

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 dimethacrylate). 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 semiconducting 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 nmol/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

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addition of PEG (polyethylen glycol), EC (ethyl cellulose), etc. into the TiO_2 layer.

Polystyrene (PS) is a synthetic polymer by thermal polymerization. It has density of $0.96 \sim 1.04 \text{ g/cm}^3$, 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 $0 \sim 4 \text{ wt}\%$ 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 $0 \sim 4 \text{ wt}\%$. We made the blocking layer of WE by mixing titanium(IV)bis(ethyl aceto acetato)-diisopropoxide and 1-Butanol into a solution, followed by spin-coating for $0 \text{ rpm} \sim 10 \text{ sec}$ and $2000 \text{ rpm} \sim 40 \text{ sec}$, 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 $0 \sim 4 \text{ wt}\%$, 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) bis-tetrabutylammonium(N719) on a TiO_2 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 $400 \sim 800 \text{ nm}$ 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, Peccell) and potentiostat (Iviumstat, Ivium) to verify interfacial resistance. The analysis was carried out in the frequency range of $10 \text{ mHz} \sim 1 \text{ MHz}$ 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 $4 \text{ wt}\%$ 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 $4 \text{ wt}\%$ 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 $0.15 \text{ ea}/\mu\text{m}^2$.

Figure 1(c) is the cross-sectional image of Fig. 1(a), indicating that the TiO_2 layer is $8.6 \mu\text{m}$ 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 $6.5 \mu\text{m}$ 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 $0.13 \text{ ea}/\mu\text{m}^2$ 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 $0 \sim 4 \text{ wt}\%$ PS beads at the visible-light range of $400 \sim 800 \text{ nm}$. 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

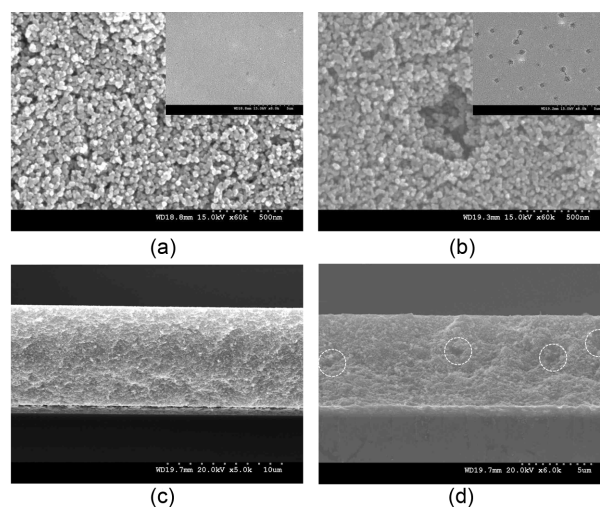


Fig. 1. FE-SEM images of (a), (b) surface section and (c), (d) cross section of TiO_2 layers with PS beads of : (a), (c) $0 \text{ wt}\%$, and (b), (d) $4 \text{ wt}\%$.

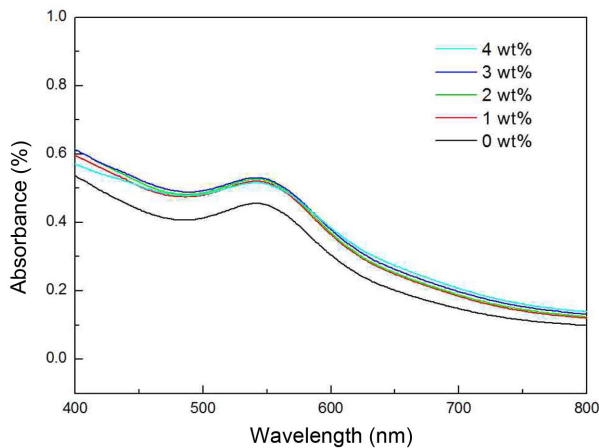


Fig. 2. Absorbance data of TiO_2 layers with PS beads of 0 ~ 4 wt% in the visible-light region.

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 1.3Ω 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_2 value decreased with the increasing amount of added PS beads; 8.6, 8.2, 8.0, 7.7, and 7.5Ω 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_3 value at higher than 10^6 Hz is related to diffusing redox species within the electrolyte. R_3 values are all about 3Ω , 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_2 as discussed before. Thus, the reduced FF is attributed to the formation of porous TiO_2 layer by PS beads addition, which subse-

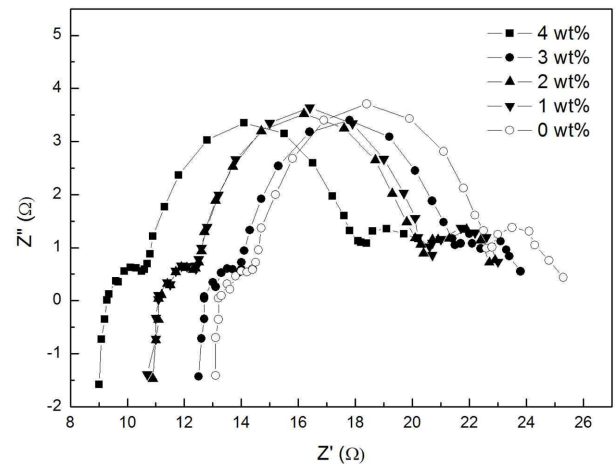


Fig. 3. Impedance of DSSCs employing TiO_2 layers with PS beads of 0 ~ 4 wt%.

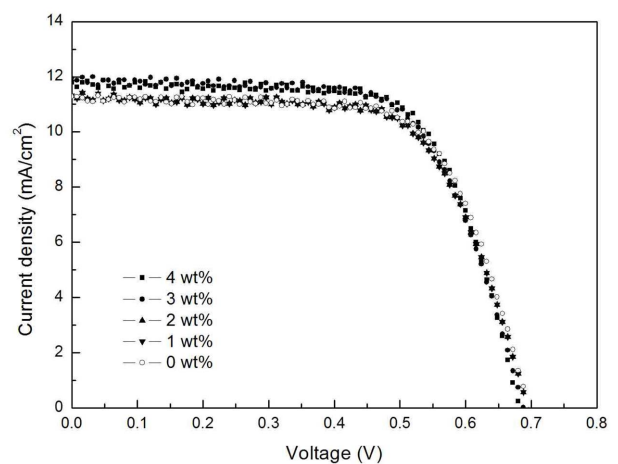


Fig. 4. Current-voltage (I-V) characteristic of DSSCs employing TiO_2 layers with PS beads of 0 ~ 4 wt%.

Table 1. Photovoltaic Properties and Energy Conversion Efficiency of DSSCs with Various Additions of PS Beads

PS bead contents	Voc (V)	Jsc (mA/cm ²)	FF	η (%)
0 wt%	0.704	11.73	0.564	4.66
1 wt%	0.700	11.08	0.653	5.07
2 wt%	0.692	11.30	0.650	5.08
3 wt%	0.684	11.95	0.635	5.19
4 wt%	0.678	11.80	0.655	5.25

quently 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

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 (η) 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 specific surface area due to a relative 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.

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