Attachment of an Organic Dye on a TiO_2 Substrate in Supercritical CO_2: Application to a Solar Cell

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(Received April 23, 1999; CL-990326)

Attachment of eosin Y onto TiO_2 electrode was carried out using super critical CO_2 as a solvent. The solar cell composed of an electrode which prepared under the condition of 493 K and 25 MPa in super critical CO_2, showed an efficient fill factor as high as 95% (a Xe lamp with a 517 nm band pass filter). The dye was supposed to keep its structure under such sever conditions. Super critical CO_2 made possible to carry out the attachment of dye at high temperature in a uniform phase.

We have been engaged in the study of a solar cell, in order to develop a substitutional solar cell for silicon. Gratzel et al. reported an efficient solar cell consisting of a porous TiO_2 semiconductor electrode sensitized with Ru-complexes.[1] We constructed similar cells using organic dyes as photo-sensitizers.[2] Among various organic dyes, eosin Y showed relatively high efficiency compared by an incident monochromatic photon-to-current efficiency (IPCE = 51%) and solar-to-energy efficiency (1.3%, AM-1.5, 100 nW/cm^2 with UV cutoff filter).[2] The manner how the dye interacts with the substrate is one of the factors which determine the efficiency. Normally, the attachment of dyes is carried out in organic solvents by refluxing at the boiling point. In other words, the temperature of attachment is restricted by the nature of the solvent. It is well known that super critical phase CO_2 (sc CO_2) is an efficient solvent for organic compounds.[3] There are several advantages in using sc CO_2 as a solvent. Compared with other organic solvents, sc CO_2 is environmentally harmless. Removal of sc CO_2 from the system is easily performed by reducing pressure. One of the most important characters is production of uniform fluid above the critical point. In other words, if we use sc CO_2 as a solvent, it may be possible to carry out attachment of an organic dye to TiO_2 in a uniform sc CO_2 at any temperature above the critical point. Such a method may not only promote attachment reaction, but also increase the amount of adsorbed dye molecules. So we conducted attachment of eosin Y to a TiO_2 electrode in sc CO_2 and constructed a solar cell and examined the performance.

A porous TiO_2 electrode was prepared as explained in our previous work.[2] Viscous slurry of TiO_2 powder (Nihon Aerosil P-25) was spread on a conducting glass support (Nihon Sheet Glass Co., F-doped SnO_2 over layer, 10 Ω/sq). Prior to the attachment of dye, the TiO_2 electrode was treated at 773 K for 1 h under the flow of N_2. As a photo-sensitizer, eosin Y (Aldrich, high purity) was used, which was found to be efficient in our previous work.[2] The attachment reaction was performed by an autoclave (Nittou Koatu Co.). Initially, appropriate amount of dye and a TiO_2 electrode was placed in the bottom of the autoclave. The reactor was connected to a CO_2 line, then was purged by CO_2 gas. Subsequently, liquid CO_2 (278 K) was poured by a liquid pump. The amount of CO_2 supplied was estimated by the flow rate and time. The reactor was closed and heated to the reaction temperature and was kept for 1 h. After the reaction, the reactor was cooled to ambient temperature and pressure was released. The dye-attached TiO_2 electrode was incorporated into a thin-layer sandwich-type solar cell with a polyethylene spacer (0.12 mm thick). As a counter electrode, a conducting glass with a thin platinum layer deposited on the surface was used. The electrolyte solution consisted of 0.5 mol dm^{-3} tetra-n-propylammonium iodide and 0.05 mol dm^{-3} iodine dissolved in a mixed solvent (ethylene carbonate: dry acetonitril = 6: 4 by volume). The efficiency of a solar cell was examined by photocurrent, photovoltage, and a potential-current curve measured by a potentiostat with a non-resistance ammeter.

Initially we tried to dissolve about 30 mg of eosin Y directly into sc CO_2. But after the attachment under the condition of 323 K and 10 MPa, no sign of dissolution was found in the reactor. It is well known that in the super critical system an entrainer promotes dissolution. Namely, a small amount of third component, which has a high affinity toward a solute and a solvent, mediates dissolution.[4] We know that methanol well dissolves eosin Y and it is well dissolved in sc CO_2. So we adopted methanol as an entrainer. We pre-dissolved 8 mg of

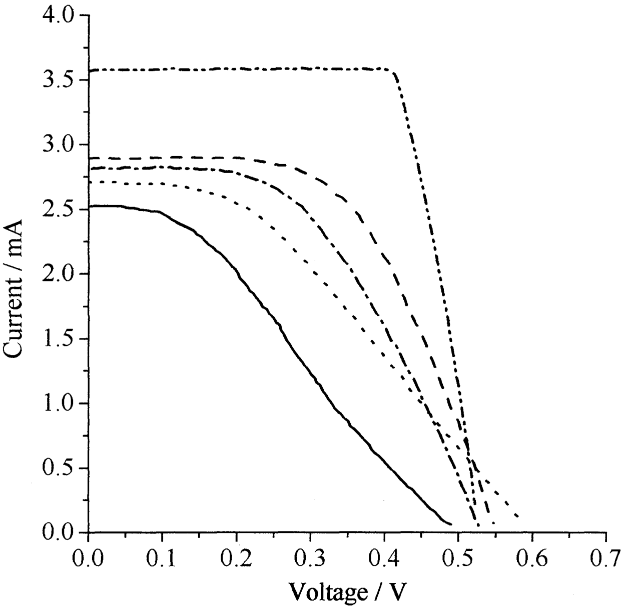

Figure 1. Potential-current curves observed under the irradiation of white light passing through a 420 nm cut off filter for solar cells prepared under the conditions as follows: ——— 353 K, 0.1 MPa (Condn.1), – – – 353 K, 25 MPa (Condn.2), ····· 373 K, 19 MPa (Condn.3), —·—·— 413 K, 25 MPa (Condn.4), —··—·· 493 K, 25 MPa (Condn.5).

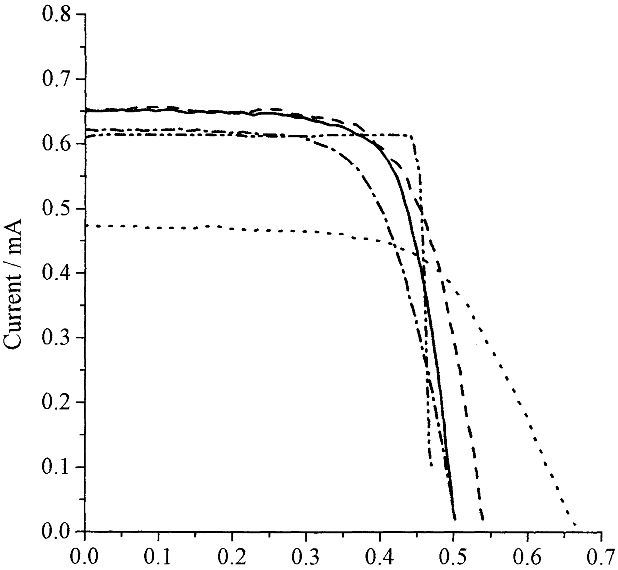

Figure 2. Potential-current curves observed under the irradiation of visible light passing through a 517 nm band pass filter for solar cells prepared under the conditions as follows: ——— 353 K, 0.1 MPa (Condn.1), – – – 353 K, 25 MPa (Condn.2), · · · · · 373 K, 19 MPa (Condn.3), –·–·– 413 K, 25 MPa (Condn.4), –··–·· 493 K, 25 MPa (Condn.5).

eosin Y into 3ml of methanol and set the solution in the reactor with a TiO_2 electrode. Subsequently, we purged the reactor with CO_2 and poured appropriate amount of liquid CO_2 into the reactor. After the reaction, we found dissolved eosin Y everywhere in the reactor, so we regarded that eosin Y could be dissolved in sc CO_2 in such conditions. Figures 1 and 2 show the resultant potential-current curves observed for solar cells prepared under various conditions. We also show the result observed for the solar cell prepared by the normal refluxing method reported in our previous work (Condn.1).[2] The absolute values for potential and current were almost the same as those for Condn.1 (Figure 1 and 2). Another property which evaluates the efficiency of a solar cell is a fill factor (ff). When the fill factor is nearly 100%, the potential-current curve forms a rectangular form. Such a solar cell not only has a very low inner resistance, but also produces little back-current. As is seen in Figures 1 and 2, a solar cell prepared under the condition 5 shows remarkably high fill factors under both a white light (Figure 1, 77%) and a 517 nm light (Figure 2, 95%), compared to those prepared under Condn.1 (Figure 1, 34% and Figure 2, 73%). Such high fill factors can be regarded as the best data ever reported. It is clear that the preparation method adopted in this work is effective for a solar cell. Judging from temperature and pressure, the attachment was carried out under super critical CO_2 for the conditions 2,3,4 and 5. And under these conditions, eosin Y was thought to be dissolved uniformly into sc CO_2, so either pressure or temperature determined the efficiency of the electrode. Under the conditions 2 and 4, the pressure was as high as that in Condn.5, but the fill factor was not so good as that in Condn.5. So we thought that temperature played an important role in this work. As mentioned above, decay of a rectangle form of the I-V curve is mainly due to an inner resistance and back current. One of the main sources of the inner resistance exists in the electron transfer from the dye molecule to the TiO_2 substrate. So it is possible to improve (decrease) the inner resistance by modification of bonding between the dye and TiO_2. Dye molecules are supposed to be anchored to TiO_2 through carboxylate bonding, which is formed by dehydration between Ti-OH and a carboxyl group in the dye. So higher reaction temperature may promote this reaction, as far as the structure of the dye endures. In the sc CO_2 system, we can freely vary the temperature keeping the whole system in a uniform phase, therefor we think that high temperature promotes formation of complete bonding between the dye and TiO_2. In Figure 1, the efficiency (short circuit current and ff) was greatly improved by treatment under Condn.5. This improvement was greater than that observed in Figure 2. So it was suggested that in addition to the promotion of TiO_2-dye bonding formation, some intrinsic change occurred either in the TiO_2 substrate or in the dye, such as reconstruction of surface structure of TiO_2 and/or modification of structure of the dye due to the sever condition under sc CO_2. And such changes might make the TiO_2 electrode prepared under Condn.5 become more sensitive toward visible light than those prepared under ordinary conditions (Condn.1). However, these ideals are yet to be identified.

We found a new method for attachment of an organic dye to TiO_2 substrate using super critical CO_2 and found the electrode prepared in sc CO_2 at 493 K under 25 MPa exhibited an ideal potential-current curve under the irradiation of visible light.

We appreciate Mr. Akio Honma (Honma Riken Co.) for technical support in construction of sc CO_2 system, and Mr. Takarou Horiguchi (Sumitomo Osaka Cement Co.) for discussion.

References and Notes

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