Development of Dye-sensitized Solar Cells Fabricated with PVDF-HFP-type Polymeric Solid Electrolytes and Titanium Dioxide Nanotubes

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Dye-sensitized solar cells (DSCs) are photoelectrochemical cells consisting of mesoporous TiO₂ electrodes sensitized with organic dyes such as ruthenium dyes, Pt counter-electrodes, and I⁻/I₃⁻ redox electrolytes. Increasing the durability and power conversion efficiency of DSCs are critical goals that will have to be met before DSCs can be put on the market on a large scale. For increasing durability, we have developed new gel-type polymeric solid electrolytes (PSEs) based on poly(vinylidenefluoride-co-hexafluoropropylene) (PVDF-HFP) to reduce leakage of the electrolyte solution, which is one of the main factors of poor DSC durability. The use of PSEs, however, is almost always accompanied by a decrease in the short-circuit current density (Jsc). We then studied the electrochemical properties of two different kinds of DSCs to determine why the conversion efficiency is lower in PSE-based DSCs than in liquid electrolyte-based DSCs. The diffusion coefficient of I₃⁻ and the cell-gap (the distance between the surface of the transparent conducting oxide substrate for the TiO₂ electrode and that of the Pt counter-electrode) of DSCs were eventually understood to be key factors affecting the Jsc. This indicates that the design of the DSC structure is quite important for achieving higher conversion efficiency in a PSE-based DSC. Further, with the aim of increasing the power conversion efficiency, we have developed ultrahigh-aspect-ratio TiO₂ nanotubes (TNTs), made by anodic oxidation of Ti metals in an extremely dilute perchloric acid solution, to establish good carrier pathways. Unlike TiO₂ nanoparticles (NPs), TNTs of suitable dimensions serve as efficient light scatterers while also providing large surface areas for charge separation. We have succeeded in enhancing the power conversion efficiency of a DSC using a TiO₂ electrode with a new bilayer structure, which consists of a light-scattering TNT layer formed upon a light-absorbing NP layer. We also found a promising application for TNTs formed on Ti substrates, i.e. their use in the fabrication of flexible, back-side illuminated DSCs. In this review we present our recent research on DSCs fabricated with PVDF-HFP-type PSEs and ultrahigh-aspect-ratio TNTs.

Keywords
Dye-sensitized solar cell, Polymeric solid electrolyte, PVDF-HFP, Titanium dioxide nanotube, Anodic oxidation, Light scatterer

1. Introduction

Organic solar cells have received considerable attention due to their great potential for use in developing low-cost, flexible, colorful, and light-weight photovoltaic devices. Organic solar cells are typically of two types: so-called Grätzel type dye-sensitized solar cells (DSCs)1,2); and organic thin-film solar cells (OPVs)3,4). DSCs offer especially high potential for development of a new field of cutting-edge solar cells, due to the great progress that has been made in increasing their conversion efficiency. Conversion efficiency of up to around 11% has already been reported and this value compares favorably with amorphous Si-based solar cells5). However, before DSCs can be marketed on a large scale, many things remain to be done, such as achieving better durability and increasing the conversion efficiency even more.

Electrolyte loss caused by the leakage and/or volatility of the electrolyte solution has been identified as one of the major problems which keeps the durability of DSCs relatively low. Various approaches to the problem have been tried thus far. These approaches include employing a gel-type electrolyte to minimize the loss, or replacing the solution with either p-type inorganic or organic semiconductors, including conductive polymers and small molecules, to prevent the loss completely6,7,8). The gel-type polymeric solid electrolyte (PSE) appears to yield successful results in terms of showing the highest
conversion efficiency among these approaches because of its high ionic conductivity. We have already proposed poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP)-based PSEs, having high ionic conductivity and mechanical strength, for DSCs\(^{12,13}\). The short-circuit current density \(J_{sc}\) of a PSE-based DSC is strongly dependent on the cell-gap, and a narrower cell-gap gives a higher \(J_{sc}\). We confirmed experimentally that the \(J_{sc}\) of a PSE-based DSC with a 20 \(\mu\)m cell-gap is about 97\% that of a liquid electrolyte-based DSC. That is to say, the design of the DSC structure is critical to achieving higher conversion efficiency in the case of PSE-based DSCs.

With the aim of increasing the conversion efficiency of DSCs, TiO\(_2\) nanotubes (TNTs)\(^{14,15}\), which establish good carrier pathways; and novel organic dyes\(^{16-18}\), which harvest sunlight efficiently, have been widely investigated. We have already developed two key materials: (1) ultrahigh-aspect-ratio TNTs made by the anodic oxidation of Ti metals in an extremely dilute perchloric acid solution\(^{19}\); and (2) novel triarylamine-functionalized ruthenium dyes\(^{20}\). TNT-based DSCs were found to provide higher light-harvesting efficiencies than conventional DSCs with TiO\(_2\) nanoparticle (NP) photoanodes. Several different triarylamine-functionalized ruthenium dyes have been synthesized, aimed at achieving efficient electron injection from the dye to the TiO\(_2\) conduction band as well as faster regeneration of the cationic dye.

In the present review, we focus particularly on topics of our recent work aimed at increasing the durability and conversion efficiency of DSCs, focusing on PVDF-HFP-type PSEs and ultrahigh-aspect-ratio TNTs.

2. DSCs Fabricated with PVDF-HFP-based PSE

2.1. Fabrication of PVDF-HFP-based PSE

DSCs are photoelectrochemical cells fabricated usually with three components as shown in Fig. 1: a TiO\(_2\) electrode sensitized with Ru-dyes, a Pt-coated counter-electrode, and a liquid electrolyte with an \(I_3^-/I^-\) redox couple. When the cell is illuminated by sunlight, the photo-excited dye produced by light absorption injects electrons into the TiO\(_2\) conduction band. These electrons lose their energy as they work in the external circuit and then reach the counter-electrode. The cationic dye that remains is reduced by \(I^-\), giving rise to \(I_3^-\), and finally \(I_3^-\) is reduced by the electrons at the counter-electrode. A DSC repeats this chain reaction to generate electricity. In order to increase the DSC’s durability, we can use a PVDF-HFP-based PSE in place of a liquid electrolyte. In this study, the PSE consisted of a PVDF-HFP-based matrix polymer and an electrolyte solution such as 0.5 mol/L 1-propyl-2,3-dimethylimidazolium iodide (DPIMP), 0.1 mol/L LiI, 0.05 mol/L I\(_2\), and 0.5 mol/L 4-t-butylpyridine (TBP) in \(\gamma\)-butyrolactone (GBL). Instead of GBL, methoxyacetonitril (MAN), 3-methoxypropionitril (MPN), and propylene carbonate (PC) are also used as polar solvents. In order to fabricate the PVDF-HFP-based PSE, the matrix polymer and the electrolyte solution were mixed using various levels of polymer content depending on the purpose of the experiment, and acetone (AC) was then added to the mixture as solvent. The mixture was stirred at 70\(^\circ\)C until the polymer was dissolved completely, and then coated onto a substrate with a doctor blade and left to dry for 20 min at room temperature. Finally, we were able to obtain a PVDF-HFP-based PSE which has good mechanical strength and ionic conductivity.

2.2. Electrochemical Properties of Quasi-solid State DSCs\(^{12a}\)

The conversion efficiency of a DSC is influenced by the diffusion coefficient of \(I_3^-\) (\(D\)), which is related to the ionic conductivity of the electrolyte. The relationship between the \(D\) and the ionic conductivity of the electrolyte can be expressed by \(\sigma = Dne^2/kT\), where \(n\) is the carrier density, \(e\) is the elementary charge of the electron, \(k\) is the Boltzmann constant, and \(T\) is the temperature\(^{21}\).

In Fig. 2, the \(J_{sc}\) values of PSE-based and liquid electrolyte-based DSCs are plotted with the \(D\). \(J_{sc}\) in-

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Fig. 1 Schematic Cross-sectional View of the DSC Fabricated with the PSE

Fig. 2 Short-circuit Current Density \((J_{sc})\) of the PSE-based and Liquid Electrolyte-based DSCs with Different Diffusion Coefficients of \(I_3^-\)
creases sharply with $D$ and levels off for larger $D$ values. A decrease in the $D$ reduces the supply of $I_3^-$ to the Pt counter-electrode, causing a depletion of $I_3^-$ at the counter-electrode and therefore decreasing the $J_{sc}$. This decrease in the $J_{sc}$ originates from the decrease in ionic conductivity as indicated by $\sigma = D\varepsilon^2/kT$. On the other hand, as Fig. 3 shows, the diffusion coefficient dependence of the open-circuit voltage ($V_{oc}$) is quite weak. It has been reported that the back-electron transfer from TiO$_2$ to $I_3^-$ reduces $V_{oc}$, which is determined by the energy difference of the Fermi energy of TiO$_2$ and the $I^-/I_3^-$ redox potential, due to a decrease in the electron density in the TiO$_2$ conduction band. In the open-circuit condition, the concentration of $I_3^-$ is expected to be constant over the entire distance between the TiO$_2$ and Pt counter-electrodes irrespective of the $D$. Hence, $V_{oc}$ is considered to be independent of $D$.

In order to gain a more detailed insight into the dependence of $J_{sc}$ on $D$, we examined the electrical impedance spectra of DSCs with five different polymer contents (matrix polymer/PSE mass%). We employed the equivalent circuit given in Fig. 4 for the curve fitting of the impedance spectra of the DSCs. Here the symbol $R_i$ ($i = 1, 2$) is the charge transfer resistance of the electrochemical reaction, $R_s$ is the series resistance composed of the resistance of the electrolyte, TiO$_2$, the sheet resistance of the fluorine-doped SnO$_2$ conducting oxide (FTO), etc.; $Z_D$ is the finite-length Warburg diffusion impedance, and CPE$_i$ ($i = 1, 2$) is the constant phase element. The impedance of the Warburg diffusion in a finite-length region and CPE$_i$ are defined by Eqs. (1) and (2), respectively.

$$Z_D = R_D \frac{\tanh(j\omega \tau)^{1/2}}{(j\omega \tau)^{1/2}}$$  \hspace{1cm} (1)

where $\omega$ is the angular frequency, $j = \sqrt{-1}$ , and $\tau = L^2/D_e$. $D_e$ is the effective diffusion coefficient of the diffusing species, and $L$ is the effective length.

$$\text{CPE}_i = \frac{1}{T_i(j\omega)^{P_i}}$$  \hspace{1cm} (2)

where $T_i$ and $P_i$ are parameters obtained by curve fitting. The resistance values of the Pt/PSE interface ($R_1$) are plotted in Fig. 5. Unlike the diffusion coefficient, $R_1$ shows a weak dependence on the polymer content. $R_1$ is the charge transfer resistance at the interface between the PSE and the Pt counter-electrode. Therefore, the decrease in $J_{sc}$, given in Fig. 2, is mainly attributable to the decrease in $D$ which decreases when the polymer content becomes higher. This fact indicates that the interface between the PSE and the Pt counter-electrode is established in good condition, otherwise $R_1$ would increase in the PSE-based DSC.

Figure 6 shows the cell-gap dependence of $J_{sc}$ for a PSE-based and a liquid electrolyte-based DSC. The $J_{sc}$ of the liquid electrolyte-based DSC is almost con-
constant in cell-gaps less than 50 μm, whereas that of the PSE-based DSC decreases monotonically with the cell-gap. The difference in cell-gap dependence between the two kinds of DSCs originates mainly from the difference in $D$. The $D$ of the PSE is smaller than that of the liquid electrolyte by a factor of about 7.6. The $J_{sc}$ of the PSE-based DSC shows a strong dependence on the cell-gap, and a narrower cell-gap gives a higher $J_{sc}$. The $J_{sc}$ of a PSE-based DSC with a 20-μm cell-gap reaches a value comparable to that of the liquid electrolyte-based DSC.

In practice, however, some of the dye used (hereafter referred to as photon-limiting). In simple theory, the maximum conversion efficiency of PSE-based DSCs could be improved even further and brought up equal to that of liquid electrolyte-based DSCs by optimizing the cell-gap structure, we confirmed that it is possible to fabricate a PSE-based DSC with a $J_{sc}$ the same as that of a liquid electrolyte-based DSC.

The melting points of the PSEs and the $J_{sc}$ of DSCs with four different polymer contents are plotted in Fig. 7. The $D$ of PSE-based DSCs increases as the polymer content decreases, whereas the melting point drops from around 120 to 90°C. This drop in melting point ultimately leads to a loss of tensile strength of the PSE and liquid electrolyte, and, in certain cases, the diffusion process of $I_3^-$ becomes the rate-determining step in the photoconversion process (hereafter referred to as diffusion-limiting).

We then derived model equations for the $J_{sc}$ of DSCs as a function of the cell-gap and $I_3^-$ diffusion coefficient, and studied their effects on the performance of DSCs. The symbols used to describe the equations are given in Fig. 8, and summarized in Table 1 for the purpose of clarity. For simplicity, in modifying the model equations, we assumed that the diffusion coefficient of $I_3^-$ in a PSE relates to that in a liquid electrolyte according to the following formula: $D_{PSE} = \alpha D_0$, where $D_{PSE}$ and $D_0$ are, respectively, the diffusion coefficients of the PSE and liquid electrolyte, and $\alpha$ is the liquid electrolyte content of the PSE, defined as the ratio by weight of the liquid electrolyte in the PSE.

When a photon-limiting current ($J_{ph}$) flows, the concentration profiles of $I_3^-$ in the TiO$_2$ nanopore region (Region I: $0 < x < \ell$) and in the bulk electrolyte region (Region II: $\ell < x < \ell + b$) are given below; $\ell$ is the TiO$_2$ film thickness and $b$ is the bulk electrolyte layer thickness. These equations can be derived by solving the corresponding one-dimensional diffusion equations of $I_3^-$ under the proper boundary conditions.

Region I: $0 < x \leq \ell$

$C_{\text{mp}}(x) = C_{\text{mp}}(\text{init}) + \frac{J_{ph}}{D_{\text{mp}}F_{\text{g}}} \left[ \frac{1}{6} \left[ \frac{1}{\ell} + \frac{2}{\ell^2} - \frac{1}{\ell^3} \right] \left[ \ln(10) \right] + \frac{1}{2[10^{\ell}-1]} \right]$

Region II: $\ell < x < \ell + b$

$C_{\text{mp}}(x) = C_{\text{mp}}(\text{init}) + \frac{J_{ph}}{D_{\text{mp}}F_{\text{g}}} \left[ \frac{1}{6} \left[ \frac{1}{\ell} + \frac{2}{\ell^2} - \frac{1}{\ell^3} \right] \left[ \ln(10) \right] + \frac{1}{2[10^{\ell}-1]} \right]$

$C_{\text{al}}(x) = C_{\text{al}}(\text{init}) + \frac{J_{ph}}{D_{\text{al}}F_{\text{g}}} \left[ \frac{1}{6} \left[ \frac{1}{\ell} + \frac{2}{\ell^2} - \frac{1}{\ell^3} \right] \left[ \ln(10) \right] + \frac{1}{2[10^{\ell}-1]} \right]$

$J_{\text{ph}}(A_0) = \frac{2}{3} A_0^2 \left[ \frac{1}{\ell} \left( \ln(10) \right)^2 + \frac{1}{\ell^2} \left( 10^{\ell} - 1 \right) \right]$
Here $C_{\text{gap}}(x)$ and $C_{\text{ob}}(x)$ are, respectively, the $I_3^-$ concentrations at a position of $x$ in the TiO$_2$ nanopore electrolyte and in the bulk electrolyte, $C_0(\text{init})$ is the initial concentration of $I_3^-$, and $\varepsilon_p$ is the porosity of TiO$_2$.

We calculated the concentration profiles of $I_3^-$ in the DSCs, employing three different sensitizing dyes and two different cell-gaps. Two of the dyes are ones commonly used in DSCs, namely bis-bis(isothiocyanato)-bis(2,2'-bipyridyl-4,4'-dicarboxylato)-ruthenium(II) bis-tetraethylammonium (N-719) and tris(isothiocyanato)-ruthenium(II)-2,2':6',2''-terpyridine-4,4',4''-tricarboxylic acid, tris-tertbutylammonium salt (black dye); and the third one is a hypothetical dye (920 nm-dye) with a sharp absorption edge at 920 nm, which is the optimal threshold for single junction solar cells. The absorption spectra of the three dyes are given in Fig. 9. The maximum or $J_{\text{ph}}$ in the ideal photon-limiting case for N-719, Black-dye, and 920 nm-dye are 16, 21, and 28 mA/cm$^2$, respectively. The $I_3^-$ concentration profiles between the electrodes are shown in Fig. 10. The concentration profiles of $I_3^-$ in the DSCs with a 50 $\mu$m cell-gap indicate that $J_{\text{sc}}$s flow under diffusion-limiting conditions in all cases since the concentration of $I_3^-$ at the Pt-counter-electrode ($x = 50$ $\mu$m) cannot be greater than zero. In contrast, the $J_{\text{sc}}$ of the DSCs with a cell-gap of 20 $\mu$m flows under photon-limiting conditions except for the PSE-based DSC fabricated with 920 nm-dye.

Based on the discussion above, we can estimate the minimum diffusion coefficient required to obtain the $J_{\text{ph}}$. The photocurrent flowing under diffusion-limiting conditions is given in Eq. (6).

$$J_{\text{lim}} = \frac{6\varepsilon_p F D_{\text{min}} C_0(\text{init})}{\ell} \left( 1 + \frac{\alpha b}{\varepsilon_p \ell} \right) \left( \frac{1}{f_{\text{PE}}} + 3 \frac{\varepsilon_p b}{\alpha \ell} + \frac{3}{2} \frac{b}{\ell} \right)$$

The minimum diffusion coefficients for DSCs can be estimated by equating $J_{\text{lim}}$ to $J_{\text{ph}}$. For instance, the diffusion coefficient of $I_3^-$ and/or I$^-$ of a 50 $\mu$m cell-gap DSC must be twice as high as the corresponding value of a 20 $\mu$m cell-gap one as shown in Table 2. Therefore, the cell-gap dependence shows clearly that narrowing the cell-gap is a simple, effective way to increase the $J_{\text{sc}}$ of PSE-based DSCs.

![Absorption Spectra of Three Different Dyes Used for DSC](image1)

![I$_3^-$ Concentration Profiles between the Electrodes](image2)

Table 2 Minimum Diffusion Coefficient of I$_3^-$ Obtained in Twelve Different DSCs

<table>
<thead>
<tr>
<th>Cell-gap [(\mu m)]</th>
<th>N-719 [(J_{\text{ph}}) (= 16) mA/cm$^2$]</th>
<th>Black-dye [(J_{\text{ph}}) (= 20.5) mA/cm$^2$]</th>
<th>920 nm-dye [(J_{\text{ph}}) (= 28) mA/cm$^2$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>solution PSE</td>
<td>solution PSE</td>
<td>solution PSE</td>
</tr>
<tr>
<td>20</td>
<td>4.4</td>
<td>6.4</td>
<td>5.6</td>
</tr>
</tbody>
</table>

2.4. Equivalent Circuit Analysis of Photocurrent in Quasi-solid State DSCs\textsuperscript{13)}

In this section, the photocurrent densities of DSCs are discussed in terms of the diffusion coefficients of I\textsubscript{3}\textsuperscript{-} and/or I\textsuperscript{-}. Figure 11 shows the current density-voltage (J-V) curves for DSCs with (a) liquid electrolytes and (b) PSEs. The characteristic feature of the J-V curves is that the overall shapes of the J-V curves are similar to each other and are analogous to conventional p-n junction solar cells\textsuperscript{22).} This means that the J-V characteristics of DSCs can be described by the equivalent circuit depicted schematically in Fig. 12. The equation for the equivalent circuit is then given by Eq. (7).

\[
J = J_0 \exp \left( \frac{q(V + R_s J)}{n kT} \right) - \frac{V + R_s J}{R_{sh}} \tag{7}
\]

Here \(J_0\) is the saturation current density, \(R_s\) is the series resistance, \(R_{sh}\) is the shunt resistance, \(q\) is the electric charge, and \(n\) is the ideality factor. The \(J_0\) is mainly determined by the back-electron transfer process from TiO\textsubscript{2} to I\textsubscript{3}\textsuperscript{-}, and the \(R_s\) is composed chiefly of the resistance of the FTO thin film, the nanoporous TiO\textsubscript{2} film, and the electrolyte. The \(R_s\) is then given by Eq. (8), since the resistance of the electrolyte is assumed to change inversely proportional to the diffusion coefficient of I\textsubscript{3}\textsuperscript{-} and/or I\textsuperscript{-} in the electrolyte.

\[
R_s = R_0 + R_1 = R_0 + \frac{a}{D} \tag{8}
\]

where \(R_0\) is the combined resistance of the FTO thin film and the nanoporous TiO\textsubscript{2} film, \(R_1\) is the resistance of the electrolyte, and \(a\) is the constant. In Fig. 13, the series resistance values of DSCs with four different electrolyte solvents are plotted with the reciprocal values of diffusion coefficient of I\textsubscript{3}\textsuperscript{-} and/or I\textsuperscript{-}. The experimental data (solid squares) fit well with Eq. (8) (solid line).

To provide insight into the effect of diffusion coefficient of I\textsubscript{3}\textsuperscript{-} and/or I\textsuperscript{-} on the photocurrent of DSCs, the operating principle of a DSC under short-circuit conditions was considered as given in Fig. 14. The operation process is composed of the following fundamental

\[\text{MAN; methoxyacetonitril, MPN; 3-methoxypropionitril, GBL; } \gamma\text{-butyrolactone, PC; propylene carbonate.} \]
steps.

Forward electron transfer process:

- The dye absorbs sunlight and an electron is excited from the HOMO (highest occupied molecular orbital) to the LUMO (lowest unoccupied molecular orbital).
- The electron is injected from the LUMO of the excited dye into the TiO2 conduction band, leaving behind oxidized cationic dye.
- The electron is extracted through the TiO2 conduction band.
- The oxidized dye is reduced by I⁻, returning back to its initial neutral state.

Backward electron transfer process:

- A portion of the injected electrons in the TiO2 re-combine with the oxidized dye and/or I₃⁻.

The series of equations for photo- and electrochemical kinetics in a DSC operating under steady state conditions is given below.

\[
\frac{d[S^+]}{dt} = \phi A \Phi - k_b [n][S^+] - k_d [\Gamma][S^+] = 0 \quad (9)
\]

\[
\ell (1 - \epsilon_f) \frac{d[n]}{dt} = \phi A \Phi - k_b [n][S^+] - k_d [\Gamma][S^+] = 0 \quad (10)
\]

\[
J_{sc} = qk_d [\Gamma][S^+] \quad (11)
\]

Here \(k_b\) and \(k_d\) are, respectively, the rate constants for the back and forward electron transfer reactions, \([n]\) the electron density in TiO₂, \([S^+]\) the oxidized dye concentration, \(\phi\) the electron injection efficiency, \(\Phi\) the incident photon flux, and \(A\) is the ratio of absorbed photon flux to \(\Phi\).

The electron concentration in the nanoporous TiO₂ at a steady state condition equals the summation of the initial concentration of electrons, \([n_0]\), at \(t = 0\) and the concentration of steadily injected electrons from the excited dye. The balance equation is then

\[
\epsilon (1 - \epsilon_f) [n] = \epsilon (1 - \epsilon_f) [n_0] + [S^+] \quad (12)
\]

where \(\ell\) is the thickness of the TiO₂ layer. The short-circuit current density is then derived from Eqs. (9)-(12) in the following form:

\[
J_{sc} = \frac{qk_b [\Gamma][n_0]}{2k_b [n_0] + k_d [\Gamma]} (13)
\]

The equation is approximated to be

\[
J_{sc} = \frac{k_d [\Gamma]}{k_b [n_0] + k_d [\Gamma]} q \Phi \Phi = \frac{k_d [\Gamma]}{k_b [n_0] + k_d [\Gamma]} J_{ph} (14)
\]

because \((k_b [n_0] + k_d [\Gamma])^2 > 4k_b \Phi \Phi / \ell (1 - \epsilon_f)\). Considering the chemical reaction between \(S^+\) and \(\Gamma\), the Smoluchowski equation gives the relationship between \(k_d\) and \(D\), that is, \(k_d = \gamma D \lambda^{235}\). With the Smoluchowski equation, \(J_{sc}\) is rewritten as a function of \(D\):

\[
J_{sc} = \frac{\gamma D \lambda [\Gamma]}{k_b [n_0] + \gamma D \lambda [\Gamma]} J_{ph} (15)
\]

**Figure 15** shows that the experimental data fit very well with Eq. (15), and the \(J-V\) characteristics of the DSC can be finally expressed by Eq. (16) using Eq. (15):

\[
J = \frac{\gamma D \lambda [\Gamma]}{k_b [n_0] + \gamma D \lambda [\Gamma]} J_{ph} - \frac{\exp \left[ (V + R_J)/nkT \right]}{1 - \exp \left[ (V + R_J)/nkT \right]} \frac{V + R_J}{R_h} (16)
\]

It was concluded that the back-electron transfer from TiO₂ to the oxidized dye also appears to influence \(J_{sc}\), particularly when the diffusion coefficient of \(I_3^-\) and/or \(\Gamma\) is low enough for the oxidized dye to be reduced before the back-electron transfer reaction occurs.
3. DSC Fabricated with Titanium Dioxide Nanotubes (TNTs)

3.1. Characteristics of TNTs\(^{(19a)}\)

TNTs have great potential for improving the conversion efficiency of DSCs since TNTs have the following characteristics as shown in Fig. 16.

- High carrier mobility because of the reduced grain boundaries where charge recombination takes place.
- High light scattering ability because of the high aspect-ratio one-dimensional nanostructure.
- High surface area for dye absorption.

TNTs with ultrahigh aspect-ratio structures can be obtained by the anodic oxidation of a Ti sheet in an aqueous perchloric acid solution. The as-prepared TNTs have amorphous structures with a diameter of 20 nm and an aspect-ratio of over 1000 : 1. After a 450°C thermal treatment, pure anatase phase TNTs can be obtained with a specific surface area of about 95 m\(^2\) g\(^{-1}\). As shown in Figs. 17 (a) and (b), the scanning electron microscope (SEM) image shows that the as-prepared TNT powder consists of bundles of TNTs having a length over 10 \(\mu\)m and a diameter over 1 \(\mu\)m, while the diameter of a single TNT is about 20 nm as shown in the transmission electron microscope (TEM) image. Since the as-prepared TNT powder cannot be dispersed in any organic solvents, it has to be treated with an acid solution because protonation of the TNT surfaces causes the TNT bundles to unravel and become unstable in dielectric solvents. Figure 17 (c) shows SEM image of the annealed TNT layer formed on the FTO substrate via the electrophoretic deposition (EPD) method\(^{(24,25)}\).

In this section, we examine the performance of DSCs fabricated using a TNT layer alone (TNT-DSC), and compare their performance with that of DSCs with NP layers (NP-DSC). Further, we investigate the performance of a DSC with a bilayer structure (NP/TNT-DSC) which uses a TNT layer as a light scattering layer. The EPD method can be used to form TNT layers for DSCs because it is a fabrication process which is non-destructive to the high aspect-ratio structure of TNTs. TNT layers were electrophoretically deposited on two different substrates of 10 \(\mu\)m-thick NP coated FTO substrates and on a bare FTO substrate as a reference.

3.2. Performance of TNT-based DSCs for Front-side Illumination\(^{(19a)}\)

In this section, we examine the performance of DSCs fabricated using a TNT layer alone (TNT-DSC), and compare their performance with that of DSCs with NP layers (NP-DSC). Further, we investigate the performance of a DSC with a bilayer structure (NP/TNT-DSC) which uses a TNT layer as a light scattering layer. The EPD method can be used to form TNT layers for DSCs because it is a fabrication process which is non-destructive to the high aspect-ratio structure of TNTs. TNT layers were electrophoretically deposited on two different substrates of 10 \(\mu\)m-thick NP coated FTO substrates and on a bare FTO substrate as a reference.

schematic of a typical experimental set-up is shown in Fig. 19. After EPD, the TNT layer was annealed at 450°C for 1 h.

Photographs of the dye-adsorbed TiO2 electrodes are shown in the inset of Fig. 20. The thicknesses of the TiO2 (TNT, NP, and SP) layers are 8 μm, 10 μm, and 4 μm, respectively. Here, SP is the light scattering particles of TiO2, having a large diameter, which is usually used for the light scattering layer. As shown in Fig. 20, the absorption spectrum of the TNT layer is similar to that of the SP layer in the range of wavelengths longer than 700 nm, where the Ru-dye shows very weak absorption. This means that the TNT and SP layers yield a similar light scattering efficiency. This is because TNTs scatter light rays as efficiently as SP TiO2, due to their orientation of the symmetry axes oblique to the incident rays. Moreover, absorption of the TNT layer is also similar to that of the NP layer in the wavelength range shorter than 600 nm, where the absorption of the Ru-dye begins. The key difference between the TNT and SP layers is that the TNT layer works not only as a light scattering layer but also as a photocarrier generation layer, while the SP layer works as a light scattering layer only.

In Fig. 21, the Jscs of the TNT-DSC and NP-DSC are plotted with the amount of adsorbed dye molecules. In this case, the liquid electrolyte was comprised of 0.5 mol/L 1-propyl-2,3-dimethylimidazolium iodide, 0.1 mol/L LiI, 0.05 mol/L I2, and 0.5 mol/L 4-t-butylpyridine in acetonitrile. The Jscs increase with increasing amounts of adsorbed dye molecules. The Jscs of the TNT-DSC were, however, slightly higher than those of the NP-DSC when compared at the same amounts of adsorbed dye molecules. The higher Jscs of the TNT layers are attributed to the combination of the two characteristics of efficient light-scattering as well as efficient electron transport properties. Figure 22 gives the incident photon-to-electron conversion efficiency (IPCE) spectra of DSCs fabricated, respectively, with (a) NP-based and (b) TNT-based photoanodes. Enhanced IPCE was observed in the TNT-based DSC in the wavelength region where Ru-dye absorption is weak. On the other hand, the IPCE values of the TNT-based DSC were smaller in the wavelength region between 300 nm and 600 nm, where the dye absorption is relatively strong. This is mainly because randomly-aligned TNTs in the photoanode increase backward light scattering. The IPCE values of a DSC with optimal TNT alignment are expected to be higher than the measured IPCE values in the entire wavelength region.

Next we discuss the photovoltaic properties of DSCs.
with a bilayer TiO$_2$ structure (NP/TNT) employing TNTs, which have been shown to serve a dual function as a light-scatterer and light-absorber, in place of a widely-used SP TiO$_2$ scatterer. The thicknesses of the TNT layer and SP layer deposited on 10 μm-thick NP layers were selected to be 8 μm and 4 μm, respectively, which allows each layer to possess similar light-scattering properties. Table 3 shows the solar cell performance of DSCs fabricated with two different bilayer TiO$_2$ electrodes (NP/TNT-DSC and NP/SP-DSC). The $V_{oc}$ of the NP/SP-DSC was slightly lower than that of the NP/TNT-DSC because the increased absorber thickness of the TiO$_2$ layer in the NP/TNT-DSC reduced the electron density in the bilayer. The $J_{sc}$ value of the NP/TNT-DSC increased by 46% relative to that of the NP/SP-DSC, whereas the $J_{sc}$ value of the NP/SP-DSC showed only a 20% increase. As a result, an enhancement of conversion efficiency from 6.95 to 7.59% has been achieved by employing the new bilayer NP/TNT photoelectrode.

### 3.3 Performance of TNT-based DSCs for Back-side Illumination

The anodic formation of a TNT layer on a Ti substrate in an extremely dilute perchloric acid solution can be used to obtain a flexible TNT/Ti photoelectrode for DSCs. A Ti substrate (0.5 mm thick, 1.5 × 1.5 cm$^2$) was anodized in an aqueous perchloric acid solution (5 × 10$^{-4}$ mol/L) in a two-electrode cell at a constant current of 30 mA. The amount of TNTs increases with anodization time, to densely cover the entire surface of the Ti substrate. The TNT layer prepared on the Ti substrate scatters incident light, resulting in the white color of the formed TNT layer.

To gain insight into the solar cell performance of TNT-based DSCs for back-side illumination, we examined three different types of DSCs as shown in Fig. 23. The TiO$_2$ electrodes used were: (1) a TNT layer on a Ti substrate annealed at 450°C for 1 h, (2) a 10 μm-thick NP layer formed on a Ti substrate by the doctor blade method and annealed at 450°C for 1 h, and (3) a 3 μm-thick NP layer formed on an annealed TNT layer by the doctor blade method, then annealed at 450°C for 1 h (NP/TNT).

The $J$-$V$ characteristics of the DSCs with TNT, NP, and NP/TNT electrodes are given in Table 4. These three different cells are referred to as TNT-DSC, NP-DSC, and NP/TNT-DSC, respectively. Although TNT and NP electrodes adsorb a similar amount of dye, TNT-DSC showed a higher $J_{sc}$ than did NP-DSC. The higher $J_{sc}$ of the TNT-DSC is attributed chiefly to the improved light harvesting efficiency of the TNT layer, which results from its superior internal light scattering properties.

The $J_{sc}$ of the cell was increased by forming the thin NP layer on top of the TNT layer. This is due to the fact that the transparent NP layer greatly reduces the back-scattering of incident light from the TNT layer, which in turn causes the dyes adsorbed in both the TNT layer and in the NP layer to fully participate in light-harvesting.

### Table 3: $J$-$V$ Characteristics of TNT-DSC, NP-DSC, NP/TNT-DSC, and NP/SP-DSC

<table>
<thead>
<tr>
<th>TiO$_2$</th>
<th>Thickness [μm]</th>
<th>$J_{sc}$ [mA·cm$^{-2}$]</th>
<th>$V_{oc}$ [V]</th>
<th>FF</th>
<th>Efficiency [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>TNT</td>
<td>11.5</td>
<td>10.3</td>
<td>0.744</td>
<td>0.736</td>
<td>5.64</td>
</tr>
<tr>
<td>NP</td>
<td>10.4</td>
<td>11.0</td>
<td>0.729</td>
<td>0.731</td>
<td>5.88</td>
</tr>
<tr>
<td>NP/TNT</td>
<td>19.5</td>
<td>15.0</td>
<td>0.736</td>
<td>0.688</td>
<td>7.59</td>
</tr>
<tr>
<td>NP/SP</td>
<td>14.3</td>
<td>13.2</td>
<td>0.746</td>
<td>0.705</td>
<td>6.95</td>
</tr>
</tbody>
</table>

*a) FF = $V_{max} I_{max}/V_{oc} J_{sc}$ where $V_{max}$ and $I_{max}$ are the maximum voltage and current at the maximum power output.*

### Table 4: $J$-$V$ Characteristics of DSCs with TNT, NP, and NP/TNT with Back-side Illumination

<table>
<thead>
<tr>
<th>TiO$_2$</th>
<th>Area [cm$^2$]</th>
<th>Adsorbed dye [10$^{-8}$ mol/cm$^2$]</th>
<th>$J_{sc}$ [mA·cm$^{-2}$]</th>
<th>$V_{oc}$ [V]</th>
<th>FF</th>
<th>Efficiency [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>TNT</td>
<td>0.232</td>
<td>10.8</td>
<td>10.1</td>
<td>0.806</td>
<td>0.645</td>
<td>5.27</td>
</tr>
<tr>
<td>NP</td>
<td>0.229</td>
<td>11.4</td>
<td>7.1</td>
<td>0.764</td>
<td>0.631</td>
<td>3.41</td>
</tr>
<tr>
<td>NP/TNT</td>
<td>0.247</td>
<td>13.2</td>
<td>12.9</td>
<td>0.775</td>
<td>0.640</td>
<td>6.41</td>
</tr>
</tbody>
</table>

*a) Same as shown in Table 3.*
4. Summary

We have developed new gel-type polymeric solid electrolytes (PSEs) based on poly(vinylidenefluoride-co-hexafluoropropylene) (PVDF-HFP), aimed at reducing electrolyte solution leakage, and fabricated PVDF-HFP-type DSCs which exhibit good durability. The use of PSEs, however, is almost always accompanied by a decrease in the short-circuit current density ($J_{sc}$). Therefore, we performed electrochemical studies on two different kinds of DSCs to determine why the conversion efficiency is lower in PSE-based DSCs than in liquid electrolyte-based DSCs. The difference in $J_{sc}$ between these DSCs was found to depend chiefly on the diffusion coefficient of $I_3^-$. The $J_{sc}$ of PSE-based DSCs has a strong dependence on the cell-gap, and a narrower cell-gap gives a higher $J_{sc}$. The conversion efficiency of PSE-based DSCs can be improved even further and brought up equal to that of liquid electrolyte-based DSCs by optimizing the cell structure as well as the ingredients of the PSEs. We also studied the photocurrent of DSCs using model equations of two types of DSCs, choosing three different sensitizing-dyes; N-719-, black-, and 920 nm-dyes. Based on the model equations, $J_{sc}$ was found to increase by either increasing the diffusion coefficient of $I_3^-$ or decreasing the cell-gap, or both. In particular, the cell-gap dependence clearly indicates that narrowing the cell-gap is a simple, effective way to increase the $J_{sc}$. Further, with the aim of increasing the power conversion efficiency, we have developed ultrahigh-aspect-ratio TNTs, made by anodic oxidation of Ti metals in an extremely dilute perchloric acid solution, to establish good carrier pathways. The TNT layers, which serve as the light-scattering layers, were formed by the EPD method and are composed of randomly aligned TNTs with a length of several micrometers and a diameter of 20 nm. The nanosized one-dimensional structure of TNTs enables the generation of photocarriers in the TNT layer and their rapid transport through the TNT layer. DSCs with TNT light scattering layers showed higher IPCE values, that is, higher conversion efficiency. These facts demonstrate a promising approach for further improvement of the conversion efficiency of DSCs. Moreover, TNT-based photoanodes could readily be applied to development of flexible solar cells, since the TNT layer can be formed on a thin Ti sheet.

References

要  旨

PVDF-HFP 系ゲルタイプ高分子固体電解質とニ酸化チタン・ナノチューブを用いた色素増感太陽電池の開発

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色素増感太陽電池は、ルテニウム色素に代表される有機色素で増感された TiO2 ナノ粒子電極、白金対極およびヨウ素レドックス電解質からなる光電気化学セルである。色素増感太陽電池が今後大規模に上市されるためには、耐久性の改善と変換効率の向上が重要課題となる。そこで、耐久性改善のために、ビニリデンフルオライド (VDF) とヘキサフルオロプロビレン (HFP) の共重合体である PVDF-HFP をマトリックス・ポリマーとしたゲルタイプ高分子固体電解質の開発を行った。この高分子固体電解質はセルを凝固体化することにより、耐久性低下の主要因である電解液の揮発防止が可能である。ただ、高分子固体電解質を用いたセルでは、短絡電流の低下が起こる。そこで、その原因を明らかにするため、高分子固体電解質および液体電解質を用いて作製したセルの電気化学特性を調べた。その結果、ヨウ素イオン拡散係数とセルギャップ（電極間距離）が短絡電流密度を決定する重要な因子であることが分かった。つまり、高分子固体電解質セル構造の最適化が、凝固体型色素増感太陽電池の高効率化に重要であることが分かった。続いて、変換効率の向上を目的として、アスペクト比の非常に大きい TiO2 ナノチューブを用いたセル作製を行った。用いたナノチューブは、チタン金属を希釈過塩素酸水溶液で陽極酸化することにより合成した。TiO2 ナノチューブはナノ粒子と異なり、電荷分離のための高比表面積を保持しつつ光学反転体として機能する。そのため、高アスペクト比の TiO2 ナノチューブを光学反転体としてナノ粒子上に形成することで、色素増感太陽電池の高効率化を達成することができた。さらに、チタン金属を基板とした対極照射型のフレキシブル太陽電池を作製することも可能であった。本総説では、筆者等が行ったゲルタイプ高分子固体電解質と TiO2 ナノチューブを用いた色素増感太陽電池のこれまでの研究開発状況を報告する。