

A Hybrid Doped Polypyrrole/Poly(vinylidene chloride-co-acrylonitrile) Solid State Gel Electrolyte for Iodine-Free Dye-Sensitized Solar Cells

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1. Introduction

Here, we presented a solid state gel electrolyte as an alternative to the liquid electrolytes used in DSSCs because the use of liquid electrolyte raises significant technological problems associated with device sealing, long-term stability and corrosive I₂. The first solid state gel electrolyte was prepared by using the propylene carbonate (PC) as the solvent, doped polypyrrole (PPy) as the hole-conducting polymer. The CO- of PC solvent and -NH of PPy combined with the amide bond, producing the ester functional group which accelerates the hole transport rate in the cells. Then, we introduced block copolymer of poly(vinylidene chloride-co-acrylonitrile) (PVDC-AN) with low transition temperature (T_g) into a PC-PPy system to change the liquid electrolyte into the gel electrolyte. The chlorine, which is present in PVDC-AN, has the largest electronegativity, which could be expected to improve the ionic transport, thus enhancing the performance of the solar cells.

2. Experimental

To prepare the electrolyte, the 200 μL doped PPy was dissolve in the PC and THF solution. 0.6 M 1-butylpyridinium iodide and 7wt% PVDC-AN was added into the solution and heated at 60 °C for 3h. 20 nm anatase TiO₂ colloid particles were prepared with the home method and mixed with resin to make the paste. The resulting TiO₂ slurry was coated on fluorine-tin-oxide (FTO, 3 mm, 10 Ω/square, Pilkington TEC8) using a doctor-blade method then annealed at 550 °C for 30 min. To absorb the dye, TiO₂ substrates were then immersed in a 0.3 mM (Bu₄N)₂- ("N719", Solaronix) in ethanol for 30 min. The dye adsorbed TiO₂ electrode and Pt counter-electrode were assembled into a sealed sandwich-type cell by heating with a hot melt of a 50 μm thick Surlyn polymer film (Surlyn, Dupont 1702). A electrolyte solution was introduced into holes drilled in the counter-electrode of the assembled cell, followed by sealing the holes using a microcover glass and Surlyn. The photocurrent (J_{sc}) and photovoltage (V_{oc}) of the DSSCs were measured with an active area of 0.15-0.25 cm² using simulated solar light at AM 1.5, produced by a 1000 W xenon lamp (Oriel, 91193). The intensity modulated photovoltage spectroscopy (IMVS) and intensity modulated photocurrent spectroscopy (IMPS) measurements were performed on a ZAHNER CIMPS system.

3. Results and Discussion

The photovoltaic performances of the PGEs on DSSCs were evaluated by using TiO₂ photoelectrodes consisting a 10 μm thick nanocrystalline TiO₂ film (≈ 20 nm-sized anatase TiO₂ particles). Figure 1 shows the current-voltage (*I* – *V*) characteristics of the gel-state DSSCs using the PGEs containing 7 wt% PVDC-AN. The energy conversion efficiency obtained for the liquid-state cell is

4.31% under the illumination of one sun (AM 1.5, 100 mW cm⁻²). For the gel-state electrolyte containing 7 wt% PVDC-AN, the energy conversion efficiency achieved is 3.85%. The introduction of PVDC-AN in the electrolyte causes slightly increase and decrease, respectively, in *J*_{SC} and *V*_{OC}. As a result, the gel-state cell can achieve an efficiency ≈ 98% the value of the liquid-state cell.

Figure 2 is the IMPS of gel and liquid based DSSCs for a photon intensity level ranging from 20 W/m² to 80 W/m². The inverse of the frequency ($\tau_d = (2\pi f_{\min}(\text{IMPS}))^{-1}$) at the minimum of the IMPS arch represents the typical time interval from photoelectron injection to photoelectron arrival at FTO. The calculated time interval is from 0.87 ms to 1.50 ms for gel based cell, which is faster than that for liquid based cells (0.50 ms ~ 0.83 ms). Therefore, the photoelectron collection process in gel EL devices is faster than that in liquid based ones.

The electron lifetime can be obtained from the IMVS plot by setting $\tau_n = (2\pi f_{\min}(\text{IMVS}))^{-1}$. Under short-circuit conditions with homogeneously absorbed light, the electron diffusion coefficient can be estimated from the relationship of $D_n = d^2/4\tau_d$, where *d* is the layer thickness of the nanocrystalline TiO₂. The diffusion coefficients obtained from the fitted IMPS responses and the electron lifetime results from the obtained IMVS values with different light intensities. The diffusion coefficient constant of gel was apparently decreased due to a short length diffusion of I⁻ and I₃⁻ ions, caused by the gel as the extended HTLs, and this is perceived as the reason for the smaller third semicircle for the cell with the gel EL, compared to the near-infinite line in the case of cell with the liquid. The gel EL at the counter electrode surface is supposed to extend up to the dye-coated TiO₂. The gel EL enables electron transfer from the counter electrode to the charge transfer intermediate and decrease the charge diffusion length in the electrolyte. In the mean while the electron life time of gel EL was longer than that of the liquid EL.

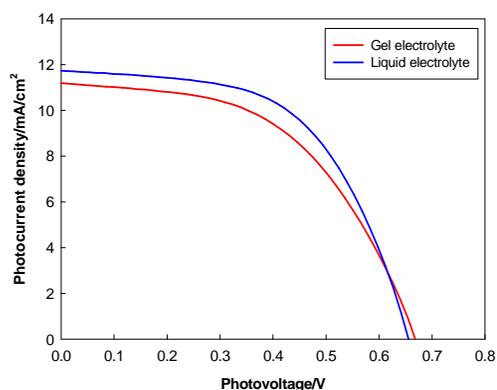


Figure 1. I-V characteristics of cells with gel and liquid electrolyte.

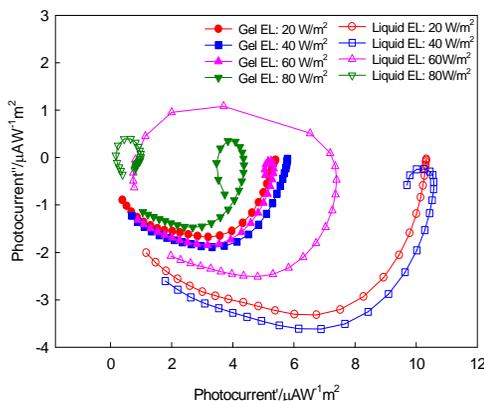


Figure 2. IMPS spectra of the gel and liquid electrolyte in the form of Nyquist plots which were measured at 530 nm light emitting diodes.