Properties of Working Electrodes with Polystyrene Beads Addition in Dye Sensitized Solar Cells

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ABSTRACT

We prepared the TiO₂ layer with 0~4 wt% of polystyrene (PS) beads having a radius of 250 nm to increase the dye adsorption and energy conversion efficiency (ECE) of a dye sensitized solar cell (DSSC). Then, we fabricated DSSCs using 0.45 cm² active area. FE-SEM was used to characterize the microstructure consisting of TiO₂ layer and PS beads. UV-VIS-NIR was used to determine the optical absorbance of working electrodes (WEs). Solar simulator and potentiostat were used to determine the photovoltaic properties. We observed that pores having a radius of 250 nm were formed with the density of 0.15 ea/µm² in TiO₂ layers after conducting the sintering process. The absorbance in visible light regime was found to increase with the increase in the amount of PS beads. The ECE increased from 4.66% to 5.25% when the amount of PS beads was increased from 0 to 4 wt%. This is because the pores of PS beads increased the adsorption of dye. Our results indicate that the ECE of the DSSCs can be enhanced by the addition of an appropriate amount of PS beads into TiO₂ layers.

Key words: Dye sensitized solar cells, Energy conversion efficiency, Polystyrene bead, TiO₂

1. Introduction

Dye-sensitized solar cell (DSSC) is considered to be the next-generation photovoltaic device, since it is cost-effective to fabricate and has the desirable compatibility to conventional glass substrates.1) However, it has a low efficiency of below 10%, compared to 25% of the conventional silicon-based solar cell, which has promoted its efficiency improvement as one of the most active fields of research.2)

Improving energy conversion efficiency (ECE) of DSSC involves in engineering for all its components such as working electrode (WE), counter electrode (CE), electrolyte, etc. Especially, most focused one has been the WE that generally based on a TiO₂ layer. To devise the TiO₂ layer more efficient, Zhang et al.3) employed carbon nano tube (CNT) into the TiO₂ layer that has a narrower band gap than that of TiO₂. They reported that its ECE increased from 3.63% to 6.34% through increasing electron mobility with adding CNT.

Another approach has directed to increasing the surface area of TiO₂ layer for dye absorption. For example, various techniques were reported such as making a thicker TiO₂ layer, and coating TiO₂ in multi-layers to provide additional area for dye adsorption.4) However, these techniques limited to improve efficiency, since the layer above a proper thickness lead to electron recombination before electrons move to the electrode.5) Therefore, it is desirable to increase dye absorption without charge recombination at the optimum layer thickness of TiO₂.

Considering the above argument, studies to fabricating porous structure were carried out to achieve high specific surface area and chemical stability at a fixed layer thickness of TiO₂. Two popular methods were often employed to have a high porosity in normal structural ceramics. One is the addition of thermoplastic polymer to a ceramic body as the foaming constituent followed by heat treatment,6) and the other is the foaming of ceramic in a slurry state followed by gas agitation.7)

Chae et al.8) formed porous zirconia ceramics of 58~75% porosity with the addition of macro-spheres of PMMA (poly methyl methacrylate-coethylene glycol dimethaerylate). Lim et al.9) used foaming and gelation processes and fabricated highly porous Al₂O₃ ceramics of 64~90% porosity by the addition of Triton X-114 as the active surfactant.

Recently, this technique of introducing porosity into structural ceramic bodies has been applied into the semiconductor TiO₂ layer of DSSC to have a porous WE and to increase its specific surface area. For example, when a thermoplastic polymer is introduced into the TiO₂ layer of DSSC, the organic matter thermally decomposes and forms a porous structure during the sintering of TiO₂ layer. Thus, the dye adsorption can be increased by increasing specific surface area of TiO₂ layer, and ECE can be enhanced.

Patel et al.10) reported an increase of dye absorption from 18.8 to 66.8 mmol/cm² on a porous TiO₂ layer with the addition of PVC (polyvinyl-chloride). Fan et al.11) reported that ECE improved from 0.61% to a maximum of 2.44% with the
addition of PEG (polyethylene glycol), EC (ethyl cellulose), etc. into the TiO$_2$ layer. Polystyrene (PS) is a synthetic polymer by thermal polymerization. It has density of 0.96 ~ 1.04 g/cm$^3$, melting point of 240°C, and decomposes at temperatures above 330°C.$^{12}$ In addition, PS has excellent formability and can be formed into nano-size beads.$^{13}$

In this study, we added 0 ~ 4 wt% PS beads of 500 nm into the TiO$_2$ layer in DSSC to confirm these arguments and to accomplish an improved ECE.

2. Experimental Procedure

In this study on DSSCs, we prepared the TiO$_2$ layer with the addition of PS beads (500 nm, Fluka) in the amount of 0 ~ 4 wt%. We made the blocking layer of WE by mixing titanium(IV)bis(ethyl aceto acetato)-disopropoxide and 1-Butanol into a solution, followed by spin-coating for 0 rpm-10 sec and 2000 rpm-40 sec, and heat treating at 500°C for 15 min.

We fabricated the semiconducting TiO$_2$ layer by mixing TiO$_2$ paste (20 nm, DSL 18NR-T of 10, Dyesol) and PS beads in the amount of 0 ~ 4 wt%, by coating it via doctor blade method, and by heat treating at 500°C for 30 min into a TiO$_2$ film. We adsorbed 0.5 mM cis-vis bis-ruthenium (II) bistetrabutylammonium(N719) on a TiO$_2$ film and completed the WE consisted of glass/FTO/blocking layer/TiO$_2$ with PS beads/dye.

The CE was prepared by RF sputter (MHS-1500, Moohan, 300 W, 13.56 MHz) to form a 100 nm-Pt film on a glass substrate using 99.99% Pt as a target. A flow of 40 sccm Ar at pressure of 5 mtorr at RT was set for the process. The prepared WE and CE were fixed at position and filled with electrolyte, finalizing DSSC device consisted of glass/FTO/blocking layer/TiO$_2$ with PS beads/dye(N719)/electrolyte/100 nm Pt/glass with active area of 0.45 cm$^2$.

We analyzed the surface microstructure of TiO$_2$ layer with PS beads in WE by FE-SEM (field emission scanning electron microscope, S-4800, Hitachi) at an accelerating voltage of 15 kV. We also observed its cross-sectional microstructure by FE-SEM at an accelerating voltage of 20 kV. Absorbance of the prepared WE was analyzed by UV-VIS-NIR (UV3105PC, Shimadzu) with an absorption-mode apparatus under medium scan speed. Average absorbance in the visible-light region of 400 ~ 800 nm was obtained by adding absorbances at each wavelength and dividing it by the number of added times.

Impedance of DSSC was determined by solar simulator (PEC-L11, Pecell) and potentiostat (Iviumstat, Ivium) to verify interfacial resistance. The analysis was carried out in the frequency range of 10 mHz ~ 1 MHz applying AC voltage and collecting the current responses. I-V (current-voltage) characteristic of DSSC was measured by the same instruments under a setup: a 100 W Xenon lamp was the illumination source at 1 sun (100 mW/cm$^2$) condition. From the I-V curves, short-circuit current density, open-circuit voltage, fill factor, and ECE were evaluated.

3. Results and Discussion

Figure 1 shows FE-SEM images of the TiO$_2$ layer without and with 4 wt% PS beads, respectively: (a) and (b) are FE-SEM images of surface at 60,000 magnification, and the insets at the upper-right corner are images of lower magnification of 8,000, and (c) and (d) are FE-SEM images of cross sections at 5,000 and 6,000 magnifications.

In case of Fig. 1(a), TiO$_2$ particles have particle size of 20 nm. As shown in the inset, the coated microstructure is relatively uniform without any macro-size pore as intended.

Figure 1(b) shows FE-SEM surface images of the TiO$_2$ layer with 4 wt% PS beads, showing uniformly distributed pores of about 480 nm compared to Fig. 1(a). Considering the size of added PS beads is 500 nm, this implies that the same size pores are formed after sintering at 500°C by thermal decomposition of added PS beads. Image in the inset indicates that the pore distribution density is about 0.15 ea/µm$^2$.

Figure 1(c) is the cross-sectional image of Fig. 1(a), indicating that the TiO$_2$ layer is 8.6 µm thick, and is structurally uniform without any macro-size pore. Fig. 1(d) is the cross-sectional image of Fig. 1(b), indicating that the TiO$_2$ layer is 6.5 µm thick which is little thinner than Fig. 1(a). This implies that more sintering shrinkage took place due to the decomposition of PS beads. We also confirmed uniformly distributed pores of 450 nm size, which have distribution density of 0.13 ea/µm$^2$ as indicated by dotted line. We confirmed that a porous structure can be formed both in interior and surface of the TiO$_2$ layer with the addition of PS beads.

Figure 2 shows absorbance curves of WEs with 0 ~ 4 wt% PS beads at the visible-light range of 400 ~ 800 nm. The absorbance of WE without PS bead is 0.297%, while they are 0.349%, 0.355%, 0.359%, and 0.362% with the additions

![Fig. 1. FE-SEM images of (a), (b) surface section and (c), (d) cross section of TiO$_2$ layers with PS beads of : (a), (c) 0 wt%, and (b), (d) 4 wt%](image-url)
of 1, 2, 3, and 4 wt% of PS beads, respectively. This increase of absorbance with the additions of PS beads is attributed to the increased dye adsorption on the porous TiO$_2$ layer. The increase in specific surface area of the TiO$_2$ layer with PS beads is in agreement with microstructure result discussed before.

Figure 3 is the Nyquist plot of real ($Z'$) and imaginary ($Z''$) terms for DSSC with the additions of 0 ~ 4 wt% PS beads into WE under applied frequency. It is evident that the curves show three half-circle ($R_1$, $R_2$, $R_3$) like an internal resistance curve of conventional DSSC. $R_1$ value represents interfacial resistance at the CE/electrolyte in the frequency region of $10^3$-$10^5$ Hz, and is about 1.3 Ω for all cases since the CE and electrolyte are the same for all DSSCs.

On the other hand, $R_2$ value represents interfacial resistance of WE in the frequency region of 1 - $10^3$ Hz. This value consists of electron transport resistance in TiO$_2$ and interfacial resistance at TiO$_2$/electrolyte. $R_3$ value decreased with the increasing amount of added PS beads; 8.6, 8.2, 8.0, 7.7, and 7.5 Ω with the additions of 0, 1, 2, 3, and 4 wt% of PS beads. This is attributed to PS beads that make the TiO$_2$ layer porous, which provide increasing specific surface area for adsorbing dye. Thus, that generate more electrons, which ultimately reduces resistance.

$R_2$ value at higher than $10^3$ Hz is related to diffusing redox species within the electrolyte. $R_3$ values are all about 3 Ω, since the electrolyte is the same. Thus, we confirmed that the addition of beads increased specific surface area for dye adsorption and generated more electrons, which reduced resistance compared to the case of bare TiO$_2$ layer.

Figure 4 is I-V data of DSSC with 0 ~ 4 wt% PS beads addition. We confirmed that the PS addition lowered fill factor (FF) compared to the case without PS beads. FF is related to the whole interfacial resistance of DSSC device, which means it depends on impedance $R_3$ as discussed before. Thus, the reduced FF is attributed to the formation of porous TiO$_2$ layer by PS beads addition, which subsequently increases specific surface area and dye absorption.

Table 1 is a summary of results for I-V curves of Fig. 4. Open-circuit voltage ($V_{oc}$) depends on both redox level of electrolyte and Fermi level of TiO$_2$ electrode. It showed little difference between devices within an error range, since each device used same electrolyte and TiO$_2$ electrode. FFs with 0, 1, 2, 3, and 4 wt% PS beads were 0.564, 0.653, 0.650, 0.635, and 0.655, respectively. It indicating a clear increasing

<table>
<thead>
<tr>
<th>PS bead contents</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>FF</th>
<th>η (%)</th>
</tr>
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<tr>
<td>0 wt%</td>
<td>0.704</td>
<td>11.73</td>
<td>0.564</td>
<td>4.66</td>
</tr>
<tr>
<td>1 wt%</td>
<td>0.700</td>
<td>11.08</td>
<td>0.653</td>
<td>5.07</td>
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<tr>
<td>2 wt%</td>
<td>0.692</td>
<td>11.30</td>
<td>0.650</td>
<td>5.08</td>
</tr>
<tr>
<td>3 wt%</td>
<td>0.684</td>
<td>11.95</td>
<td>0.635</td>
<td>5.19</td>
</tr>
<tr>
<td>4 wt%</td>
<td>0.678</td>
<td>11.80</td>
<td>0.655</td>
<td>5.25</td>
</tr>
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trend with the amount of PS beads. However, short-circuit current density ($J_{sc}$) was about same for all cases within an error range.

ECE ($\eta$) of the device without PS bead was 4.66%, while efficiencies of devices with 1, 2, 3, and 4 wt% PS beads were 5.07%, 5.08%, 5.19%, and 5.25%, respectively. It is implied that the device with 4 wt% PS bead is found to be superior by 1.12 times compared to the case without any PS bead. We interpreted the result with the identical reasoning as explained before. However, when PS bead addition is excessive being higher than 5 wt%, the ECE can be seen to rather decrease, which was considered to be a result of reduction in the fraction of TiO$_2$ layer with increasing pores. In summary, we successfully fabricated DSSC devices of enhanced ECE by adding a proper amount of PS beads into the TiO$_2$ layer.

4. Conclusions

We employed 0 ~ 4 wt% of PS beads into the TiO$_2$ layers of WEs of DSSCs, and characterized their properties. Microstructure analysis revealed that a uniform porosity was developed throughout the TiO$_2$ layer. The absorbance increased with the amount of added PS beads. The ECEs of DSSCs improved with the addition of PS beads. This is attributed to PS beads that make the TiO$_2$ layer porous, which provide increasing specific surface area for adsorbing dye. Thus, that generate more electrons, which ultimately reduces resistance. By employing the appropriate amount of PS beads, we demonstrated an improvement on ECE of DSSC.

REFERENCES