Dye-sensitized Solar Cells Using Nanocomposite Ion-gel

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Dye-sensitized solar cells (DSCs) are expected to be the next-generation solar cell because they can be fabricated at a low cost and use no harmful materials. There are several tasks, which must be undertaken to attain practical use, and as one of those tasks, it is necessary to improve electrolyte materials for improvement of long-term stability and reliability of the cells. We investigated the properties of a nanocomposite ion-gel electrolyte that was a gelated ionic liquid electrolyte with several nanoparticles. The nanocomposite ion-gel type cell successfully attained both increase in conversion efficiency and quasi-solidification of the electrolyte. Energy conversion efficiency of the quasi-solid state-type cell with 5 mm × 9 mm photo-electrode size was η = 6.4% under optimized conditions. In this report, details of the photovoltaic property of the cell are described. In addition, technological subjects in the fabrication of practical DSCs devices are also introduced.

1. Introduction

Recently, photovoltaic generation is attracting attention as clean energy, and production of solar cells is increasingly growing. Dye-sensitized solar cells (DSCs)¹ are expected as a next-generation solar cell because of their favorable characters which are as follows: low fabrication costs, simple manufacturing process, use of no toxic materials, and so forth. For practical use, it is necessary to improve energy conversion efficiency and long-term stability of the cells. In addition, enlargement of cell size is also required. We have reported our investigation of electrolyte materials² ³ and development of device fabrication technology⁴ to achieve the above-mentioned tasks. In this report, we focus on a nanocomposite ion-gel electrolyte as a novel electrolyte material for DSCs. Its unique properties that have not been observed in conventional electrolyte systems and device fabrication technology for utilizing the novel electrolyte system are described.

2. Outline of Ion-gel Type DSCs

A typical structure of DSCs is shown in Fig. 1. It has a photo-electrode and an oppositely placed counter-electrode. The former is composed of a semiconductor mesoporous film on a transparent substrate and sensitizing dyes adsorbing on the semiconductor surface. The latter is covered with a thin Pt layer. An electrolyte solution including I⁻/I³⁻ redox couples fills up the intervening space between both electrodes. Some volatile organic solvents (e.g. acetonitrile) are employed as an electrolyte solvent and its evaporation deteriorates the output of cells during long-term operation. Leakage of the electrolyte also harms the reliability of DSCs. Non-volatile electrolytes and solid (or quasi-solid)-state electrolytes have been studied to solve these problems (Table 1)⁵ - ⁹. Ionic liquids and ion-gels, which mean gelated ionic liquids, seem to be suitable as electrolyte materials. Ionic liquids that entirely consist of cations and anions keep the liquid state stably in a wide range of temperature including room tem-

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Fig. 1. Structure of a Dye-sensitized Solar Cell.
Temperature. They are drawing interest as an electrolyte material for DSCs because of their favorable properties such as negligible vapor pressure, non-flammability and high ionic conductivity. The ionic liquid-based electrolyte can be quasi-solidified physically or chemically by addition of proper gelators. The quasi-solid electrolyte, called ‘ion-gel electrolyte’, is free from solvent evaporation and electrolyte leakage. Therefore, the ion-gel electrolyte is believed to be one of the best suited materials to realize practical DSCs. However, the output of ion-gel type cells is often low compared with the result of a conventional volatile electrolyte system. Increase of energy conversion efficiency is an important task for application of the ion-gel electrolyte. In addition, due to its poor flowability, development of technology to fill up a cell with the ion-gel electrolyte uniformly is also necessary.

3. Methods for Cell Fabrication and Measurement

Typical conditions of test cell preparation are shown as follows.

Glass substrates with a fluoride-doped SnO₂ (FTO) film or an FTO/ITO double layer were used as transparent electrodes. TiO₂ nanoparticles-dispersed paste (Ti Nanoxide T, Solaronix) was spread on the above-mentioned substrates. After drying the wet film on the substrate, the film was sintered at 450°C. A light-reflecting layer that consisted of several hundred nanometers-sized TiO₂ particles was deposited over the prepared mesoporous TiO₂ layer by the same procedure. As a sensitizing dye, N₃ dye (Ru (2,2’-bipyridyl-4,4’-dicarboxylate)₂ (NCS)₅) was used. As a counter-electrode, an FTO substrate on which platinum had been deposited by sputtering was used.

Electrolyte solution was composed of 1-ethyl-3-methylimidazolium iodide (except for the case of HMIm-I applying), LiI, I₂, and 4-tert-butylpyridine that was dissolved in an ionic liquid. As ionic liquids, 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (EMIm-TFSI), 1-hexyl-3-methylimidazolium iodide (HMIm-I), or 1-ethyl-3-methylimidazolium dicyanamide (EMIm-DCA) was applied (Fig. 2).

Preparation procedure of a nanocomposite ion-gel electrolyte is described below. The ionic liquid-based electrolyte solution described above, and several amounts of nanoparticles (1-10 wt%) were diligently grinded in a mortar. The mixture was centrifuged with a centrifugal acceleration of about 2,000G to separate the excess liquid component from the gel phase, and then a paste-like nanocomposite ion-gel electrolyte was obtained.

In preparation of test cells, the photo-electrode and the counter-electrode were clamped together directly. The nanocomposite ion-gel electrolyte was spread on the photo-electrode before clamping. Photo-electrode size was 9 mm × 5 mm except for a large-sized cell.

Photovoltaic measurement was carried out using a solar simulator (ESS-150A, Eiko Seiki) with AM 1.5 adjusted spectra and 100 mW/cm² irradiation strength.

4. Ion-gel Type DSCs Using Polymer Gelator

As the first step of ion-gel electrolyte development, photovoltaic properties of ion-gel type DSCs using a polymer gelator were investigated. Poly(vinylidene-fluoride-co-hexafluoropropylene) (PVdF-HFP), which is a relatively familiar gelator, was used to gelate the ionic liquid-based electrolyte. It can stably gelate various kinds of ionic liquids with addition of only a little amount (Fig. 3). Preparation procedure of a nanocomposite ion-gel electrolyte is described below. The ionic liquid-based electrolyte solution described above, and several amounts of nanoparticles (1-10 wt%) were diligently grinded in a mortar. The mixture was centrifuged with a centrifugal acceleration of about 2,000G to separate the excess liquid component from the gel phase, and then a paste-like nanocomposite ion-gel electrolyte was obtained.

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Table 1. Examples of Solid-/Quasi-solid Electrolytes for DSCs Reported Previously (Non-volatile Electrolyte System)

<table>
<thead>
<tr>
<th>Electrolyte (Hole conductor)</th>
<th>Composition</th>
<th>Institution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ion-gel (Ionic liquid + Gelator)</td>
<td>HMIm-I+Low molecular weight gelator (Hydrogen bond-type)⁵</td>
<td>Osaka Univ.</td>
</tr>
<tr>
<td></td>
<td>MImI+PVdF-HFP (Polymer gelator)⁶</td>
<td>EPFL etc.</td>
</tr>
<tr>
<td>Chemical-gel</td>
<td>MImI+PVP/Multi-functional halide⁷</td>
<td>Institute of Technology</td>
</tr>
<tr>
<td>Others</td>
<td>MImI+Silica⁸</td>
<td>EPFL</td>
</tr>
</tbody>
</table>

| Solid state | CuI, CuSCN etc.⁹ | IFS Sri Lanka, Shizuoka Univ. etc. |

HMIm-I; 1-Hexyl-3-methylimidazolium iodide
MImI; 1-Methyl-3-propylimidazolium iodide
PVdF-HFP; Poly(vinylidenefluoride-co-hexafluoropropylene)
PVP; Polyvinylpyridine

Electrolyte solution was composed of 1-ethyl-3-methylimidazolium iodide (except for the case of HMIm-I applying), LiI, I₂, and 4-tert-butylpyridine that was dissolved in an ionic liquid. As ionic liquids, 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (EMIm-TFSI), 1-hexyl-3-methylimidazolium iodide (HMIm-I), or 1-ethyl-3-methylimidazolium dicyanamide (EMIm-DCA) was applied (Fig. 2).

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Figure 4 shows I-V characteristics of DSCs including a result of the PVdF-HFP ion-gel system. Initially, as shown in the figure (Polymer gel B), photocurrent of the prepared cell was rather low in comparison with the result of a conventional volatile electrolyte system. Increase of energy conversion efficiency is an important task for application of the ion-gel electrolyte. In addition, due to its poor flowability, development of technology to fill up a cell with the ion-gel electrolyte uniformly is also necessary.
Ion-gel electrolyte systems using polymer gelators, as represented by the PVdF-HFP, or several low molecular gelators have a capability equal to the liquid electrolyte system, but it is difficult to exceed that output. This restriction might be unavoidable for those conventional ion-gel systems. But energy conversion efficiency of DSCs using ionic liquids has been still inferior to the case of a volatile electrolyte system (Fig. 4). Hence, it is necessary to reduce the gap in cell output.

5. Development of Nanocomposite Ion-gel Electrolytes

5.1 Photovoltaic Properties

We found unique and favorable properties of a nanocomposite ion-gel electrolyte that was a quasi-solid ionic liquid-based electrolyte gelated by several nanoparticles. It was possible to increase energy conversion efficiency of the cell compared with that before gelation. Although studies on application of single walled-carbon nanotubes or silica nanoparticles have been reported as similar ion-gel preparation with nanoparticles, the property of improvement of DSCs output by gelation has not been known yet.

The nanocomposite ion-gel electrolyte was a paste-like form as shown in Fig. 3. It was very thixotropic and possible to spread easily on the photo-electrode using a paddle.

Figure 5 shows I-V characteristics of the prepared nanocomposite ion-gel type DSCs. All values of short-circuit current ($I_{sc}$), open-circuit voltage ($V_{oc}$), and fill factor (FF) were better than those obtained by...
the corresponding liquid electrolyte system in contrast with the result of the conventional ion-gel system. Energy conversion efficiencies of cells after and before gelation were $\eta = 5.7\%$ and $\eta = 4.7\%$, respectively.

Photovoltaic properties of cells using nanocomposite ion-gel electrolytes gelated by various kinds of nanoparticles (Fig. 6) were studied. Although the degree of enhancement was different depending on the kind of nanoparticles, these systems other than that applying TiO$_2$ also showed improvement of output (Table 2). At this time, the performance of cases using a metal oxide such as TiO$_2$ and SiO$_2$ is especially superior. Correlation between energy conversion efficiency and nanoparticle size was also investigated in the TiO$_2$ nanoparticle system. As shown in Fig. 7, efficiency was increased in every case but apparent dependence on particle size was not observed. We supposed that nanoparticles in the nanocomposite ion-gel were not primary particles because of their aggregation. When it was considered from our assumption of the charge transport mechanism in the nanocomposite ion-gel electrolyte (described in detail later), electrolyte properties would be influenced by the size if nanoparticles were dispersed as primary particles in the electrolyte. We are expecting further improvement of the output by controlling the dispersion condition.

The influence of applied ionic liquids was studied. Figure 8 presents energy conversion efficiencies of cells using nanocomposite ion-gel electrolyte with several ionic liquids, which was improved after electrolyte gelation for every ionic liquid system. Especially, the cell with EMIm-DCA (investigated at Yokohama National University)\textsuperscript{12} based electrolyte gelated by TiO$_2$ (P25) nanoparticles showed energy conversion efficiency of $\eta = 6.4\%$ that was notably superior for the ion-gel type DSCs (Fig. 9). This result was more than 90% of the output in the volatile electrolyte system as described above. It was expected that investigations of the composition or mixing

![Fig. 6. FE-SEM Images of Nanoparticles Using Gelation.](image)

![Fig. 7. Dependence of Energy Conversion Efficiency on the TiO$_2$ Particle Size in the Nanocomposite Ion-gel Electrolyte.](image)

![Fig. 8. Comparison of Energy Conversion Efficiency of Nanocomposite Ion-gel Type Cells Using Several Ionic Liquids.](image)
condition of the electrolyte might enable further increase of energy conversion efficiency.

5.2 Discussion of Charge Transport

Apparent diffusion coefficients ($D_{\text{app}}$)\(^1\) of $I^{-}/I_{3}^{-}$ redox couples in the nanocomposite ion-gel electrolyte were estimated to consider the mechanism of the increase of output with gelation. $D_{\text{app}}$ that indicated the charge transfer rate in the electrolyte was evaluated by carrying out cyclic voltammetry measurement using a platinum microelectrode. Calculated values of $D_{\text{app}}$ are listed in Table 3. After gelation, $D_{\text{app}}$ values increased obviously; therefore, enhancement of the charge transfer rate with nanocomposite ion-gel formation was suggested.

In an electrolyte solution including $I^{-}/I_{3}^{-}$ redox couples, charges were transported by physical diffusion of carriers as the most simplified style like the drawing in Fig. 10(a). In ionic liquids, a conjugated charge transport reaction that was based on not only the physical diffusion but also an exchange reaction occurred with an increase of $I^{-}/I_{3}^{-}$ concentration (Fig. 10(b))\(^1\). In the case of the exchange reaction-based process, rapid charge transfer was enabled even in a viscous ionic liquid because physical species transfer was not virtually necessary for the charge transport. Since acceleration of the physical diffusion rate with the formation of the nanocomposite ion-gel was also difficult, we considered that the charge transport based on the exchange reaction was enhanced in the nanocomposite ion-gel electrolyte. At this time, we assume a model like the drawing in Fig. 11. Imidazolium cations might adsorb on the additional nanoparticles surface\(^4\) and then counter-anions ($I^{-}/I_{3}^{-}$) gathered around them. It was supposed that such dense and oriented $I^{-}/I_{3}^{-}$ region played the role of a rapid charge transport path with exchange reaction. In the conventional electrolyte system, unfortunately, dense $I^{-}/I_{3}^{-}$ composition was not utilized effectively because of decreasing output attributed to light absorption or recombination by $I_{3}^{-}$ ions. On the other hand, in the nanocomposite ion-gel system, it was considered that enhancement of the charge transport based on the exchange reaction was enabled without an increase of absolute $I^{-}/I_{3}^{-}$ concentration by the

\[ J_{sc} = 11.2 \text{ mA/cm}^2 \]
\[ V_{oc} = 809 \text{ mV} \]
\[ \text{FF} = 0.70 \]
\[ \eta = 6.4\% \]

Fig. 9. I-V Characteristics of the Nanocomposite Ion-gel Type DSC with EMIm-DCA + P25 System.

Table 3. Apparent Diffusion Coefficients; $D_{\text{app}}$ of $I^{-}/I_{3}^{-}$ before and after Gelation

<table>
<thead>
<tr>
<th>Ionic liquid</th>
<th>Nanoparticles for gelation</th>
<th>Apparent diffusion coefficient $D_{\text{app}}$ ($\times 10^{-7} \text{ cm}^2/\text{s}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EMIm-TFSI</td>
<td>without particles</td>
<td>3.7</td>
</tr>
<tr>
<td>TiO$_2$ (P25)</td>
<td></td>
<td>6.0</td>
</tr>
<tr>
<td>Carbon black</td>
<td></td>
<td>4.7</td>
</tr>
<tr>
<td>HMIm-I</td>
<td>without particles</td>
<td>1.5 – 1.6</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td></td>
<td>2.8 – 3.2</td>
</tr>
</tbody>
</table>

Fig. 10. Schematic Drawing of Charge Transport Mechanisms in Ionic Liquid.

Fig. 11. Schematic Drawing of a Proposed Charge Transport Mechanism in the Nanocomposite Ion-gel Electrolyte.
mechanism above-described mechanism.

5.3 Device Fabrication Technology

Although nanocomposite ion-gel electrolytes have several attractive properties, such as nonvolatility, quasi-solid state and high output, there were some tasks to be undertaken for the device fabrication as practical DSCs. For example, development of electrolyte-filling technology and enlargement of cells were needed.

Typically, except for open cells for laboratory use, DSCs have a cell package structure as shown in Fig. 12(a). The electrolyte solution was injected into the cell via an opening on the backside by pressure difference or capillary phenomenon. But, it was difficult to apply those electrolyte-filling methods for electrolytes with poor fluidity like the nanocomposite ion-gel, so we developed a novel cell package (Fig. 12(b)). In this cell package, the photo-electrode and the counter-electrode were put into an outer case after sandwiching the electrolyte layer between two electrodes and then the outer case was sealed. It has the following advantages:

1) Easy to fill up with a viscous electrolyte (e.g. spreading by a blade or a print method).
2) No limitation regarding electrode distance attributed to spacer (i.e. a sealing polymer) thickness.
3) Possible to seal a cell without excess heat or pressure on the electrode surface.

Figure 13 shows a view of a nanocomposite ion-gel type DSC module with 450 mm × 300 mm size fabricated by the novel cell package application. It had six unit cells in a package. On the photo-electrode of each unit-cell, current collecting grids were formed by screen-printing to increase conductivity of substrates. Output of the large-sized cell was markedly improved in comparison with that of the simple large-sized cell without grids owing to a decrease in internal resistance. Energy conversion efficiency of the unit cell was \( \eta = 3.2\% \) At this time, the gap of output between the present large-sized cells and mini-cells is still wide. We consider that optimization of design of current-collecting grids and decrease in generation variation within a cell would improve the photovoltaic property of the DSCs modules.

6. Conclusion

Our test cells were successfully achieved by both increase in conversion efficiency and quasi-solidification of the electrolyte by applying the nanocomposite ion-gel electrolyte. In addition, the outer case-type cell package and the highly conductive transparent electrode with current collecting grids were also developed as an essential technology for DSCs device fabrication. Test modules of nanocomposite ion-gel type large-sized DSCs were fabricated based on these technologies. Recently, attention to the development of practical DSCs modules is increasingly growing on a global scale. We will also undertake early practical application of DSCs through further investigation to achieve the energy conversion efficiency and the long-term stability of the devices.

This work was partially supported by the New Energy and Industrial Technology Development Organization (NEDO) under the Japanese
Government.

References