Efficient and Stable Photovoltaic Characteristics of Quasi-Solid State DSSC using Polymer Gel Electrolyte Based on Ionic Liquid in Organosiloxane Polymer Gels

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Abstract. Dye-Sensitized Solar Cell (DSSC) is still one of the promising solar cell types among the third generation of solar cells because of easiness of fabrication and variety of available materials. In this type of solar cell, the electrolyte is one of the important components for regenerating excited dyes and transporting electric charge carriers to the counter electrode. Indeed, the power conversion efficiency of DSSC can be then significantly affected by the chemical and physical properties of the electrolyte. The simplest electrolyte system of an I3/I- redox couple in an organic solvent, however, has some drawbacks due to corrosive properties, volatile and leakage problem. Use of solid phase or gel phase electrolyte may overcome those problems, but it is often considered to suppress the efficiency due to low ion diffusion. Here, we report the photovoltaic characteristics of DSSC using polymer gel electrolyte (PGE), which is composed of ionic liquid and an organosiloxane polymer gel. The better cell performance with power conversion efficiency of about 6% has been obtained by optimizing the mesoporous size of the TiO2 layer and the PGE viscosity.

1. Introduction
Dye-Sensitized Solar Cells (DSSCs) is organics solar cells with dye molecules as the light absorbers. Since the first report in 1991 by O’Regan and Gratzel [1], DSSCs have received much attention for several decades because of the easiness of fabrication and low-cost production [2-3]. In a conventional DSSC, regeneration of excited dyes was performed by using I3/I- redox couple dissolved in an organic solvent. Such solution may cause several problems including the leakage and volatilization of the liquid solvent, possible desorption of the adsorbed photosensitizers, and corrosion of the Pt counter electrode. Those critical effects may hamper the long-term performance of DSSC [4]. In order to solve those problems, other types of electrolytes have been introduced, such as solid state and quasi-solid state (QSS) electrolyte. In the last decade, quasi-solid state electrolytes have been much investigated because...
of their stability and large ionic conductivity. However, the overall energy conversion efficiencies of quasi-solid DSSCs are usually lower than liquid DSSCs, which commonly be assigned due to poor ion diffusion and poor interfacial contact with its TiO$_2$ mesoporous layer [5,6]. Tao et al. fabricated QSS-DSSC with PCE of 9.61 % by using electrolyte based on a low molecular mass organo-gelator (LMOG) material [7]. The best record efficiency for QSS-DSSC was about 10.1% as reported by Suzuka’s group by using TEMPO polymer gel electrolyte [8]. In this report, we present the improvement on the performance of DSSC using polymer gel electrolyte (PGE), which is composed of ionic liquid and an organosiloxane hybrid polymer gel (HPG), by optimizing the mesoporous structure of the TiO$_2$ layer and controlling the viscosity by adjusting the crosslinking degree of HPG. In the previous work, we have shown that the performance and efficiency of this kind of quasi-solid-state DSSC may crucially be affected by scarce penetration of the PGE into the mesoporous TiO$_2$ layer [9].

2. Experiments

2.1. Fabrication of photoelectrode

For preparing DSSC working electrode, FTO glass (15Ω/sq, Solaronix) was firstly washed with detergent. Then it was followed by cleaning in an ultrasonic bath with acetone and isopropanol (1:1) for 15 minutes and drying. Afterwards, a series of TiO$_2$ layers were deposited onto the top of FTO by the same method as in the previous work [9, 10]. In this work, the layer was then treated in 40 mM Ti-isopropanoxide solution in isopropanol and sintered at 500°C for 30 min. After natural cooling to 80°C, the TiO$_2$ electrodes were immersed in 0.7 mM N719 dye solution in ethanol for 24 h in dark condition.

2.2. Electrolyte

PGE used here is consisted of HPG and Imidazolium Ionic Liquid (IIL) (Mosalyte TDE 250, Solaronix). The HPG was synthesized from 3(trimethoxysilyl)propyl methacrylate (TMSPMA, Sigma-Aldrich) via the sol-gel method in a mix solution of ethanol, distilled water, and acetic acid with 1:10:0.1:0.25 in a volume ratio. The solution was then stirred and heated at 45 °C for 17h and 24h. The mixing process of HPG and IIL was carried out at room temperature with 1:1 in a volume ratio.

2.3. DSSC assembly and Characterization

The photoanode and the Pt drilled counter electrode (Dyesol) were sealed together with a 25 µm Surlyn (Solaronix) spacer. The PGE was then injected into assembled cells. In this research three different electrolytes were used, namely pure ionic liquid (DSSC L), DSSC PGE 17h and DSSC PGE 24h. The morphology of TiO$_2$ nanoparticles and the thickness of the layer were observed by SEM, and its porosity analyzed by PoreDizM70 Matlab program. The current-voltage characteristics and EIS measurements were carried out by the same instruments as in our previous works. [9-11] The viscosity measurements of electrolytes by using a Brookfield viscometer.

3. Results and Discussion

3.1. Porosity of TiO$_2$

The performance of the fabricated DSSC was strongly influenced by the mesoporous structure of TiO$_2$ layer. Figure 1 shows a typical SEM image of the mesoporous TiO$_2$ layer prepared in this work and its porosity analyzed by PoreDizM70 Matlab program. From this SEM image, the mean pore diameters are estimated to be about 60 nm while the particle sizes are about 30-40 nm.

3.2. Photovoltaic Performances of DSSC

Figure 2 shows the current density-voltage (J-V) curves of DSSCs fabricated in this work. The parameter performances of DSSC including PCE are summarized in Table 1. It can clearly be seen that the performance of DSSC using ionic liquid is slightly better than the DSSCs using PGE with PCE of about 6%. This efficiency reduction is commonly observed in DSSCs with PGE, which often attributed due to
the high viscosity and low ion diffusion as well as poorer electrolyte interfacial contact TiO\textsubscript{2}. Recently, we have also emphasized again the crucial effect of scarce electrolyte penetration into the mesoporous layer due to that electrolyte rheology. In order to investigate the stability, the cells were also measured after one month (34 days) after the cell fabrication.

![Typical SEM image of TiO\textsubscript{2} mesoporous film used in this work.](image)

**Figure 1.** Typical SEM image of TiO\textsubscript{2} mesoporous film used in this work.

**Table 1.** The parameter photovoltaic performances of DSSC using PGE and IL (as comparison)

| Sample   | TiO\textsubscript{2} thickness | J\textsubscript{sc} (mA/cm\textsuperscript{2}) | Voc (V) | Efficiency (%) |
|----------|---------------------------------|---------------------------------------------|---------|---------------|
|          | H+1    | H+34 | H+1    | H+34 | H+1    | H+34 |
| DSSC L   | 17     | 14.7 | 11.8   | 0.675 | 0.74  | 6.04  | 5.21 |
| DSSC 17h | 17     | 15.8 | 14.6   | 0.638 | 0.68  | 5.25  | 5.65 |
| DSSC 24h | 17     | 16.6 | 16.2   | 0.625 | 0.66  | 5.70  | 5.73 |

3.3. Impedance Characteristics

Analysis of electrochemical impedance spectroscopy (EIS) spectra is important to be done as it can provide some information on the processes of transport and transfer, diffusion, and accumulation of charge carriers as well as loss recombination of charge carriers. [2, 6, 11] In order to explain and analyze the EIS spectra of DSSC, we must estimate the parameter from EIS spectra by fitting with its equivalent circuit model. From this analysis, we can deduce the physical processes and the related parameters of the device. Fig. 3 represents the Nyquist plot of DSSC measured under 0.6V DC bias voltage and light condition at one day (fresh) and one month after fabrication for (a) DSSC using liquid electrolytes, (b) DSSC with PGE using HPG synthesized for 17h, (c) DSSC with PGE using HPG synthesized for 24h. The Nyquist plot can be well fitted with an equivalent circuit as shown in Fig. 3 (d) and the
The impedance spectrum of each solar cell exhibit three semicircles with almost similar impedance magnitude. Each semicircle can be described, from high frequency to low frequency, as followings. The first semicircle corresponds to the charge transfer processes at the counter electrode/electrolyte interfaces, the second semicircle corresponds to transport electron in the TiO$_2$ mesoporous, while the third semicircle corresponds to diffusion process from electrolyte.

**Figure 3.** Nyquist plots of DSSC with different electrolytes measured at the 1$^{st}$ day after the fabrication and measured at the 34$^{th}$ days after the fabrication. (a) DSSC with liquid electrolyte, (b) DSSC with PGE synthesized for 17h, (c) DSSC with PGE synthesized for 24h, (d) equivalent circuit

![Nyquist plots of DSSC](image)

**Table 2.** The equivalent circuit parameters of DSSCs using PGE and IL, which were measured at two different times after preparation, namely after one day (H+1) and after around one month (H+34).

| Condition | DSSC Liquid | DSSC 17h | DSSC 24h |
|-----------|-------------|----------|----------|
| Rs [$\Omega$] | 29.4 | 29.4 | 35.5 | 33.3 | 26.8 | 24.0 |
| $R_{v1}$ [$\Omega$] | 10.17 | 30.3 | 5.8 | 10.4 | 6.7 | 9.2 |
| $R_{v2}$ [$\Omega$] | 8.5 | 10.6 | 7.5 | 10.2 | 6.1 | 6.8 |
| $R_{v3}$ [$\Omega$] | 5.8 | 11.1 | 6.4 | 7.6 | 6.8 | 8.6 |
| $C_{dl1}$ [µF] | 403.2 | 390.3 | 473.4 | 456.8 | 519.5 | 467.8 |
| $C_{dl2}$ [µF] | 65.8 | 33.6 | 51.5 | 42.9 | 52.3 | 44.7 |
| $L$ | 0.3 | 0.8 | 1.6 | 0.3 | 0.4 | 1.1 |
| $r_k$ [$\Omega$] | 4.9 | 3.8 | 180.5 | 16.2 | 243.3 | 255 |
| $r_m$ [$\Omega$] | 227.6 | 61.9 | 447.8 | 347.8 | 350.6 | 164.5 |
| $Y_m[S^*s^a]$ | 26.6 | 44.9 | 27 | 34.6 | 12.4 | 6.9 |
| $a$ | 0.9 | 0.8 | 1 | 0.9 | 1 | 1 |

### 3.4. Viscosity

Figure 4 shows the curve of viscosity vs. shear stress of the ionic liquid, PGE, and HPG. The viscosity of the ionic liquid is relatively larger than the others. The PGE shows similar viscosity characteristics with the ionic liquid. However, HPG used here shows a Newtonian behavior where its viscosity does not significantly influence by the changing of shear rate. The PGE using HPG synthesized for 17h have
larger viscosity than PGE using HPG synthesized for 24h. This result shows that the viscosity characteristics in these PGEs are dominated by the ionic liquid content, which has strong ionic interaction, and are not by the HPG cross-linking degree. Based on their photovoltaic characteristics in the present work, the DSSC with PGE 24h produces better working performance than the DSSC with PGE 17h, which has less cross-linking and higher viscosity in contrary to our previous report before [9]. It should be noted, however, the TiO\textsubscript{2} layer has in the present work has a more porous structure by avoiding preparing the layer in a multi-step process.

Figure 4. The viscosity characteristics of PGEs and HPG that were synthesized in 17h and 24h.

4. Conclusion
The performance enhancement of quasi-solid state DSSC using PGE studied here was achieved by optimizing the mesoporous structure of TiO\textsubscript{2} layer and controlling the crosslinking degree of HPG as indicated by its viscosity. The PCEs of DSSCs with PGEs are almost close to the PCE of the reference cell with pure ionic liquid, which is about 6%. The performance of DSSC with PGE 24h, which has smaller viscosity and has a presumably higher crosslink degree, shows better performance than that of PGE 17h because the TiO\textsubscript{2} layer in the present work has more porous structure. It should be also noted that DSSC with PGE has better stability than the DSSC with pure IL because of less electrolyte leakage.

5. References
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