

전자선 조사를 통한 염료감응형 태양전지의 분해 연구

Application of electron beam irradiation for studying the degradation of dye sensitized solar cells

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Abstract: The effect of electron beam irradiation on dye sensitized solar cell (DSSC) has been studied to examine degradation of DSSC. The high-energy electron beam irradiation affects on the materials and performance of dye sensitized solar cells. We have checked the effects of electron beam irradiation of TiO₂ substrate with and without dye adsorption on the photovoltaic performances of resulting DSSCs and also studied the structural and electrical properties of polymers after irradiation. All solar cells materials were irradiated by electron beams with an energy source of 2MeV at different dose rates of 60 kGy, 120 kGy, 240 kGy and 900 kGy and then their photoelectrical parameters were measured at 1 sun (100 mW/cm²). It was shown that the efficiency of DSSC was decreased as increasing the dose of e-beam irradiation due to lowering in TiO₂ crystallinity, decomposition of dye and oxidation of FTO glasses. On the other hand, the performance of solid-state DSSC with polyethylene oxide based electrolyte was improved after irradiation of e-beam due to enhancement of its conductivity and breakage of crosslinking.

1. Introduction

The production of electrical power on spacecrafts and satellite is so critical and expensive when using batteries, radiator and other power system devices in comparison with solar cell. The solar devices also fail to produce longer time stability due to existence of a large amount of ionizing irradiation rays on there. In 1974, the silicon solar cell power generator based Satellite-VI (ETS-VI) was tested. When it passes through the Van Allen radiation belts, the power generated by its silicon solar cell array has been dropping rapidly [1]. Laboratory radiation testing of the same Si space cells has been carried out in order to clarify the mechanism which caused such severe radiation degradation [2]. Generally, electron beams with energies in the MeV range are used in research and industry to develop new materials and to change the physical and chemical properties of materials of technological interest. These beams are also used to study the effects of space-ionizing radiation in solar cell power modules found in spacecraft and satellites [3]. Recently, investigations of the radiation damage caused by 1-MeV electrons demonstrated that the open circuit potential (V_{OC}) of the solar cell was changed only [4]. However, high-energy proton irradiation leads the degradation of all parameters of solar cell [5].

Although dye-sensitized solar cell (DSSC) was well known as a promising cheap photovoltaic device, much more improvement in terms of stability and

energy conversion efficiency should be intensively done before bringing it to practical applications [6-7] and give suitable future energy source. Dye sensitizer and electrolyte in DSSC is subject to affect by the high-energy ray irradiation. The effects of such irradiation on the performance of DSSC are also worthwhile for the application of DSSC in space stations. Generally, the use of liquid electrolyte causes several problems such as leakage, evaporation of electrolyte and dye degradation. Several methods [8-10] have been made to overcome these problems and improved the long term stability and energy production. In this study, we have examined materials properties and photovoltaic performance of irradiated fabricated solar cells after electron beam irradiation with the basis of photochemical analysis.

2. Experimental

2.1. Support material and chemical reagents

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

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2.2 Preparation of TiO₂ electrodes and Fabrication of dye sensitized solar cell

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. 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. To fabricate the DSCs, thus prepared TiO₂ thin film electrodes were immersed in the ethanolic solution of 0.3mM N-719 *cis*-bis(isothiocyanato) bis (2,2'-bipyridyl-4,4'-dicarboxylato)-ruthenium(II) at room temperature for 24 h. 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 TCO glass. The Pt electrode was placed over the dye-adsorbed TiO₂ electrode and the edges of the cell were sealed with 5-mm wide stripes of 60- μ m thick sealing sheet (SX 1170-60, Solaronix). Sealing was accomplished by hot-pressing the two electrodes together at 100°C. The redox electrolyte, consisting of 0.3 M LiI, 15 mM I₂, and 0.2 M tert-butyl pyridine in acetonitrile, was introduced into the cell through one of two small holes drilled in the counter electrode. The holes were then covered and sealed with a small square of sealing sheet and microscope objective glass. The resulting cell had an active area of about 0.25 cm². In order to determine the effects of electron beam, DSSCs, TiO₂ powder, dye, PEO, TiO₂ film with and without dye adsorption were subjected to the irradiation using 2-MeV electrons source at different dose rate ranging from 60 kGy to 900 kGy with a rate of 15 kGy/min (the e-beam line of the Korea Atomic Energy Research Institute (KAERI)).

3. Result and Discussion

3.1. FT-IR studies

Figure-1 shows the FT-IR spectra of the ruthenium dye (N-719) molecules adsorbed TiO₂ film after electron-beams irradiation. The FT-IR spectrum of dye adsorbed TiO₂ surface exhibits a weak band at 2110 cm⁻¹ linked to ν (NCS). Whereas, irradiated dye adsorbed TiO₂ samples showed weaker peak in that region because of splitting in isothiocyanato group under high energy radiation, which means that the thiocyanato groups interact with the surface and that all of them are non equivalent. Strong bands at 1606 and 1360 cm⁻¹ are attributed to antisymmetric ν_{as} (COO⁻) and symmetric ν_s (COO⁻), respectively. Irradiated samples of 240 kGy and 900 kGy are showed the splitting of the peak at 1606 cm⁻¹, which resulting from oxidation and breaking of Ti-O and carboxylic group linkage or ester linkage between titania and carboxylic group. We can also see that a steady decrease in the peak intensities of irradiated samples as increasing the dose of irradiation, which is due to decomposition of dye molecules. A weak band at 1720 cm⁻¹ corresponding to ν (C=O) is present, and

other bands linked to the bipyridine rings are located at 1536, 1456, and 1415 cm⁻¹. The splitting of ν (C=O) indicates that dye molecules on TiO₂ surface are decomposed under high dose of e-beam, which may suppress photocurrent density and the performance of DSSCs.

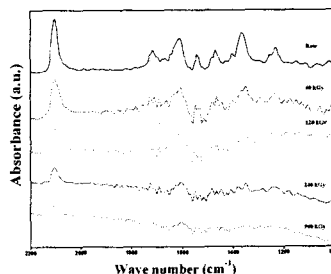


Fig. 1. FT-IR spectra of the dye adsorbed TiO₂ film before and after irradiation of electron beams

On the other hand, the IR spectra of raw and irradiated PEO samples show three main peaks at between 900-3000 cm⁻¹ regions. The most prominent band is ascribe to C-O stretch at 1250-900 cm⁻¹, which is not due to ester (-C=O) or alcohol (-C-OH) because this spectra are not shown C=O peak and O-H peaks. Other two peaks are -CH₂- bend at 1395 cm⁻¹ and sp³ C-H stretch at 2950-2750 cm⁻¹ region. After irradiation of electron beam, there is no change in IR peaks as compare to raw samples, only intensity of peaks decreases with increasing the doses of electron beam, which means e-beam irradiation affect only in the transition phase of polymers.

3.2. XRD Studies

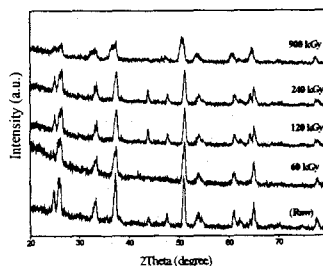


Fig. 2. XRD pattern of TiO₂ film on FTO before and after electron beam irradiation

XRD patterns of TiO₂ films before and after electron beam irradiation are shown in Fig. 3. After irradiation, TiO₂ film shows the lower intensity of anatase and rutile peak as compare to raw sample. It shows decreasing of crystallinity under high energy radiation. The 60 kGy sample shows the highest anatase peaks in comparison to other dosed samples (120, 240, 900 kGy doses), which is lower than raw TiO₂. Therefore, it is clear that crystallinity of TiO₂ materials are changed after electron beam irradiation. The UV-Vis DRS absorption spectra of raw TiO₂ powder and irradiated TiO₂ powder as a function of

high energy radiation are also consistent: in UV-Vis DRS absorption spectra, raw and all irradiated samples absorbed same absorbance of the light i.e. 300-400 nm, which suggests that all of the samples are active in UV region. Hence, the band gap energy was not changed after irradiation of electron beam on the TiO₂ substrate.

3.3 Differential Scanning calorimetry (DSC) studies

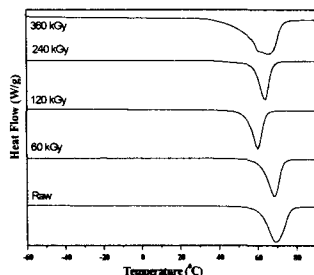


Fig. 3. DSC pattern of polyethylene oxide

DSC studies carried out for the irradiated PEO as shown in Fig. 3 and Table 1. From Fig. 3, PEO samples are showing very weak signal of T_g , indicating the amorphous phase of polymers.

Table 1. DSC data of irradiated PEO

Samples	ΔH_m (J/g)	T_m ($^{\circ}$ C)	% of crystallinity
60 kGy	119.46	66.3	60.6
120 kGy	79.62	64.2	40.5
240 kGy	76.67	63.7	38.9
360 kGy	56.01	61.8	28.4

The melting temperature (T_m) of the irradiated PEO samples decreases as increases the doses of irradiation with a difference of 3.2 - 3.8 $^{\circ}$ C. From Table 1, the melting enthalpy and crystallinity of irradiated samples are decreased as increasing the doses of electron beam, indicating the degradation of polymer or shortening of scissoring chain under irradiation. Since the curve area of melting endotherm is related to crystallinity in the polymer. Therefore, electron beam irradiation results in the degradation of chains and reduction of the molecular weight of polymer, which is related to the crystallinity of the polymer. The conductivities of polymers were enhanced by e-beam irradiation due to changing in crystallinity and shortening of polymer chain.

3.4 Effect of electron beam irradiation on the photovoltaic performance of resulting DSSCs.

Summary of I - V measurements of the DSSCs are presented in Table 2 and 3. Whatever DSSCs fabricated with the irradiated TiO₂ substrate before or after dye adsorption, the overall conversion

efficiencies were decreased drastically as increasing the irradiation dose. The efficiency reduction was more prominent on the DSSCs fabricated with irradiated TiO₂ after dye adsorption due to the severe degradation of adsorbed dye molecules as compare to the deformation of TiO₂ itself. Hence, it clear that the higher energy irradiation causes the damage of surface morphology of TiO₂ particles and severe decomposition of dye absorbed on TiO₂, which suppressed the photovoltaic properties.

Table 2. Summary of I-V measurement for DSSCs fabricated with irradiated TiO₂ substrate.

Samples	V_{oc} (Volt)	J_{sc} (mA/cm ²)	FF	η (%)
Raw	0.7	16.2	56%	6.38
60 kGy	0.71	7.09	65%	3.18
120 kGy	0.68	4.59	65%	2.04
240 kGy	0.68	5.40	65%	2.38
900 kGy	0.68	5.18	68%	2.38

Table 3. Summary of I-V measurement for DSSCs fabricated with irradiated TiO₂ substrate after dye adsorption.

Samples	V_{oc} (Volt)	J_{sc} (mA/cm ²)	FF	η (%)
60kGy	0.64	4.79	66%	2.02
120kGy	0.515	1.64	64%	0.54
240kGy	0.31	0.301	53%	0.06
900kGy	0.045	0.112	41%	0.00 24

However, incase of solid state DSSC with irradiated PEO electrolyte, the performance of cell was improved as compared to the DSSC fabricated with raw PEO electrolyte, which is attributed to the conductivity enhancement and crystallinity decreasing under irradiation.

4. Conclusions

The high energy irradiation causes the damage of surface morphology of TiO₂ particles and severe decomposition of dye absorbed on TiO₂, which suppressed the photovoltaic properties. However, the overall conversion efficiencies were enhanced on the solid state DSSC with PEO electrolyte irradiated at 60 kGy, which is believed due to the conductivity enhancement and crystallinity decreasing under irradiation. The application of irradiation technology in DSSC may open to development of promising solid state DSSC.

Acknowledgements

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