Quasi-solid Polymer Electrolytes Based on Polyacrylonitrile and Plasticizers for Indoline Dye Sensitized Solar Cells of Efficiency 5.3%

Oliver A. Ileperuma,[1] G. R. Asoka Kumara,[2] and Kenji Murakami*[1]
[1]*Research Institute of Electronics, Shizuoka University, 3-5-1 Johoku, Hamamatsu 432-8011*
[2]*Department of Materials Science, Shizuoka University, 3-5-1 Johoku, Hamamatsu 432-8561*

(Received September 13, 2007; CL-071013; E-mail: rskmura@ipc.shizuoka.ac.jp)

Fabrication of quasi-solid solar cells based on nanostructured TiO_2 sensitized by the organic dye indoline is reported here. The electrolyte is based on polyacrylonitrile polymer with ethylene carbonate and propylene carbonate as plasticizers incorporating tetrabutylammonium iodide (0.70 M) and iodine (0.14 M). A conversion efficiency of 5.3% was achieved under AM 1.5 irradiation ($100\,mW\,cm^{-2}$).

Dye-sensitized solar cells (DSCs) based on mesoporous TiO_2 have attracted attention owing to their ease of production from relatively impure materials as low cost alternatives to silicon photovoltaics.[1,2] They are based on a highly porous network of TiO_2 particles sensitized by a ruthenium bipyridine dye such as [*cis*-Ru^{II}(2,2′-bipyridyl-4,4′-dicarboxylic acid)$_2$(NCS)$_2$] along with a liquid electrolyte containing the redox electrolyte which is typically I_3^-/I^-. Use of a liquid electrolyte results in practical problems for their long term use and attempts have been made to overcome this problem by the use of quasi-solid polymer materials,[3,4] gelling agents,[5,6] and also both organic[7] and inorganic[8] hole conductors. Furthermore, ruthenium dyes are relatively expensive and there is interest to search for cheaper alternatives for efficient panchromatic dyes. Some recent developments in this area are the use of two organic dyes, indoline,[9] and coumarin[10] which respectively give efficiencies of around 8 and 6% for their derivatives when used in nanocrystalline TiO_2 solar cells. These organic dyes offer the advantages of easy synthesis, extremely high extinction coefficients compared to the commonly used ruthenium dyes and cheaper production costs.

Again, the technical difficulties of using a liquid electrolyte still remain and the use of an organic hole transport material, *spiro*-OMeTAD, in a solid-state TiO_2 solar cell sensitized by the indoline dye D102, yielding solar cells with an overall efficiency of over 4% has been reported.[11] Similarly, solid-state solar cells of the type TiO_2/indoline/CuI where CuI is employed as a hole conductor, with an efficiency of 4.2% have been reported.[12] This type of solid-state cell seems to work better with indoline when compared to the ruthenium N3 dye where the latter gave only an efficiency of 3.2% under identical experimental conditions. These high efficiencies can be attributed to the strong absorption of the dye coupled with its high extinction coefficient. It is interesting to study the use of quasi-solid polymer electrolytes which have been extensively studied with DSCs employing ruthenium dyes with this system. We report here the first quasi-solid indoline sensitized TiO_2 solar cell employing a gel polymer electrolyte reaching efficiencies of over 5%.

Colloidal TiO_2 films used for this work were fabricated as previously described.[13] Indoline dye (D149, 4×10^{-4} M) optimized with chenodeoxycholic acid kindly provided by Mitsubishi Paper Company Ltd. was adsorbed from *tert*-butyl alcohol/acetonitrile (1:1). The polyacrylonitrile based electrolytes had the following composition: propylene carbonate (PC, 0.750 g), ethylene carbonate (EC, 0.525 g), polyacrylonitrile (PAN, 0.225 g), *n*-$Bu_4N^+I^-$ (0.70 M), and I_2 (0.14 M). The redox species concentrations are based on the volume of the propylene carbonate plasticizer. We avoided using *tert*-butylpyridine in these electrolytes since it dissolves the organic dye. These components were ultrasonically mixed and the contents were heated with stirring to about 120 °C when a viscous gel is obtained which was pressed between two glass plates to give films of about 1 mm in thickness. A strip of the polymer film was placed on the indoline adsorbed TiO_2 layer photoelectrode (area $0.25\,cm^2$) and heated to around 80 °C and a platinum mirror electrode was firmly pressed over the polymer film. The *I–V* characteristics of the cells fabricated under simulated sunlight (AM 1.5, $100\,mW\,cm^{-2}$) and photocurrent action spectra ($50\,\mu W\,cm^{-2}$) were recorded with a calibrated solar cell evaluation system (JASCO, CEP-25BX).

Figure 1 shows the *I–V* characteristics of the quasi-solid solar cell fabricated with the polyacrylonitrile electrolyte and the photovoltaic parameters measured were, open-circuit voltage (V_{oc}) = 690 mV, short-circuit photocurrent density (J_{sc}) = 13.4 $mA\,cm^{-2}$, fill factor (ff) = 0.57, and efficiency (η) = 5.3%. The corresponding values reported[9] for this type of solar cell using the standard liquid electrolyte are $V_{oc} = 693\,mV$, $J_{sc} = 18.5\,mA\,cm^{-2}$, ff = 0.62, and $\eta = 8.0\%$. The V_{oc} values are almost identical and the lower efficiency of the quasi-solid cell arises due to the lower J_{sc} values. This can be attributed to the barriers to movement of ions through the tubular structure of polymer matrix. We obtained a higher photocurrent density and a comparable fill factor when compared to the results ob-

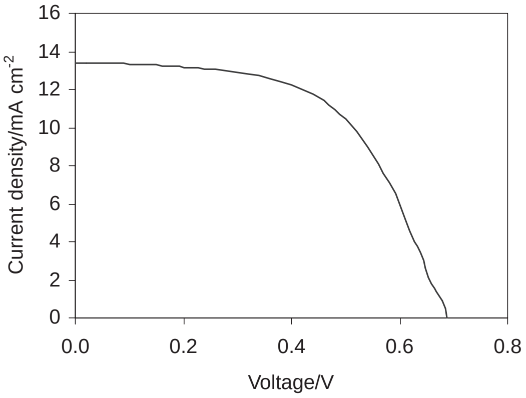

Figure 1. *I–V* characteristics of TiO_2 cells sensitized with indoline dye under AM 1.5 irradiation ($100\,mW\,cm^{-2}$) with the PAN polymer electrolyte (area of the electrode, $0.25\,cm^2$).

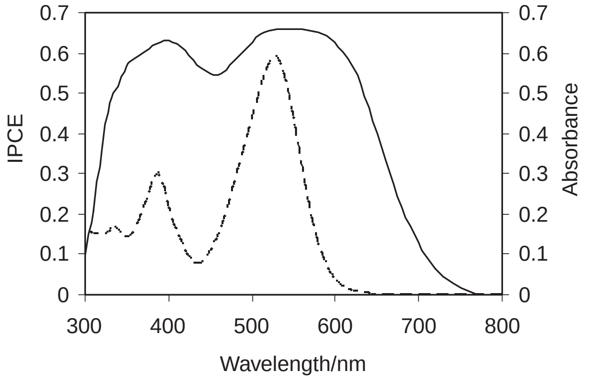

Figure 2. Photocurrent action spectra of TiO_2 cells sensitized with indoline dye (solid line) and absorption spectrum of indoline dye (broken line).

tained on the solid-state cell using indoline dye along with *spiro*-OMeTAD organic hole collector.[11] The higher V_{oc} value even in the absence of *tert*-butylpyridine is remarkable and the possibility exists for a way forward to further improve this solar cell if an alternate way to suppress the dark current by blocking surface states of TiO_2 can be achieved.

Figure 2 shows the IPCE values obtained and the absorption spectrum of indoline dye (D149) in *tert*-butyl alcohol/acetonitrile. As observed for many DSCs with organic dyes, the photocurrent action spectra are broad and red shifted and this is attributed[12,14] to the formation of J aggregates and these are not susceptible to concentration quenching. The IPCE values reach more than 60% in the range from 410 to 600 nm and this is attributed to the efficient charge injection from the dye to the TiO_2 upon photoexcitation. The large photocurrents in the case of indoline dyes is due to the panchromatic harvesting of a major part of the visible region of the solar spectrum and the higher extinction coefficients of the two absorption bands at 390 and 526 nm.

The composition of the polymer electrolyte selected for this particular study having optimal conductivity was based on our experience of using such polymer electrolytes with TiO_2/Ru-dye systems.[3] It was found that the ratio of the polymer used along with the plasticizers gives optimal ionic conductivity. While the use of gelators gives electrolytes with high ionic conductivity similar to the liquid electrolyte,[6] polymer electrolytes such as PAN offer strongly adhesive self sealing films for solar cell devices. These plasticized polymer electrolytes offer the advantages of the cohesive properties of a solid along with the diffusive nature of liquids. They hold a fair amount of liquid between their pores and the analogous poly(vinylidene fluoride-*co*-hexafluoropropylene) shows no difference in the conversion efficiencies between the quasi-solid and the liquid electrolytes for a nanoporous TiO_2 cell sensitized with Ru N719 dye.[4] Thus, there is no barrier to charge transport inside the polymer network which appears to be the case with the PAN polymer as well. The advantage of these polymer electrolytes is their inherent thermal stability and the cells can survive at a temperature of around 70 °C for hours without any softening of the solid. Similar gel electrolytes which can withstand a temperature of 100 °C have been reported.[15] Ion transport in the polymer is dominated by the mobility of the plasticizer molecules trapped within the polymer network rather than through an ion hopping mechanism.[3] We have found that the use of 0.70 M (n-Butyl)$_4$N$^+$I$^-$ with 0.14 M I_2 gave the best results. The ionic conductivity determined for this polymer film from impedance measurements was 3.34×10^{-3} S cm^{-1} which indicates the high ionic conductivity of this medium. We also observe that the polymer films hold the electrodes strongly without the need of external sealants and with the more viscous electrolytes used, work better at higher temperatures.

In conclusion, we have made the first attempt at replacing the conventional liquid electrolytes of organic dye sensitized TiO_2 based DSCs with a quasi-solid polymer gel electrolyte giving efficiencies of around 5.3%.

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