Carbon Nanotubes Counter Electrode for Dye-Sensitized Solar Cell

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The counter electrode of the dye-sensitized solar cell plays a role in reduction of the electrolyte that oxidized at the photovoltaic electrode. So far the counter electrode has used platinum from the perspective of reduction capability and corrosion resistance to the electrolyte. However, the material of a high corrosion resistance and low cost has been demanded because platinum still has issues of the insufficient corrosion resistance to the iodide electrolyte and of cost. The carbon materials are potential candidates to solve these issues. Thus, we have developed carbon nanotube owing to its attractive characteristics. We report the development of an electrode of a superior reduction capability with the carbon nanotubes that are utilized as the counter electrode of the dye-sensitized solar cell in this study.

1. Introduction

Dye-sensitized solar cells (DSCs) are expected to be low-cost solar cells for worldwide use. They are becoming reliable alternatives to other photovoltaic cells because of their high energy conversion efficiency and low production cost 12). DSCs consist of three main elements: a working electrode, a liquid electrolyte, and a counter electrode. The working electrode is fabricated from titanium oxide (TiO2) nanoparticles on the surface of which dye is adsorbed. DSCs using TiO2 provide the highest conversion efficiency owing to its highest light absorption as compared to other materials (ZnO, NiO, SnO2) 3). The typical liquid electrolyte consists of iodide/triiodide ions (I-/I3-) as a redox couple. Platinum (Pt) is used usually as a counter electrode because Pt has high catalysis for electrolyte reduction. Even though DSC with a Pt counter electrode achieved high energy conversion efficiency up to 11.1%4), the cost issue of Pt reduces the fascination of DSC development.

Carbon materials are attractive for use as a counter electrode instead of Pt owing to their low cost, high conductivity, corrosion resistance to iodide ions, and high catalysis for I3- reduction. The carbon materials, such as hard carbon spherule, porous carbon, mesoporous carbon, and carbon powder, were used for DSCs as the counter electrodes in the previous studies5)-11). The conversion efficiencies of DSCs with the carbon materials were less than those with Pt counter electrode 5)-11). Therefore, further development of the carbon counter electrodes is required to manufacture highly efficient DSCs for commercial use in the future.

Carbon nanotubes (CNTs) have been a candidate material for counter electrodes because of their characteristics or properties such as high conductivity and high specific surface area compared to other carbon materials. Previous studies 12)13) investigated the DSC performance with CNT counter electrodes using low-conduction substrates, such as an FTO glass and a PTFE membrane, suggesting that CNT counter electrodes during I3- reduction show low impedance. The studies also suggested that the high surface area and low sheet resistance of CNT make CNTs a promising replacement for highly energy-efficient DCSs. However, a CNT counter electrode with a high-conduction substrate that has a higher capability has still not been investigated.

In this work, we present the CNT counter electrode for DSC use, on the metal substrate of which CNTs were grown directly. The electrochemical properties of Pt and CNT electrodes were measured by CV. A Pt wire served as a counter electrode, and a silver-silver nitrate couple in
acetonitrile was used as a reference electrode. The liquid electrolyte filled in the CV cell includes 5 mM 1,2-dimethyl-3-n-propylimidazolium iodide, 2 mM iodine, and 100 mM tetrabutylammonium tetrafluoroborate in 3-methoxypropionitrile. All measurements were performed under ambient atmospheric conditions.

The DSC cell was composed of a 5 mm $\times$ 5 mm TiO$_2$ photovoltaic electrode on a FTO glass and a CNT counter electrode with a 30 µm spacer, as shown in Fig. 1. TiO$_2$ film was coated with N749 (black dye) by immersing for up to 24 hr. The electrolyte was prepared with 0.05 M of iodine, 0.1 M of lithium iodide, 0.6 M of 1,2-dimethyl-3-n-propylimidazolium iodide, and 0.3 M of 4-tert-butylypyridine in acetonitrile. The impedance spectra and the current-voltage (I–V) curves of the DSC cells were obtained under irradiation (100 W/cm$^2$, AM 1.5) generated by using a solar simulator.

3. CNT counter electrodes

Figure 2 shows SEM pictures of CNTs produced a thin CNT about 20 nm in diameter and a thick one about 100 nm in diameter were obtained when the thickness of the CNT was 800 nm.

4. Electrochemical property of CNT counter electrodes

The electrochemical property of CNT counter electrodes was found to be preferable to that of a Pt electrode for use in DCS counter electrodes. The cyclic voltammograms of CNT counter electrodes in I$^-$/I$_3^-$ electrolyte were compared with that of a Pt counter electrode, as shown in Fig. 3. The CNT counter electrodes had a low I$_3^-$ reduction potential of about $-0.4$ V, which was smaller than that of Pt counter electrode ($-0.5$ V). The separation of redox peak potentials ($\Delta E_p$) of I$^-$/I$_3^-$ of CNT counter electrodes was smaller than that of the Pt counter electrode. This indicates that the redox reaction rate of the CNTs is higher than that of Pt. Moreover, CNT counter electrodes showed a higher current density at the I$_3^-$ reduction peak than that of the Pt counter electrode. This suggests that an increase in the effective area of catalysis enhances current density because the surface area of CNT counter electrodes is much larger than that of the Pt counter electrode. These advantages due to enough regeneration of iodide ions support to achieve a high conversion efficiency of DSC. Because recent experiments suggested that controls of the diameter and the vol-

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Panel 1. Abbreviations, Acronyms, and Terms.

DSC—Dye Sensitized Solar Cell
CNT—Carbon Nanotube
MPCVD—Microwave Plasma Enhanced Chemical Vapor Deposition
CV—Cyclic Voltammetry
ume of CNT improve the electrochemical properties of electrodes\textsuperscript{19}, there is enough room for further improvement.

5. Electrochemical impedance spectroscopy of DSC

5.1 Each internal resistance element of DSC

The electrochemical impedance spectroscopy is suitable to demonstrate the inside mechanism of a DSC. According to a previous study\textsuperscript{10}, the impedance of each internal resistance element of a DSC to which bias voltage was applied was characterized by using an equivalent circuit. Three semicircular shapes are attributed to impedance related to a charge transfer process occurring at the counter electrode (Z\textsubscript{1}), at the TiO\textsubscript{2}/dye/electrolyte interface (Z\textsubscript{2}), and in Nernstian diffusion within the electrolyte (Z\textsubscript{3}), where R\textsubscript{h} is the sheet resistance of FTO and R\textsubscript{n} (n= 1, 2, 3) corresponds to the internal resistance (Fig. 4). Among these internal resistances, R\textsubscript{1} is an index to develop a good counter electrode because the charge transfer process of the electrolyte on the counter electrode surface is essential.

5.2 Impedance of DSC cells using by CNTs counter-electrode

The impedance measurement of DSC cells is shown in Fig. 5. Although electrochemical properties of CNT measured from the CV measurement were excellent, CNT charge transfer impedance of the electrode redox reaction (Z\textsubscript{1}) was equivalent to the Pt counter electrode. This difference is thought to affect the structure of the CNT layer, and charge transfer impedance of thin CNT counter electrodes was less than that of the Pt counter electrode\textsuperscript{10}. This is due to the impedance component of CNT layer structure, which suggests the possibility of increasing the Z\textsubscript{1}. In future, a good performance of impedance can be expected of CNT by optimizing the layer; low charge transfer resistance of CNT counter electrodes is a promising alternative to Pt counter electrodes.

6. Cell performance of DSC using CNT counter electrode

The CNT counter electrode that had electrochemical properties superior to those of Pt counter electrode achieved a high conversion efficiency (\(\eta\)), which was comparable to that of the Pt counter electrode, taking into account the incident light availability. The I–V curves of DSC with the CNT counter electrode and the Pt counter electrode are presented in Fig. 6. The photovoltaic characteristics of all the DSCs are listed in Table 1. The CNT counter electrode achieved a \(\eta\) of 8.99\%, which was 90\% of the \(\eta\) with Pt. The 10\% loss of the \(\eta\) of CNTs is attributed to the absorption of light through the photovoltaic electrode. In contrast, for the DSC using the Pt counter electrode, the light transmitted through the photovoltaic electrode can be utilized.

![Fig. 4. The illustration of an electrochemical impedance spectrum of DSC.](image)

![Fig. 5. The Nyquist plots of the CNT electrode and the Pt electrode.](image)

![Fig. 6. The I–V characteristics of DSC with the counter electrodes of CNT and Pt.](image)

<table>
<thead>
<tr>
<th>Counter electrode</th>
<th>(J_{sc}) (mA/cm\textsuperscript{2})</th>
<th>(I_{sc}) (mA)</th>
<th>(V_{oc}) (V)</th>
<th>FF</th>
<th>(\eta) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt</td>
<td>18.67</td>
<td>4.67</td>
<td>0.713</td>
<td>0.747</td>
<td>9.95</td>
</tr>
<tr>
<td>CNT</td>
<td>17.39</td>
<td>4.35</td>
<td>0.711</td>
<td>0.727</td>
<td>8.99</td>
</tr>
</tbody>
</table>
because it reflects on the Pt surface. However, the electrochemical advantage of CNT counter electrode over Pt will compensate this disadvantage, when the photovoltaic electrode requires quick and full regeneration of I on the counter electrode in future. In addition, the electrochemical stability of CNTs toward iodide ions, which is expected to be superior to that of Pt, is also advantageous to achieve the long life of DSC for commercial use.

7. Conclusion

We succeeded to grow CNTs directly on metal substrates by MPCVD and described the application of CNT electrode to counter electrode DSC. The electrochemical properties of CNT counter electrodes, which were improved by controlling the size and the amount of CNTs, have been revealed to be superior to those of a Pt counter electrode. The impedance measurement has demonstrated that the charge transport impedance of I-/I3 redox reaction on a CNT counter electrode is fundamentally smaller than that of a Pt counter electrode. The conversion efficiency of the CNT counter electrode was comparable to that of a Pt counter electrode. This study suggests that the CNTs directly grown on the metal substrate are promising as the counter electrode of a highly efficient DSC.

References