# Quasi-Solid-State Dye-Sensitized Solar Cells Using Nanocomposite Gel Polymer Electrolytes Based on Poly(propylene carbonate)

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Poly(propylene carbonate) (PPC) is synthesized from the copolymerization of CO_2 and propylene oxide. Novel nanocomposite gel polymer electrolytes (GPEs) are prepared by utilizing PPC, organic solvents containing a redox couple, and aluminum oxide nanoparticles for application in dye-sensitized solar cells (DSSCs). The quasi-solid-state DSSC assembled with optimized nanocomposite GPEs exhibits a relatively high conversion efficiency of 6.16% at 100 mW cm^{-2} and better stability than DSSC with liquid electrolyte.
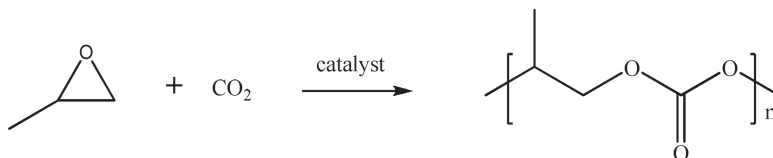
1. Introduction

Dye-sensitized solar cells (DSSCs) have been considered one of the promising alternatives to conventional solar cells because of their low cost, easy fabrication, and relatively high energy conversion efficiency.[1,2] An impressive conversion efficiency of 11% has been achieved for a DSSC with an organic solvent-based liquid electrolyte.[3] However, the potential problems caused by the liquid electrolyte, such as leakage or evaporation of the solvents, are considered critical factors that limit the long-term operation and practical use of DSSCs. Therefore, considerable efforts have been made to replace liquid electrolytes with polymer electrolytes,[4–11] inorganic p-type semiconductors,[12,13] and organic hole transport materials.[14,15] Among these approaches, the use of gel polymer electrolytes (GPEs) that exhibit high ionic conductivity at room temperature appears to provide successful results in terms of conversion efficiency. Several types of GPEs based on different kinds of polymers have been studied in the DSSCs, such

as poly(acrylonitrile),[16,17] poly(ethylene oxide)(PEO),[18–20] and poly(vinylidene fluoride-*co*-hexafluoropropylene) (P(VdF-*co*-HFP)).[21–24] The DSSCs employing ternary component GPE based on PEO exhibited relatively high conversion of 7.2%.[20] Recently, Dai group has reported an excellent conversion efficiency of 8.01% in quasi-solid-state DSSCs assembled with P(VdF-*co*-HFP)-based GPE containing liquid crystal under 1 Sun illumination.[24] However, reports about the photovoltaic performance of quasi-solid-state DSSCs assembled with new polymer materials are limited. In order to achieve high conversion efficiency and stability of DSSCs, it is important to find fairly stable polymer materials that are compatible with polar organic solvents in liquid electrolyte.

Herein, we propose a novel nanocomposite GPE based on poly(propylene carbonate) (PPC) for quasi-solid-state DSSCs. PPC is one of the synthetic polymers that utilize CO_2 as a direct starting material for polymer synthesis[25]; thus, the use of PPC to fabricate quasi-solid-state DSSCs can be one of the most challenging subjects in the CO_2 fixation field. PPC is highly compatible with carbonate-based organic solvents presently used in DSSCs, because it contains a carbonate group in the backbone. Thus, it can hold liquid electrolytes very well and improve the interfacial contact between electrolyte and electrode, resulting in an enhancement of the photovoltaic performance of the DSSCs. Moreover, PPC-based polymer electrolyte films are transparent due to the amorphous nature of PPC, unlike PEO or P(VdF-*co*-HFP). In this work, high-molecular-weight

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PPC is synthesized from CO_2 and propylene oxide, and the nanocomposite GPEs are prepared with PPC, aluminum oxide nanoparticles and organic solvents containing a redox couple. The photovoltaic performance of quasi-solid-state DSSCs with these nanocomposite GPEs is investigated and compared with that of liquid electrolyte-based DSSC.

2. Experimental Section

2.1. Materials

Aluminum oxide (particle size of 2–4 nm), ethylene carbonate (EC), γ-butyrolactone (γ-BL), propylene oxide, tetrahydrofuran (THF), lithium iodide, iodine, 4-*tert*-butylpyridine (TBP), hexachloroplatinic acid, isopropyl alcohol, PEO (average $\overline{M}_v$: 300 000), and P(VdF-*co*-HFP) (average $\overline{M}_w$: 400 000) were purchased from Sigma–Aldrich. TiO_2 paste, *cis*-diisothiocyanato-bis(2,2′-bipyridyl-4,4′-dicarboxylato) ruthenium (II) bis(tetrabutyl ammonium) (Ruthenium 535 bis-TBA)(N719) and hot melting film were purchased from Solaronix. Fluorine-doped tin oxide (FTO) glass was purchased from Pilkington. All commercial reagents were used as received. Carbon dioxide was purified by a molecular sieve column in order to remove water to below 10 ppm.

2.2. Synthesis of Poly(propylene carbonate)

A bomb reactor (3 L) equipped with a mechanical stirrer was purged with nitrogen. Propylene oxide (1300 mL) was charged into the reactor in a nitrogen atmosphere. A solution of GreenPol catalyst (224 mg) in propylene oxide (50 mL) was added using a cannula. CO_2 gas was charged at 18 bar and room temperature, and the reactor was then heated to 70 °C. After the temperature reached 70 °C, the pressure of the CO_2 inside the reactor was increased to 30 bar, and a pressure drop was observed as the polymerization proceeded. After polymerization for 2 h, the CO_2 gas was cut, and the viscous polymer solution was then transferred to a 5 L reservoir tank and diluted with propylene oxide. The light yellow polymer solution was filtered through a short pad of silica gel (50 g) previously wetted with dichloromethane (100 mL). The colorless filtrate of the polymer solution was further purified by successive dissolution in THF and precipitation with ethyl alcohol. The purified PPC was then dried in a vacuum oven at 90 °C. The chemical structure of PPC was confirmed by a ^{1}H NMR spectrum using a VARIAN (Mercury 300) NMR spectrometer with $CDCl_3$ as the solvent. The chemical shift of tetramethylsilane was used as an internal standard reference. Gel permeation chromatography (GPC) was carried out using a Waters instrument calibrated with the monodisperse polystyrene standards.

2.3. Cell Assembly and Measurements

GPE solution consisting of PPC, liquid electrolyte, and Al_2O_3 nanoparticles was prepared as follows. Proper quantities of PPC and liquid electrolyte were dissolved in anhydrous THF. The liquid electrolyte used in this study was a solution of 0.5 M LiI, 0.05 M
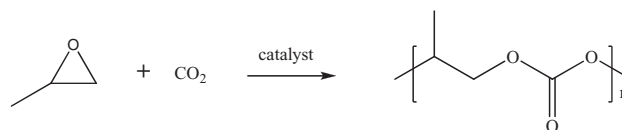

Figure 1. Reaction scheme for synthesis of PPC from CO_2 and propylene oxide.

I_2, and 0.05 M TBP dissolved in a mixed solvent of EC/γ-BL (50:50 by volume). After the polymer dissolved completely, a predetermined amount of aluminum oxide particles was added, and the solution was ball milled and sonicated to uniformly disperse the inorganic particles. Nanocrystalline TiO_2 paste was cast onto an FTO glass using a doctor blade and was then sintered at 450 °C for 30 min. Its thickness was optimized at 12 μm, and it was sensitized overnight with Ruthenium 535 bis-TBA dye solution. The counter electrode was prepared by spin-coating 0.01 M H_2PtCl_6 in isopropanol onto the FTO glass and sintering at 450 °C for 30 min. The GPE solution was cast with a doctor blade onto the TiO_2 electrode, and then left to evaporate THF slowly at room temperature. After THF evaporated, the cell was fabricated by sealing TiO_2 electrode and Pt counter electrode together using hot melting film. The thickness of the nanocomposite GPE film was in the range of 40–60 μm, and the cell geometry was 0.5 × 0.5 cm^2. The photovoltaic performance of the DSSCs was evaluated using a xenon light source (100 mW cm^{-2}) with an AM 1.5 filter in a solar simulator at ambient temperature. The light intensity was calibrated with an NREL-calibrated Si solar cell. A black mask with an aperture of 0.25 cm^2 was placed over the cells during irradiation, and an antireflection glass was placed on the front glass cover of the cells. A two-electrode electrochemical cell consisting of nanocomposite GPE sandwiched between two Pt electrodes was used to measure the diffusion coefficient of the tri-iodide ion from the diffusion-limited current measurements at a scan rate of 5 mV s^{-1}.[26,27]

3. Results and Discussion

PPC is an alternating copolymer, which can be obtained from the copolymerization of CO_2 and propylene oxide, as depicted in the reaction scheme of Figure 1. The scheme is very useful for conversion of carbon dioxide into PPC, which may solve the emission of CO_2 from industries and municipal wastes.

The ^{1}H NMR spectrum of the synthesized PPC is shown in Figure 2. The characteristic peaks in the spectrum were assigned as follows: ^{1}H NMR ($CDCl_3$), δ(ppm) 1.35(d, 3H; —CH_3), 4.24(m, 2H; —CH_2—), 5.13(d, 1H, —CH—). The peak positions were consistent with those reported previously for PPC,[28] and the relative intensity of the corresponding protons was 3.01:2.02:1.0, confirming the molecular structure of the PPC. The by-product poly(propylene oxide) has been observed at 1.16 ppm (d, 3H; —CH_3), 3.58 ppm (2H; —CH_2CH—) and 3.45 ppm (1H; —CH_2CH—) in the ^{1}H NMR spectrum.[29–31] The absence of these peaks
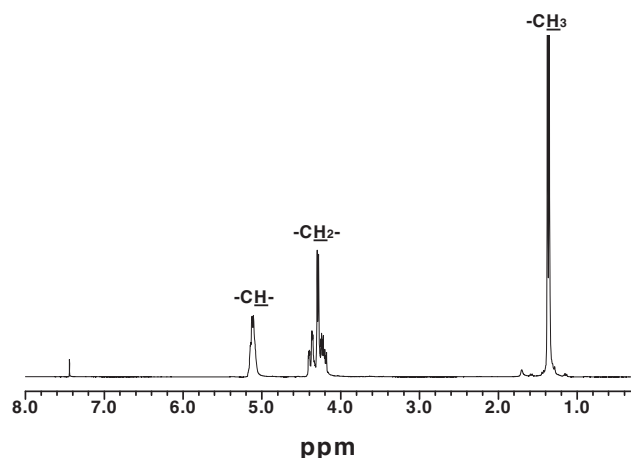
Figure 2. ^{1}H NMR spectrum of poly(propylene carbonate) in $CDCl_3$.

indicates that there are no poly(propylene oxide) units present in the polymer product. The number average molecular weight and weight average molecular weight of the PPC were measured by GPC to be 273 000 and 375 000, respectively, and the glass transition temperature (T_g) was found to be 41.7 °C in the DSC measurements.

Before applying the PPC-based nanocomposite GPE to the DSSC, the gelation of liquid electrolyte by PPC was confirmed. For the comparative purpose, different polymer materials such as P(VdF-*co*-HFP) and PEO were also dissolved at a same concentration (20 wt%) in a mixed solvent of EC/γ-BL. Figure 3 shows the images of GPEs prepared with P(VdF-*co*-HFP), PEO, and PPC, respectively. In case of P(VdF-*co*-HFP), the gel formation was not possible due to the incompatibility of polymer toward organic solvents. When PEO or PPC was used as a host polymer for preparing GPE, the electrolyte became non-fluidic due to the formation of stable polymer gel. There was no phase separation between the polymers and organic solvents
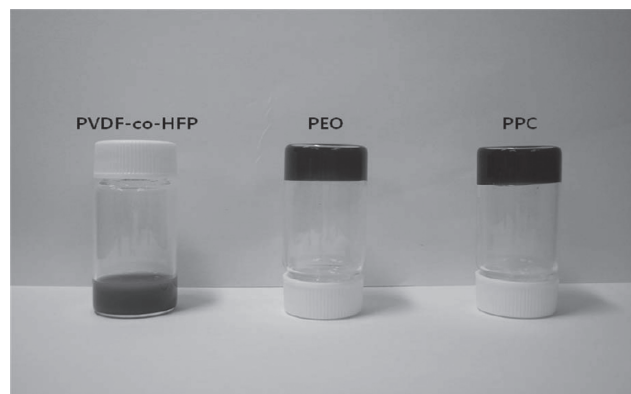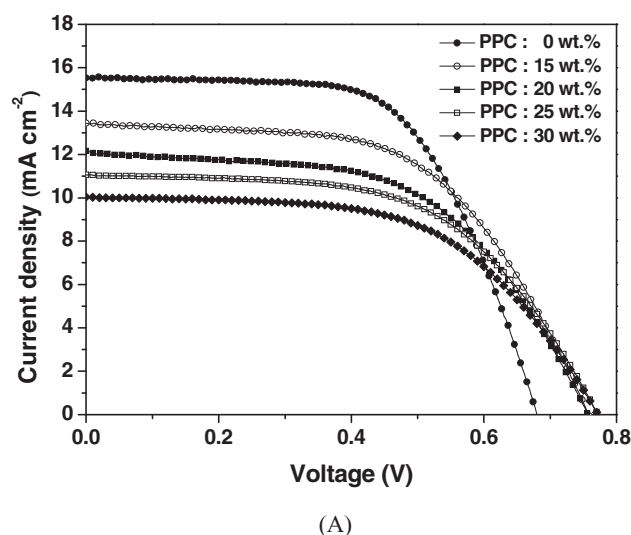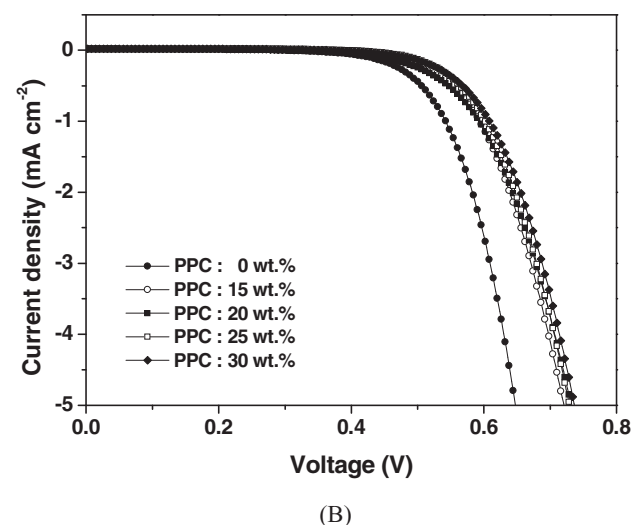

Figure 3. Images of GPEs prepared with P(VdF-*co*-HFP), PEO, and PPC, respectively. The used solvent was a mixed solvent of EC/γ-BL(50/50) and polymer concentration was 20 wt%.

(A)

(B)

Figure 4. A) Photocurrent–voltage curves of DSSCs assembled with liquid electrolyte and GPEs containing different amounts of PPC at 100 mW cm^{-2} and B) dark current–voltage curves of DSSCs assembled with liquid electrolyte and GPEs.

during long-term storage because the polymers were highly compatible with polar organic solvents such as EC and γ-BL. These results suggest that strong physical interactions between PPC and organic solvents occurred to form the stable gel electrolyte as PEO-based gel electrolyte system, thereby preventing the flow of the resulting electrolyte.

The photovoltaic performance of DSSCs using GPEs without Al_2O_3 nanoparticles was evaluated. Figure 4A shows the photocurrent density–voltage curves of the DSSCs with the GPEs containing different amounts of PPC. The photocurrent density–voltage curve of the DSSC prepared with liquid electrolyte is also shown for comparison. The open circuit voltages (V_{oc}) of the DSSCs

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assembled with GPE were higher than that of the liquid electrolyte-based DSSC. When the GPE was cast onto the surface of the TiO_2 electrode, the gel polymer formed on the TiO_2 electrode may suppress back electron transfer from the conduction band of the TiO_2 to the I_3^- ion, which increased the open circuit voltage. In order to investigate the dark reaction, the dark current of the cells was measured and depicted in Figure 4B. The dark current was significantly reduced by introducing PPC into the liquid electrolyte. This indicates that the charge recombination at the dyed TiO_2 electrode/electrolyte interface is effectively suppressed, which results in an increase of V_{oc}. The increase of V_{oc} may also result from the Lewis base nature of PPC, because the flat band potential of TiO_2 shifts negatively with the increase of the basicity of the electrolyte.[32] On the other hand, the short circuit current densities (J_{sc}) of DSSCs assembled with GPE were lower than that of DSSC assembled with liquid electrolyte. The gelation of liquid electrolyte by the addition of PPC lowered the ionic conductivity of the electrolyte. Indeed, the ionic conductivity of GPE was decreased due to the reduction of ionic mobility as well as diffusion coefficient of I^-/I_3^- ions, when the PPC content increased, as shown in Figure 5. The decrease in diffusion coefficient reduces the supply of I_3^- ions to the Pt counter electrode causing a depletion of I_3^- ions at the electrode surface and hence decreases the J_{sc} of the DSSC.[7–9] As a result, the value of J_{sc} is gradually decreased with increasing PPC content. Consequently, the conversion efficiency decreased as PPC content increased. Because the complete gelation of the liquid electrolyte failed at 15 wt% PPC, the PPC content was set at 20 wt% for further studies. The cell assembled with GPE containing 20 wt% PPC exhibited a conversion efficiency of 5.08%, which was higher than that (4.48%) of the cell prepared with GPE gelled by same amount of PEO (see Figure 3).
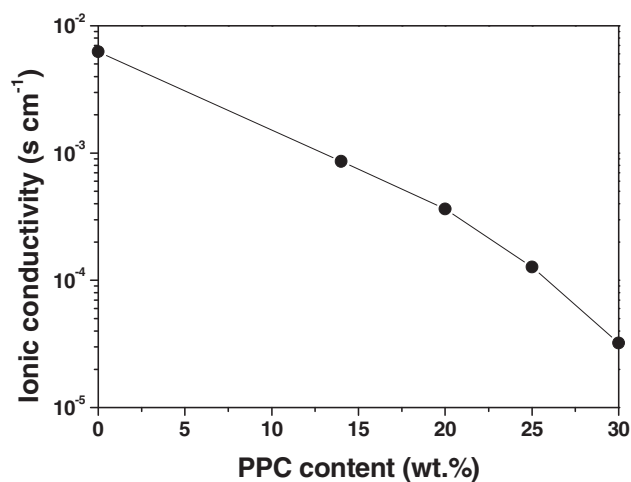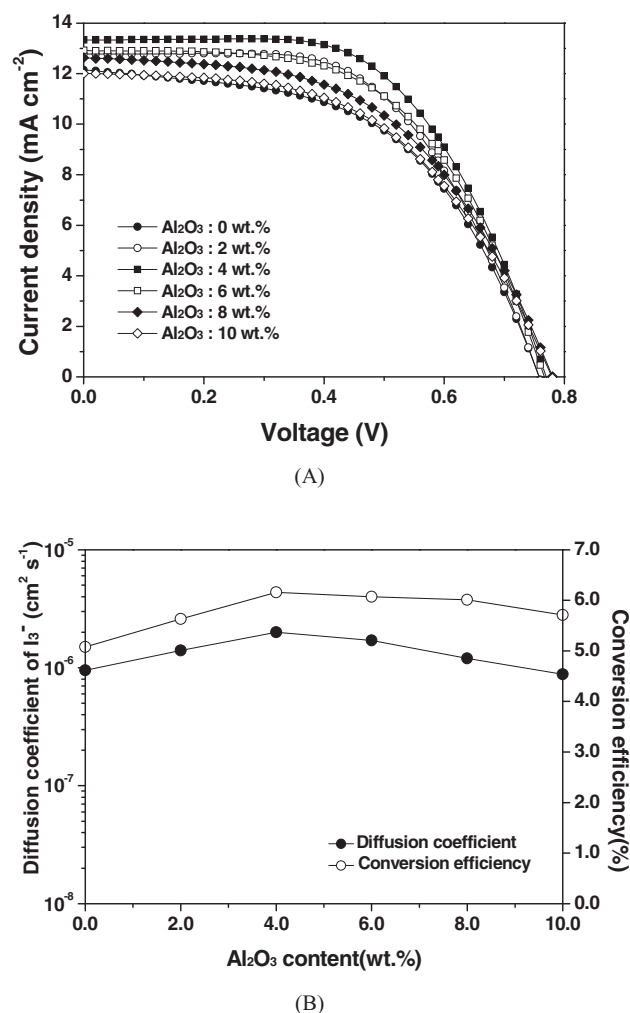
(A)

(B)

Figure 6. A) Photocurrent–voltage curves of DSSCs assembled with nanocomposite GPE containing different amounts of Al_2O_3 and B) diffusion coefficient of I_3^- and conversion efficiency versus Al_2O_3 content.

The addition of inorganic nanoparticles into the electrolyte has been an effective way to improve the photovoltaic performance of DSSCs assembled with gel electrolytes.[23,33–36] In this work, we introduced nanosized Al_2O_3 particles into the GPE to enhance the cell performance by increasing the ionic conductivity of GPE as well as increase the stability of the DSSCs by solidifying the gel electrolyte. Figure 6A shows the photocurrent–voltage curves of DSSCs assembled with nanocomposite GPE containing different amounts of Al_2O_3.

The J_{sc} and conversion efficiency (η) of the DSSC increased with the addition of Al_2O_3 up to 4 wt% and decreased with further addition. An increase in J_{sc} with Al_2O_3 content was related to improved diffusion of I_3^- in the nanocomposite GPE, as depicted in Figure 6B. An increase in the diffusion coefficient with the addition of Al_2O_3 is related to the generation of free volume at the nanoparticle

Figure 5. Ionic conductivities of GPEs as a function of PPC content.

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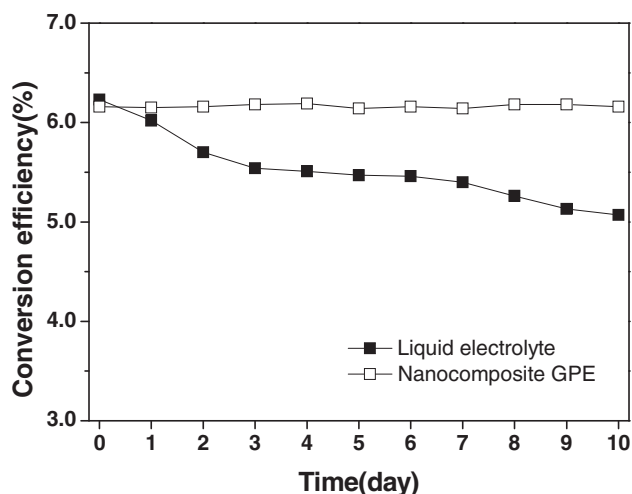
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Figure 7. Conversion efficiency variation as a function of time for DSSCs assembled with liquid electrolyte and nanocomposite GPE containing 4 wt% Al_2O_3.

interface.[35] Also, as previously reported,[23,37] charge can transport effectively in the channels of the nanocomposite gel polymer network, and a special mechanism (a Grotthuss-like exchange mechanism) may contribute to the effective charge transport. A decrease in diffusion coefficient beyond 4 wt% Al_2O_3 may be attributed to the blocking effect on the transport of charge carriers by the aggregation of Al_2O_3 nanoparticles. The optimum Al_2O_3 content that achieved the highest conversion efficiency was about 4 wt%. Notably, the high conversion efficiency (6.16%) of the DSSC assembled with nanocomposite GPE was achieved at 4 wt% Al_2O_3, which is comparable to that of the corresponding liquid electrolyte-based DSSC (6.23%).

Figure 7 shows the variation in the conversion efficiency of DSSCs assembled with liquid electrolyte and nanocomposite GPE containing 4 wt% Al_2O_3, as a function of time. The conversion efficiency in the liquid electrolyte-based DSSC decayed continuously with time during the period of investigation. After 10 d, the cell lost 19% of its initial conversion efficiency. On the contrary, the conversion efficiency of the quasi-solid-state DSSC assembled with nanocomposite GPE remained almost constant. The organic solvents containing a redox couple were well encapsulated in the quasi-solid-state DSSC due to the physical gelation of electrolyte in the cell. The adhesive nature of GPEs also promoted favorable interfacial contact between the dye-adsorbed TiO_2 electrode and the platinum counter electrode, providing more stable performance than the DSSC assembled with liquid electrolyte.

4. Conclusion

PPC was successfully synthesized from the copolymerization of CO_2 and propylene oxide. The nanocomposite GPEs consisted of PPC, Al_2O_3 nanoparticles, and liquid electrolyte were prepared and applied to the quasi-solid-state DSSCs. The quasi-solid-state DSSC assembled with the nanocomposite GPE containing 4 wt% Al_2O_3 nanoparticles exhibited a high conversion efficiency of 6.16% at 100 mW cm^{-2} and better stability than the DSSC with liquid electrolyte. It is thus expected that PPC synthesized from CO_2 is a promising polymer material for making GPEs for quasi-solid-state DSSCs.

[1] B. O'Reagan, M. Gratzel, *Nature* **1991**, *353*, 737.
[2] M. Gratzel, *Nature* **2001**, *414*, 338.
[3] M. Gratzel, *J. Photochem. Photobiol. A: Chem.* **2004**, *164*, 3.
[4] F. Cao, G. Oskam, P. C. Searson, *J. Phys. Chem.* **1995**, *99*, 17071.
[5] S. Murai, S. Mikoshiba, H. Sumino, S. Hayase, *J. Photochem. Photobiol. A* **2002**, *148*, 33.
[6] P. Wang, S. M. Zakeeruddin, I. Exnar, M. Gratzel, *Chem. Commun.* **2002**, 2972.
[7] T. Asano, T. Kubo, Y. Nishikitani, *J. Photochem. Photobiol. A* **2004**, *164*, 111.
[8] K. M. Lee, C.-Y. Hsu, W.-H. Chiu, M.-C. Tsui, Y.-L. Tung, S.-Y. Tsai, K.-C. Ho, *Sol. Energy Mater. Sol. Cells* **2009**, *93*, 2003.
[9] Y. Wang, *Sol. Energy Mater. Sol. Cells* **2009**, *93*, 1167.
[10] J. S. Park, Y. H. Kim, M. Song, C. H. Kim, M. A. Karim, J. W. Lee, Y. S. Gal, P. Kumar, S. W. Kang, S. H. Jin, *Macromol. Chem. Phys.* **2010**, *211*, 2464.
[11] O. Winther-Jensen, V. Armel, M. Forsyth, D. MacFarlane, *Macromol. Rapid Commun.* **2010**, *31*, 479.
[12] G. R. A. Kumara, S. Kaneko, M. Okuya, K. Tennakone, *Langmuir* **2002**, *18*, 10493.
[13] C. N. Zhang, K. J. Wang, L. H. Hu, F. T. Kong, L. Guo, *J. Photochem. Photobiol. A* **2007**, *189*, 329.
[14] K. Murakoshi, R. Kogure, Y. Wada, S. Yanagida, *Sol. Energy Mater. Sol. Cells* **1998**, *55*, 113.
[15] W. Zhang, Y. Cheng, X. Yin, B. Liu, *Macromol. Chem. Phys.* **2011**, *212*, 15.
[16] G. Wang, X. Zhou, M. Li, J. Zhang, J. Kang, Y. Lin, S. Fang, X. Xiao, *Mater. Res. Bull.* **2004**, *39*, 2113.
[17] D. W. Kim, Y. B. Jeong, S. H. Kim, D. Y. Lee, J. S. Song, *J. Power Sources* **2005**, *149*, 112.
[18] Y. J. Kim, J. H. Kim, M. S. Kang, M. J. Lee, J. Won, J. C. Lee, Y. S. Kang, *Adv. Mater.* **2004**, *16*, 1753.
[19] O. A. Illeperuma, M. A. K. L. Dissanayake, S. Somasundaram, L. R. A. K. Bandara, *Sol. Energy Mater. Sol. Cells* **2004**, *84*, 117.

[20] M. S. Kang, K. S. Ahn, J. W. Lee, *J. Power Sources* **2008**, *180*, 896.

[21] P. Wang, S. M. Zakeeruddin, J. E. Moser, M. K. Nazeeruddin. T. Sekiguchi, M. Gratzel, *Nat. Mater.* **2003**, *2*, 402.

[22] V. Suryanarayanan, K. M. Lee, W. H. Ho, H. C. Chen, K. C. Ho, *Sol. Energy Mater. Sol. Cells* **2007**, *91*, 1467.

[23] Z. Huo, S. Dai, K. Wang, F. Kong, C. Zhang, X. Pan, X. Fang, *Sol. Energy Mater. Sol. Cells* **2007**, *91*, 1959.

[24] M. Wang, X. Pan, X. Fang, L. Guo, C. Zhang, Y. Huang, Z. Huo, S. Dai, *J. Power Sources* **2011**, *196*, 5784.

[25] S. Inoue, H. Koinuma, T. Tsuruta, *J. Polym. Sci. B* **1969**, *7*, 287.

[26] A. Hauch, A. Georg, *Electrochim. Acta* **2001**, *46*, 3457.

[27] M. Zistler, P. Wachter, P. Wasserscheid, D. Gerhard, A. Hinsch, R. Sastrawan, H. J. Gores, *Electrochim. Acta* **2006**, *52*, 161.

[28] Y. Niu, W. Zhang, H. Li, X. Chen, J. Sun, X. Zhuang, *Polymer* **2009**, *50*, 441.

[29] J. H. Jung, M. Ree, T. Chang. *J. Polym. Sci. Part A: Polym. Chem.* **1999**, *37*, 3329.

[30] L. J. Gao, M. Xiao, S. J. Wang, F. G. Du, Y. Z. Meng, *J. Appl. Polym. Sci.* **2007**, *104*, 15.

[31] Y. Z. Meng, L. C. Du, S. C. Tiong, Q. Zhu, A. S. Hay, *J. Polym. Sci. Part A: Polym. Chem.* **2002**, *40*, 3579.

[32] T. Suresh, J. Joseph, K. M. Son, R. Vittal, J. Lee, K. J. Kim, *Sol. Energy Mater. Sol. Cells* **2007**, *91*, 1313.

[33] P. Wang, S. M. Zakeeruddin, P. Comte, I. Exnar, M. Gratzel, *J. Am. Chem. Soc.* **2003**, *125*, 1166.

[34] H. Usui, H. Matsui, N. Tanabe, S. Yanagida, *J. Photochem. Photobiol. A* **2004**, *164*, 97.

[35] M. S. Kang, J. H. Kim, J. Won, Y. S. Kang, *J. Phys. Chem. C* **2007**, *111*, 5222.

[36] S. J. Lim, Y. S. Kang, D. W. Kim, *Electrochem. Commun.* **2010**, *12*, 1037.

[37] W. Kubo, K. Murakoshi, T. Kitamura, S. Yoshida, M. Haruki, K. Hanabusa, H. Shirai, Y. Wada, S. Yanagida, *J. Phys. Chem. B* **2001**, *105*, 12809.

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