.032	0.50:0.20	2.46
f	0.346	0.008	1.50:0.05	4.33
g	0.230	0.008	1.00:0.05	3.87
h	0.161	0.008	0.70:0.05	3.27

Table 2
Photovoltaic performance of TiO_2 DSCs employing different electrolytes under AM 1.5 radiation. [The electrolyte is PC (50%), EC (35%) and PAN (15%) by weight, TiO_2 electrode area 0.25 cm × 0.25 cm and thickness 14 μm.].

No.	Electrolyte	J_{SC} (mA cm^{-2})	V_{OC} (V)	FF	η (%)
1	a	13.92	0.666	0.553	5.09
2	b	15.34	0.707	0.528	6.00
3	c	17.41	0.707	0.528	6.49
4	d	16.85	0.674	0.529	6.01
5	e	14.69	0.618	0.512	4.64
6	f	15.96	0.751	0.616	7.27
7	g	16.50	0.737	0.547	6.64
8	h	12.34	0.706	0.566	4.93

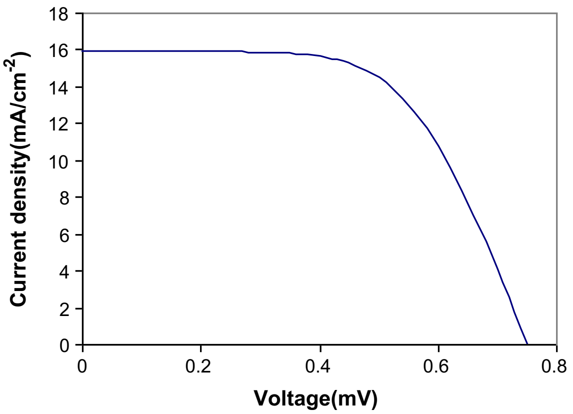

Fig. 3. Photocurrent–voltage curve obtained for N719-dye sensitized TiO_2 solar cell under AM1.5 (100 mW cm^{-2}) with the polymer gel electrolyte with composition: PAN:EC:PC = 0.15:0.35:0.50 and n-$Bu_4N^+I^-$ (1.50 M), I_2 (0.05 M), and TBP (0.5 M).

3.3. Photocurrent characteristics

Table 2 shows the photovoltaic performances of the different electrolyte compositions studied and Fig. 3 gives the *I*–*V* curve for the electrolyte composition giving the highest solar cell efficiency using the tertiary butyl ammonium iodide under a white light intensity of 100 mW cm^{-2} (AM 1.5). The Ru-dye coated TiO_2 plates were checked for their quality using the standard liquid electrolyte based on acetonitrile media and the photovoltaic characteristics obtained for a 0.25 cm × 0.25 cm area cell were: J_{SC} = 20.56 mA cm^{-2}, V_{OC} = 0.739 V, FF = 0.66 and η = 10.06 (%).

It is evident from Table 2 and the data for the liquid electrolyte that the observed differences in solar cell performance are mainly due to a lowering of the short-circuit current density and the fill factor. Both these parameters depend on the ionic conductivity of the electrolyte where low conductivities retard the electrode reactions at the counter electrode. In addition, the layer of the polymer gel between the two electrodes is thicker (0.3–0.4 mm) compared to the liquid electrolyte (~0.1 mm) which increases series resistance of the cell and reduces photocurrent. This is further aggravated by the hindrances to the movement of ions imposed by the polymer network.

The V_{OC} value, which is the difference between the Fermi level of TiO_2 and the potential of the redox couple, depends mainly on the molar ratio of the I^-/I_2 couple. The increase of V_{OC} with increasing the molar ratio of the redox couple is evident from the data in Table 2. Increase in the V_{OC} values when the liquid electrolyte is replaced by a quasi-solid electrolyte has been reported [19] and we observe a marginal increase in the V_{OC} value only for the optimum electrolyte composition, *f*. However, at the higher iodide concentrations used by us, the rate of the dark reaction due to reduction of triiodide ion by conduction band electrons accumulated on TiO_2 effectively is increased which results in lowering of the V_{OC} values for most electrolyte compositions.

These results were obtained after optimizing the concentrations of the iodide and the iodine in the polymer electrolyte and it was found that optimal solar cell performance is obtained when the I^-/I_2 ratio was 30:1 at concentrations of 1.50 M and 0.05 M, respectively. This is quite surprising since the ratio of these two components generally used by other workers in this area for gel polymer electrolytes are 0.50 M and 0.05 M. In a related study, of a solar cell using the liquid electrolyte, the highest efficiencies were observed at a fairly high iodide concentration of 1.5 M when 1,2-dimethyl-3-*n*-propylimidazolium iodide (DMHImI) was used and attributed to the strong adsorption of the DMHIm cation on the TiO_2 surface [24]. The quasi-solid electrolytes appear to require a higher concentration in the electrolyte composition compared to the liquid electrolytes. Yanagida et al. [25] found relatively higher efficiencies for organic liquid free solidified pure ionic liquids using organic gelators where the high efficiencies are attributed to the Grotthus type of mechanism caused by rather packed polyiodide species in the electrolyte. Such an explanation is attractive to explain our results where optimum efficiency is obtained at higher iodide concentrations.

The decrease of V_{OC} and the increase of J_{SC} with temperature are now well established with optimum cell performances observed at 60 °C [26]. We have also noticed a fair increase in the cell performance after a few minutes of illumination where J_{SC} increases substantially by about 30% while the other parameters showed a slight decrease. This can be attributed to a slight heating effect during illumination of the cell. Also, we noticed that keeping a fabricated cell for a day improves its performance and the best results were obtained when such a cell is either heated slightly or illuminated with AM1.5 radiation for a few minutes. It is conceivable that increased conductivity owing to a lowering of viscosity and the slow pore filling by the viscous electrolytes with increase in temperature are the most likely reasons for these trends. Similar effects have been noted for large area solar (625 cm × 625 cm) cells with polymethyl methacrylate gel polymer electrolytes where an initial decrease in the cell performance was observed which was followed up with an unexpected recovery when left for several hours in the dark [27]. Our cells were not sealed and hence volatility of iodine is also a factor and the yellow color of the polymer film gradually fades upon standing under exposure to ambient sunlight for several weeks. There was a general decrease of cell performance after 30 days where the quantum efficiency dropped from 7.27% to 6.27%. The optimum efficiency of these types of solar cells is at a temperature of ca. 60 °C which represents a practical temperature reached on roof top solar panels. Thus, the gel polymer electrolytes have a critical advantage over cells employing electrolytes containing organic liquids such as acetonitrile.

4. Conclusions

We have demonstrated that a PAN polymer matrix provides an efficient medium for the transport of ions combining high conductivity and ample free volume for the mobility of solvent. The ionic conductivity varies with temperature according to VTF type behavior. Iodide ion conductivity is significantly enhanced owing to the use of a large tetrabutyl ammonium cation and its adsorption on the TiO_2 surface. The cell fabricated gave an efficiency of 7.27% at room temperature and this could further increase at elevated temperatures.

References

[1] B. O'Reagan, M. Grätzel, A low-cost high-efficiency solar cell based on dye-sensitized colloidal TiO_2 films, Nature 353 (1991) 737–740.

[2] M.K. Nazeeruddin, A. Kay, I. Rodicio, R. Humphrey-Baker, E. Müller, P. Liska, N. Vlachopoulos, M. Grätzel, Conversion of light to electricity by cis-X_2-bis(2,2′-bipyridyl-4,4′-dicarboxylate)ruthenium(II) charge transfer sensitizers (X = Cl^-, Br^-, I^-, CN^-, and SCN^-), J. Am. Chem. Soc. 115 (1993) 6382–6390.

[3] Z.S. Wang, T. Yamaguchi, H. Sugihara, H. Arakawa, Significant efficiency improvement of the black dye-sensitized solar cell through protonation of TiO_2 films, Langmuir 21 (2005) 4272–4276.

[4] Y. Chiba, A. Aslam, Y. Watanabe, N. Koide, L. Han, Dye-sensitized solar cells with conversion efficiency of 11.1%, Jpn. J. Appl. Phys. Part 2: Lett. Exp. Lett. 45 (2006) L638–L640.

[5] M. Grätzel, Conversion of sunlight to electric power by nanocrystalline dye-sensitized solar cells, J. Photochem. Photobiol. A 164 (2004) 3–14.

[6] A.F. Noguira, M.A. de Paoli, I. Montanari, R. Monkhouse, J. Nelson, J. Durrant, Electron transfer dynamics in dye-sensitized nanocrystalline solar cells, J. Phys. Chem. B 105 (2001) 7517–7524.

[7] O.A. Ileperuma, M.A.K.L. Dissanayake, S. Somasunderam, Dye-sensitized photoelectrochemical solar cells with polyacrylonitrile based solid polymer electrolyte, Electrochim. Acta 47 (2002) 2801–2807.

[8] O.A. Ileperuma, M.A.K.L. Dissanayake, S. Somasunderam, L.R.A.K. Bandara, Photoelectrochemical solar cells with polyacrylonitrile-based and polyethylene oxide-based polymer electrolytes, Sol. Energy Mater. Sol. Cells 84 (2004) 117–124.

[9] Z. Lan, J. Wu, D. Wang, D.S. Hao, J. Lin, Y. Huang, Quasi-solid-state dye-sensitized solar cells based on gel polymer electrolyte with poly(acrylonitrile-*co*-styrene)/NaI + I_2, Sol. Energy 80 (2006) 1483–1488.

[10] M.S. Kang, J.K. Kim, J. Won, Y.S. Kang, Dye-sensitized solar cells based on cross linked poly(ethyleneglycol) electrolytes, J. Photochem. Photobiol. A 183 (2006) 15–21.

[11] P. Wang, S.M. Zakeeruddin, R. Humphry Baker, J.E. Moser, M.K. Nazeeruddin, T. Sekiguchi, M. Grätzel, A stable quasi-solid-state dye-sensitized solar cell with an amphiphilic ruthenium sensitizer and polymer gel electrolyte, Nat. Mater. 2 (2003) 402–407.

[12] T. Kato, T. Kado, S. Tanaka, A. Okazaki, S. Hyase, Quasi-solid dye-sensitized solar cells containing nanoparticles modified with ionic liquid type molecules, J. Electrochem. Soc. 153 (2006) A626–A630.

[13] U. Bach, D. Lupo, P. Comte, J.E. Moser, F. Weissörtel, J. Salbeck, H. Sreizer, M. Grätzel, Solid-state dye-sensitized mesoporous TiO_2 solar cells with high photon-to-electron conversion efficiencies, Nature 395 (1998) 583–585.

[14] K. Tennakone, G.R.A. Kumara, A.R. Kumarasinghe, K.G.U. Wijayantha, P.M. Sirimanne, A dye-sensitized nanoporous solid-state photovoltaic cell, Semicond. Sci. Technol. 10 (1995) 1689–1693.

[15] A.M. Stephan, Review on gel–polymer electrolytes for lithium batteries, Eur. Polym. J. 42 (2006) 21–42.

[16] Y.K. Sun, S.H. Jin, Synthesis and electrochemical characteristics of spinel phase $LiMn_2O_4$-based batteries, J. Mater. Chem. 8 (1998) 2399–2404.

[17] F. Cao, G. Oskam, P.C. Searson, A solid state dye-sensitized photoelectrochemical cell, J. Phys. Chem. 99 (1995) 17071–17073.

[18] K. Abraham, in: B. Scrossati (Ed.), Applications of Electroactive Polymers: Highly Conductive Polymer Electrolytes, Chapman & Hall, London, 1993, pp. 75–112.

[19] R. Komiya, L. Han, R. Yamanaka, A. Islam, T. Mitae, Highly efficient quasi-solid state dye-sensitized solar cell with ion-conducting polymer electrolyte, J. Photochem. Photobiol. A 164 (2004) 123–127.

[20] G.R.A. Kumara, S. Kaneko, A. Konno, M. Okuya, K. Murakami, B. Onwona-agyeman, K. Tennakone, Large area dye-sensitized solar cells: material aspects of fabrication, Prog. Photovolt.: Res. Appl. 14 (2006) 643–651.

[21] S. Ito, T.N. Murakami, P. Comte, P. Liska, C. Gratzel, M.K. Nazeeruddin, M. Gratzel, Fabrication of thin film dye-sensitized solar cells with solar to electric power conversion efficiency over 10%, Thin Solid Films 516 (2007) 4613–4619.

[22] A. Usami, Theoretical simulations of optical confinement in dye-sensitized nanocrystalline solar cells, Sol. Energy Mater. Sol. Cells 64 (2006) 73–83.

[23] K. Abraham, M. Alamgir, Li^+-conductive solid polymer electrolyte with liquid-like conductivity, J. Electrochem. Soc. 137 (1990) 1657–1658.

[24] K. Hara, T. Nishikawa, M. Kurashige, H. Kawauchi, T. Kashima, K. Sayama, K. Aika, H. Arakawa, Influence of electrolyte on the photovoltaic performance of a dye-sensitized TiO_2 solar cell based on a Ru(II) terpyridyl complex photosensitizer, Sol. Energy Mater. Sol. Cells 85 (2006) 21–30.

[25] W. Kubo, K. Murakoshi, T. Kitamura, S. Yoshida, M. Haruki, K. Hanabusa, H. Shirai, Y. Wada, S. Yanagida, Quasi-solid-state dye-sensitized TiO_2 solar cells: effective charge transport in mesoporous space filled with gel electrolytes containing iodide and iodine, J. Phys. Chem. B 105 (2001) 12809–12815.

[26] Y. Liu, A. Hagfeldt, X.-R. Xiao, S.-E. Lindquist, Investigation of influence of redox species on the interfacial energetics of a dye-sensitized nanoporous TiO_2 solar cell, Sol. Energy Mater. Sol. Cells 55 (1998) 267–281.

[27] M. Biancardo, K. West, F.C. Krebs, Optimizations of large area quasi-solid-state dye-sensitized solar cells, Sol. Energy Mater. Sol. Cells 90 (2006) 2575–2588.