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Plastic dye-sensitized solar cells and solidification with nano-carbon materials

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1. Introduction

Dye-sensitized solar cell (DSC) is a sole utility-type photovoltaic cell manufactured in the ambient atmosphere. It enables a dramatic cost reduction by realizing roll-to-roll printing process for electrode fabrication using flexible substrate. Further, lightweight flexible DSC is highly useful not only for attachment on round surfaces but also for applications to ubiquitous powers for consumer electronics.

Carbon materials have been extensively used in electrochemical devices for their high electro-conductivity, chemical stability. Soft and porous nature of particulated carbon materials enables its applications to flexible DSCs.

This review shows recent advancements in devising flexible DSCs and solidification of the DSC structure by using nano-carbon materials.

2. Plastic DSC as flexible photovoltaic device

Conventional high-efficiency DSC has been based on the use of glass electrodes (SnO_2 transparent conductive glass). Record efficiency in energy conversion now reached 11%,[1] which can compete with thin-film silicon solar cells. Flexible DSC is a new type DSC, now rapidly evolving as a power source in the field of plastic electronics. Its efficiency level is presently 5-6%, which is not sufficient to replace the conventional Si-based solar panel for roof top applications but is useful to power household electric appliances and handy devices by replacing batteries.

We have fabricated high-efficiency plastic DSCs by new method of coating TiO_2 mesoporous layer at low temperatures that allow use of low-cost plastic support.[2]

Fig. 1 TiO_2-coated ITO-PEN film for dye-sensitized plastic photo-electrode showing high hardness against writing by pencil (upper) and ball-point pen (lower).

Indium–tin–oxide (ITO)-coated polyethylene naphthalate (PEN) was selected as a transparent conductive plastic electrode (thickness, 200 μm; sheet resistance, 13 Ω $sq.^{-1}$; transmittance, 80%). Tg of PEN, 121 ℃, requires that electrode processing be made in a temperature range less than 150 ℃. For coating, a special TiO_2 nanocrystalline paste was prepared that contains no binder materials (insulator) and works without the sintering process, by mixing TiO_2 nano-particles of various average sizes (30–150 nm) and aqueous colloidal TiO_2 sol as an inter-particle connection agent in a mixed solvent of water and t-butanol. Large TiO_2 particle (average size, 250 μm) was mixed to enhance light harvesting effect by optical scattering. Doctor-blade coating of the binder-free TiO_2 paste on an ITO-PEN sheet and drying at 110–125℃ gave a meso-porous TiO_2 layer tightly attached to the ITO surface, ensuring anti-scratching pencil hardness of more than H (Fig. 1).

Dye sensitization of the TiO_2-coated ITO-PEN by Ru bipyridyl complex dyes, N719 or N712, gave the photo-electrode. This was combined with a platinum-coated glass counterelectrode by insertion of an organic electrolyte. Electrolyte composition, typically, was 0.4 M LiI, 0.4 M tetrabutylammonium iodide (TBAI), 0.04 M I_2, 0.3 M N-methylbenzimidazole (NMB) in a mixture of acetonitrile (AN) and 3-methoxypropionitrile (MPN) (vol. ratio 1:1).

Small test cell (0.24 cm^2 irradiation area) gave highest conversion efficiencies of 5.8% (1 sun = 100 mW cm^{-1}) and

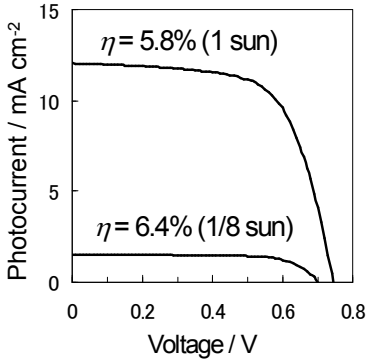

Fig. 2 I–V characteristics for N719-sensitized plastic electrodes under irradiation of strong light (1 sun) and weak light (1/8 sun).

6.4% (1/8 sun) for different irradiation intensities.[2] This high performance was achieved using 60 nm TiO_2 as a main nano-particle. Fig. 2 shows the photocurrent (I) – voltage (V) characteristics obtained with N719 under 1 sun and 1/8 sun irradiation with solar simulator (Peccell Technologies, L11). Fig. 3 exhibits spectral sensitivity of the cell in terms of external quantum efficiency of photocurrent (EQE), indicating that the cell utilizes visible light of wavelengths up to 800 nm.

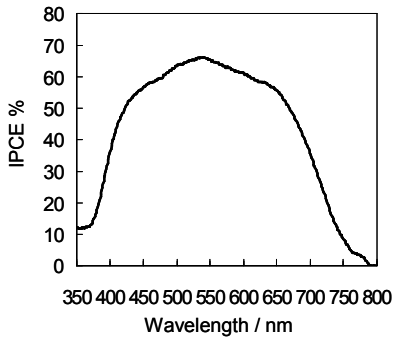

Fig. 3 Photocurrent action spectrum of plastic DSC.

Based on this method we have manufactured a large area full-plastic DSC module with series DC connection of unit cells.[3] Long strip-shaped unit cells (for example, 1.6 x 30 cm, 1.0 x 27 cm) are connected at the long edge side where conductive Ag grids for current collection were mounted also by low-temperature process at <120 ˚C. Counterelectrode was Ti/Pt alloy-coated transparent PEN film.[4] Fig. 4 shows an example of integrated plastic module which outputs 7.2V and maximal efficiency of 4%.

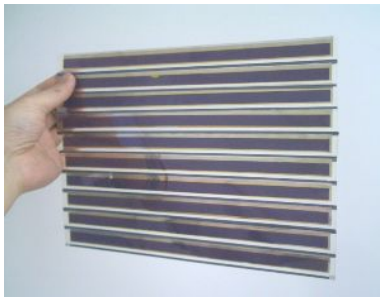

Fig. 4 Full-plastic DSC module (27 x 20 cm, 60 g).

3. Carbon-based solid-state plastic DSCs

Solidification of DSC leads to improvement of cell durability by eliminating the leakage of liquid electrolytes. Carbonaceous materials give an ease in creating good physical contact with soft organic materials. They also function as efficient carrier collectors at the porous TiO_2 surface. We have prepared a high-viscosity coating paste comprising polyaniline-loaded carbon black (PACB) powders (20 wt % polyaniline) and an ionic liquid. Ionic liquid is particularly 1,3-ethyleneoxy derivative of imidazolium iodide (EOI). The paste is free of volatile components and iodine. A thick layer of the paste (90 μm) was sandwiched between the dye-sensitized TiO_2 layer and a counterelectrode. PACB acts as hole collector, counter-electrode, and cathode catalyst, simultaneously. At the junction of PACB and dyed TiO_2 surface, carbon is placed very close to the dye separated by thin PA layer. PA (p-type conductor) rectifies the hole transfer at the interfaces of dye–PACB (solid–solid) and EOI–PACB (liquid–solid). Fig. 5 depicts the structure of PACB-based solid-state DSC and the carrier transfer processes across the mesoscopic junction. The mesoscopic interior is filled with EOI, which adsorbes the TiO_2 surface and conducts carrier transfer by electron exchange mechanism.[5]

The PACB-based solid-state photocell, devised on glass electrodes, achieves highest conversion efficiency of 4.07% (1/4 sun).[6] To make a plastic-based solid-state DSC, our optimization for cabon materials reached to use of single wall carbon nanotube (SWCNT). SWCNT mixed with EOI gave an iodine-free viscous paste for coating. On full-plastic cell fabrication using ITO-PEN films for working and counter-electrodes, we obtained conversion efficiency of 2.4%.[7] This is the first example of solid-state plastic DSC. Figure 7 shows the thin body of the carbon-based full-plastic DSC. We also confirmed relatively high stability of the above full-plastic cell unless the flexible body is mechanically deformed.

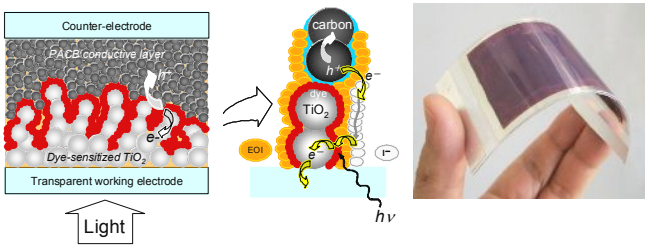

Fig. 5 Schematic illustration of the carrier transfer processes in the PACB-based DSC (left) and full-plastic solid-state DSC prepared with SWCNT (right).

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