

Enhanced performance of solid state dye sensitized solar cells with e-beam irradiated composite polymer electrolytes

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전자빔 조사를 통한 고체형 염료감응형 태양전지의 성능 향상
모드 샤희르 아크탈, 전지민, 이현철, 김기주, 양오봉*
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Introduction

Recently, solid polymer electrolytes (SPEs) are receiving a great interest in order to use as solid state alternatives for electrochemical device applications such as lithium ion battery¹, fuel cells² and photovoltaic devices³. Among them, polyethylene oxide (PEO) based electrolytes have given much attraction due to their high thermal stability and stable ionic conductivity at ambient temperature. Many efforts have already been made to improve the ionic conductivity, thermal and mechanical properties of polymer by adding inorganic salts, nanofillers, and bulk inorganic molecules. Some irradiation technologies such γ -rays, e-beam and ion radiations have been widely reported to produce remarkable changes in the physical and chemical properties of polymers^{4,5}. Permanent modifications in the electrical, optical and mechanical properties of polymers and composite materials have been observed after ion irradiation^{6,7}. In this paper, we were used electron beam irradiation with a source 1.3 MeV and dose rate of 15 kGy/min.

However, the use of polymer electrolytes in dye-sensitized solar cells has been a viable and promising alternative for the high performance, long-term stability and successful removal of the traditional liquid electrolytes^{8,9}. In the present study, we are attempted to prepare a noble heteropolyacids (HPAs)-polymer composite material with mixed solvent chloroform and methanol (8:2). The properties of prepared composites were improved by the irradiation of electron beam (e-beam) with energy 1.3MeV at doses from 40-200 kGy. Finally, the modified composite with iodine/iodide was applied as a polymeric electrolyte for the fabrication of solid-state dye sensitized solar cell. Our results shows typical photocurrent-voltage (I-V) curves of fabricated DSSCs with V_{OC} of 0.588 volt and I_{SC} of 9.68 mA/cm² with 3.35% overall conversion efficiency under 100mW/cm² illumination in 120 kGy irradiated sample.

Experimental

Commercial titanium dioxide powder (P25, Degussa) was used as TiO₂ sources. Ruthenium 535 bis-TBA dye (Solaronix) as a sensitizer and other chemicals were analytical grade and used as received. The transparent conducting oxide (TCO) glass substrate was supplied by Hartford glass company Inc. (TEC-8, FTO-coated glass, 8 Ω /sq, 80% transmittance in the visible light).

Preparation of TiO₂ electrodes

For the preparation of TiO₂ thin-film, TiO₂ slurry was prepared by the incremental addition of 2 ml of aqueous polyethylene glycol (Junsei, average MW of 20,000) solution to 0.5 g of TiO₂ powder in a mortar under vigorous grinding with pestle. Each 0.1 ml of the aqueous polyethylene glycol solution was added after the previous mixture had formed a uniform and lump-free paste. Thus prepared uniform slurry was coated on TCO glass by a doctor blade technique. After natural drying at room temperature, the thin film was calcined in static air at 450°C for 30 min.

Preparation of gel electrolyte

The preparation of HPAs/PEO is already reported in literature. The synthesized composite was dispatched on a circular frame and finally irradiated by electron beam with 1.3MeV source. Gel electrolyte was prepared by using irradiated composite HPA/PEO (7%) with liquid electrolytes (LiI 0.3M, I₂ 0.015M and t-butyl pyridine 0.2M in acetonitrile). Lastly, the mixture placed on stirrer and stirred over a period of 24 hours for complete dispersion silica into liquid electrolyte

Fabrication the Cells

To fabricate the DSSCs, thus prepared TiO₂ thin film electrodes were immersed in the dye solution of 0.3 mM ruthenium 535 bis-TBA in dry ethanol at room temperature for 24 hrs. The dye-adsorbed electrodes were then rinsed with ethanol and dried under a nitrogen stream. Pt counter electrodes were prepared by electron beam deposition of Pt (60 nm thickness) on ITO glass. The working electrode is immersed in liquid electrolyte for 2~6 hours under dark condition. Electrodes were rinsed with acetonitrile and dried at room temperature. The resulting dye adsorbed film was seal with a Pt-sputtered conducting glass by a spacer (surlyn) and the gel electrolyte was introduced into the cell through one of two small holes drilled in the counter electrode.

The prepared sample was characterized by FE-SEM, (Hitachi 4700), FT-IR, DSC (TA analyzer), and ionic conductivity (digital conductometer). The photochemical characterization of DSSCs including photocurrent density was measured by using a scanning potentiostat (EG&G 273). The device was connected in a two-electrode configuration: the dye adsorbed TiO₂ film on TCO glass was connected as the working electrode and the Pt-coated TCO glass was used as the pseudo-reference (circuited with the counter electrode). Photocurrent–Voltage (I–V) curve was measured by using two computerized digital multimeters (Model 2000, Keithley) and a variable load. The light source was a 1000-W halogen lamp (Philips lighting) and its radiant power was adjusted with respect to Si reference solar cell (Fraunhofer Institute for Solar Energy System; Mono-Si + KG filter) to about one-sun light intensity (100 mW/cm²).

Results and discussion

Morphology of composite after irradiation

From FE-SEM images of sample surfaces before and after electron beam irradiation as shown in Fig.1,

it is observed that electron beam irradiation changes the surface morphology of HPA/PEO. The highly dense microstructure and uniform distributed tiny HPA molecules on polymer of raw samples are highly damaged and disordered by e-beam irradiation. As increases the doses of e-beam, increases the damage of composite surface which is due to degradation of polymers. After irradiation, we can also see some tiny particles in damage surface which reveal the no damage in HPA molecules. Therefore, e beam radiation could only change the morphology of polymer (PEO) and no serious change in HPA molecule.

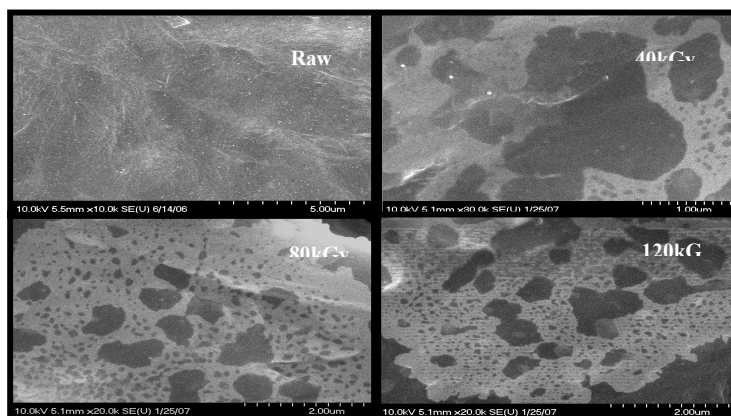
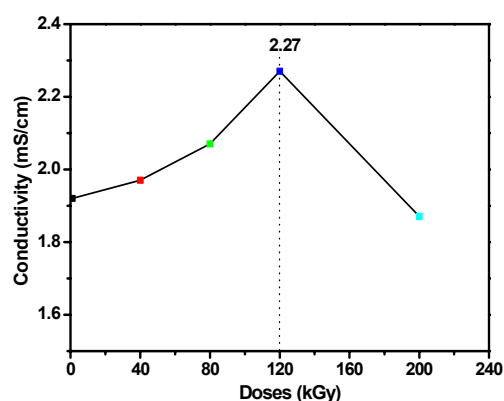


Fig. 1 FE-SEM images of composite before and after e-beam irradiation

Ionic conductivity

The ionic conductivity of irradiated samples is shown in fig. 2 and table 1. From the figure, the ionic conductivity of composites increases as increasing the dose of irradiation due to degradation of polymer in composite and lowering in crystallinity.



Samples	Conductivity (m S/cm)
Raw	1.92
40 kGy	1.97
80 kGy	2.07
120 kGy	2.27
200 kGy	1.87

Table 1 Ionic conductivity of samples

Fig.1 Ionic conductivity of composite electrolyte

Upon e-beam irradiation, the interaction between HPAs and PEO may decrease, which affect the ion conduction of composite and ionic mobility as well as. In case of 120kGy, it achieved high conductivity of 2.27 mS/cm because the reduction and breaking of polymer chains are provided the better pathway for electron mobility after irradiation. At higher 200 kGy dose, the damage of polymer surface in composite is more severe than the former irradiated samples. In general, the high

crystallinity of polymer is unfavorable for ionic conduction in other words high crystallinity (DSC of samples not mention) of polymer affects the conductivity of polymer electrolyte.

Photovoltaic properties

The current-voltage characteristics of irradiated HPAs/PEO based quasi-solid state DSSCs were shown in fig. 2. Table-2 shown the averaged data which is extracted from I-V curve measurements of different doses irradiated based DSSCs under 1 sun ($100\text{mW}/\text{cm}^2$). The maximum efficiency (3.35%) with an I_{SC} of $9.68\text{ mA}/\text{cm}^2$, V_{OC} of 0.588 volt and fill factor 58.9 achieved from 120 kGy sample. It is higher than raw, 40, 80 and 200 kGy irradiated samples. 120 kGy samples shows highest ionic conductivity, low crystallinity and improved surface morphology in compare to raw one, these factors enhance the photocurrent density, voltage and overall conversion efficiency.

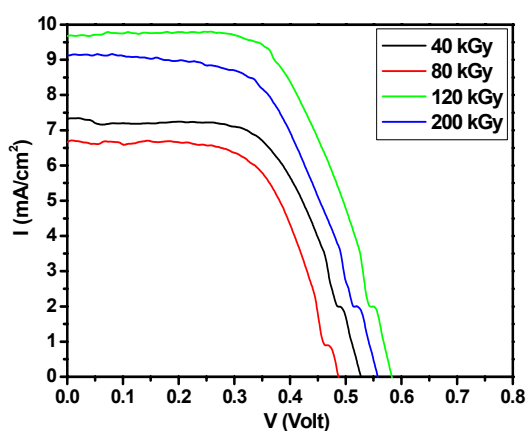


Table 2 summary of IV-curve of DSSCs

Samples	$I_{\text{SC}}(\text{mA}/\text{cm}^2)$	V_{OC} (Volt)	FF (%)	η (%)
Raw	9.70	0.524	65.6	3.1
40 kGy	7.59	0.515	61.4	2.4
80 kGy	6.57	0.516	64.2	2.17
120 kGy	9.68	0.588	58.9	3.35
200 kGy	9.36	0.558	57.3	2.95

Fig.2 IV curve of irradiated composite based DSSCs

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