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Effect of gamma ray irradiation on thermal and electrochemical properties of polyethylene separator for Li ion batteries

Ki Jae Kim, Yeon Hwa Kim, Jun Ho Song, Yong Nam Jo, Jeom-Soo Kim, Young-Jun Kim*

Advanced Batteries Research Center, Energy IT Division, Korea Electronics Technology Institute, Gyeonggi-do, 463-816, Republic of Korea

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ABSTRACT

Polyethylene separator is irradiated by gamma ray to investigate the effect on electrochemical and thermal properties of polyethylene separators. Applied irradiation dose was 50, 100, 150 and 200 kGy. It is observed that the melt integrity temperature is increased as the higher dose of irradiation is applied. In case of non-irradiated PE separator, shut-down temperature is about 133 °C and melt integrity temperature is 146 °C. On the other hand, the separator with irradiation dose of 200 kGy, shut-down temperature is about 136 °C and melt integrity temperature is about 166 °C. Thermal shrinkage test is performed at 150 and 120 °C for 1 h each. It is observed that the irradiated separator has better thermal shrinkage resistance than the non-irradiated one because of the cross-link of polyethylene formed by gamma ray irradiation. Therefore, it can be concluded that the cross-link of polyethylene formed by gamma ray irradiation is strongly effective against thermal shrinkage. The electrochemical test is performed at high rate using the irradiated separator and the non-irradiated one to investigate any trade-off. The high rate discharge characteristic of the irradiated separator is better than that of the non-irradiated one. FTIR spectral analysis of the irradiated and non-irradiated separators is performed and ionic conductivity was measured to understand the reason.

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1. Introduction

Lithium ion batteries have been widely applied to not only many mobile devices such as cellular phone, personal computers and PDA but also various class electric vehicles such as light electric vehicle, hybrid electric vehicle and plug-in hybrid electric vehicle because of their high specific energy and power. The separator which is one of the main components plays a key role in lithium ion batteries. The main function of the separator is to prevent the positive and negative electrodes from electrical short circuits and at the same time allow rapid transport of ionic charge carriers that are needed to complete the circuit during the passage of current in an electrochemical cell [1]. In addition, they should be good electrical insulators, have mechanical and dimensional stability, and have electrochemical resistance towards electrolyte and electrode materials [1]. The property of separator affects the cycle life and the safety of lithium ion batteries.

Micro-porous membrane made of polyethylene (PE) is the most widely used as separators for lithium ion batteries because of their thin thickness, small pore size and good electrochemical stability [2]. But the heat resistive properties of PE are not good enough which limits its use in power batteries because of safety problems [2–4]. PE membrane will soften or melt as the temperature reaches 120 °C or higher [5]. The volumetric shrinkage of the separator could cause internal short circuits, which may cause thermal runaway of batteries. Most of researches have been focused on increasing energy and power density of lithium ion batteries. It is important for separators to have dimensional stability at elevated temperature to ensure the safety of lithium ion batteries. Therefore, many researches have been focused on improving thermal property of the separator in recent years [6–8]. In these reports, non-woven membrane or an inorganic composite membrane showed improved thermal property as a separator. Although it has a good thermal property, non-woven separator has several problems to commercialize for lithium ion battery. It is very difficult to control pore size, uniformity and the thickness. Inorganic composite membrane has cost issue over the commercial PE because ceramic and co-polymer are coated on the surface of PE. Therefore, it is important to improve the thermal properties of the PE separator without major cost increase and performance trade-off.

High energy irradiation is very useful technique to modify the properties of polymer such as structure and surface of polymers. It has been reported that polyethylene treated by high energy irradiation showed improved thermal properties because of modified

* Corresponding author at: Advanced Batteries Research Center, Energy IT Division, Korea Electronics Technology Institute, #68 Yatap-dong, Bundang-gu, Seongnam-si, Gyeonggi-do, 463-816, Republic of Korea. Tel.: +82 31 789 7456; fax: +82 31 789 7479.
E-mail address: yjkim@keti.re.kr (Y.-J. Kim).

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Table 1
Gurley number of the non-irradiated and irradiated separators.

	Gurley (s)
Non-irradiated separator	238
50 kGy irradiated separator	236
100 kGy irradiated separator	235
150 kGy irradiated separator	235
200 kGy irradiated separator	237

surface morphology of the PE [9]. Another group reported that thermal shrinkage was improved when the PE is treated by an electron beam irradiation [10,11].

The present study reports the effect of gamma ray irradiation on thermal and electrochemical properties of PE separator for Li ion batteries.

2. Experimental

Basic properties of micro-porous PE separator made by the wet process and obtained from Asahi Kasei Chemicals are given in Table 1. The liquid electrolytes (Ukseung Chemical Co., Ltd.) used were 1.0 M lithium hexafluorophosphate ($LiPF_6$) in a 3:7 (v/v) mixture of ethylene carbonate (EC) and ethyl methyl carbonate (EMC) with 3 wt% vinylene carbonate (VC) additive. The positive electrode was prepared by coating a slurry consisting of $LiCoO_2$ (95%) (Umicore, Korea), PVDF binder (3%) and Super-P (2%) on the surface of aluminum foil with 3 reverse roll coater. The negative electrode slurry of graphite (97.5%) (Sodiff. Co., Ltd., Korea), CMC (1%) and SBR (1.5%) was coated on the surface of a copper foil with 3 reverse roll coater. The coated electrode was dried under vacuum condition at 120 °C for 12 h. The thickness of the electrodes is 78 ± 3 μm and 72 ± 3 μm for positive and negative electrodes, respectively. The capacity per unit square for positive electrode is 3.8 ± 0.1 mAh cm^{-2} and that for negative electrode is 4.1 ± 0.1 mAh cm^{-2}.

To change the PE separator microstructure and surface morphology, gamma irradiator with a ^{60}Co source was used for this experimental. The PE separator was irradiated by gamma rays at the dose rate of 10 kGy h^{-1} and applied radiation dose was 50, 100, 150 and 200 kGy. Gamma ray irradiation was carried out under air condition and at room temperature. To measure the gurley number of separator, gurley type densometer (Toyoseiki) was used. The gurley number expresses the time required for 100 cm^3 air to pass through a specific area of separator.

Thermal analysis of non-irradiated PE separator and irradiated PE separators was carried out using a DSC STAR system (Mettler Toledo) under nitrogen atmosphere at a heating rate of 10 °C min^{-1}. In order to measure the thermal shrinkage properties of the separator, the separators with 5 cm × 5 cm ($W \times L$) were stored in an oven at 120 and 150 °C for 1 h. The degree of thermal shrinkage of separators was calculated from the dimensional change of separator by using Eq. (1):

$$\text{Shrinkage}\,(\%) = \frac{W_i - W_f}{W_i} \times 100 \quad (1)$$

where W_i is the initial area and W_f is the final area of the separator.

The shut-down properties of the non-irradiated and irradiated separators were obtained by measuring the impedance of the separator at 1 kHz using Hioki 3560C AC Hitester while the temperature is linearly increased. To see the effect of separators on the cell impedance, a pouch type cell was assembled using a $LiCoO_2$ positive electrode and a graphite negative electrode.

FTIR of non-irradiated and irradiated separators was recoded by a BOMEM MB100 Spectrometer in a wave number range of 4000–400 cm^{-1} at ambient conditions. Morphology change of non-irradiated and irradiated separators was observed by FE-SEM (JSM-7000F, JEOL) after Pt coating.

Table 2
Shut-down temperature and melting integrity temperature of the non-irradiated and irradiated separator obtained from shut-down test.

	Shut-down (SD) temp. (°C)	Melting integrity (MI) temp. (°C)	ΔT (SD Temp. – MI temp.) (°C)
Non-irradiated separator	132.8	146.2	13.4
50 kGy irradiated separator	140.1	158.2	18.1
100 kGy irradiated separator	137.2	153.7	16.5
150 kGy irradiated separator	137.9	160.0	22.1
200 kGy irradiated separator	135.9	166.4	30.5

The separators were sandwiched between two Li metal electrodes and soaked in a liquid electrolyte in 2032 coin type cells to measure the ionic. The ionic conductivity was obtained from the measuring electrolyte resistance by AC impedance technique using Solatron 1280C over frequency range from 0.1 Hz to 20,000 Hz with an amplitude of 10 mV. Then, the ionic conductivity was calculated from the relation $\sigma = d/RA$, where d and A are thickness and area of the separator, respectively, and R is electrolyte resistance obtained from the AC impedance test.

To examine electrochemical properties of the non-irradiated and irradiated separators, cycle life and rate discharge test were performed by Maccor 8500 instrument using 2032 coin cells. Coin cells were cycled between 3.0 V and 4.2 V and discharged with various rates of discharge current at room temperature.

3. Results and discussion

Microstructures of the non-irradiated and irradiated separators are given in Fig. 1. The pore structure of irradiated separator is slightly changed by gamma ray irradiation. It is well-known that polymer such as PE or polypropylene (PP) occurs cross-linking of polymeric chains by irradiation [9,10,12]. To confirm the cross-link or other reaction onto PE separator after gamma ray irradiation, FTIR spectral analysis was performed. Fig. 2 shows the FTIR spectra of the non-irradiated and irradiated separators. All of samples show typical PE separator characteristic bands: C–H stretching vibrations at 2850–3000 cm^{-1} and C–H bending vibration at 1465 cm^{-1}. It can be found that, however, the molecular structural change occurs indicated by a peak at 1720 cm^{-1} corresponding to the carbonyl band as shown in Fig. 3. In case of non-irradiated separator, carbonyl band is not observed. The intensity of this peak increases with increase of the gamma ray irradiation dose. It has been reported that carbonyl band was observed onto PE separator exposed gamma ray irradiation under air environment [12,13]. The modified PE separators have a cross-linking structure and a carbonyl band. These changes, however, do not affect to the gurley number which is one of basic properties of a separator for Li ion batteries. The results are given in Table 1.

The shut-down test was performed on non-irradiated and irradiated separators to understand the effect of the gamma ray irradiation on the thermal properties of the separator. The results of test are shown and summarized in Fig. 4 and Table 2, respectively. In case of non-irradiated separator, shut-down temperature and melting integrity temperature are about 133 and 146 °C, respectively. The temperature difference between shut-down and melting integrity is about 13 °C in this case. For irradiated separators, the shut-down temperature is slightly increased and melting integrity temperature is increased by more than 10 °C. Shut-down temperatures of the 50, 100, 150 and 200 kGy gamma ray irradiated

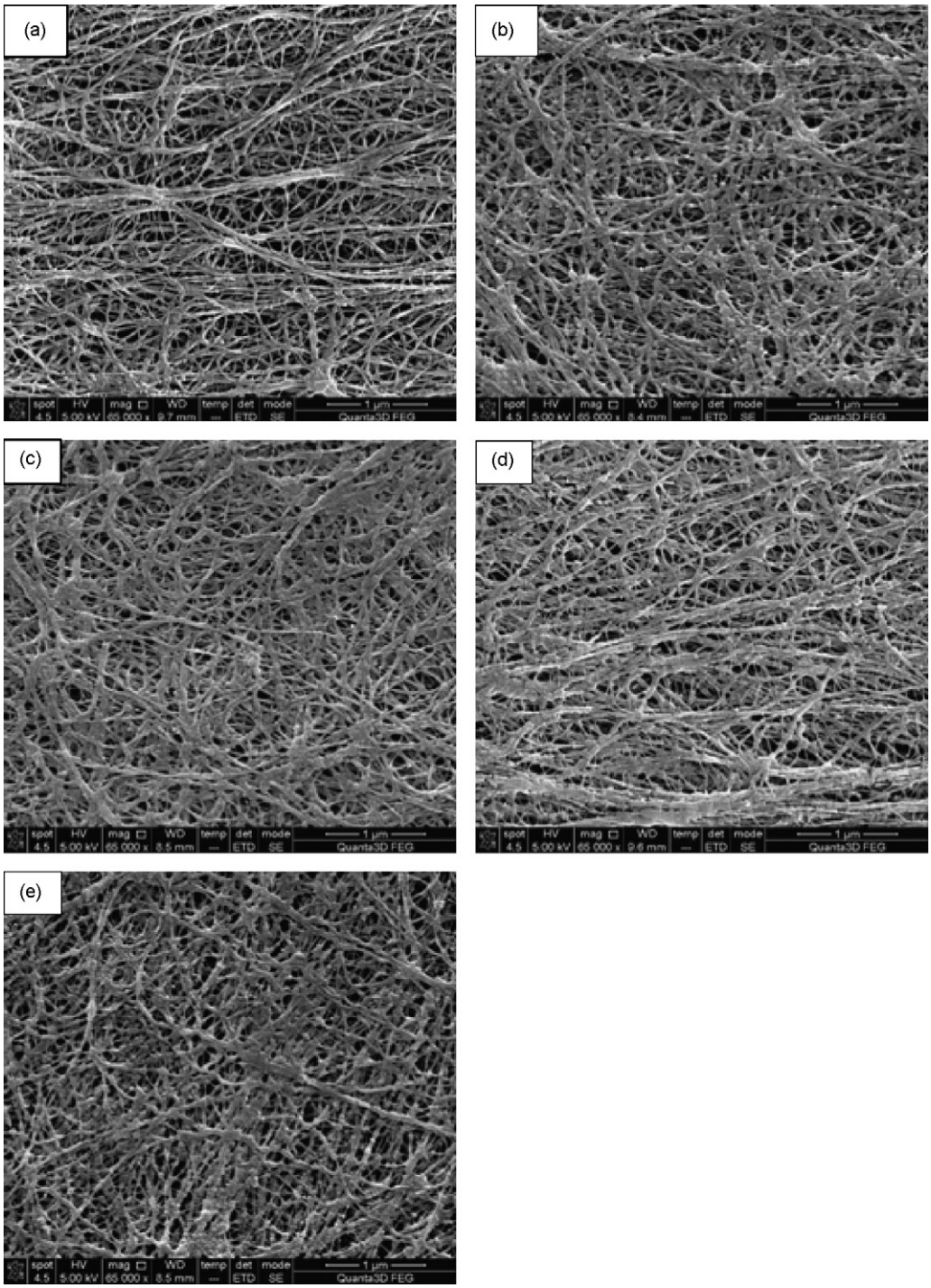

Fig. 1. SEM image of the non-irradiated and irradiated separators: (a) non-irradiated separator, (b) 50 kGy irradiated separator, (c) 100 kGy irradiated separator, (d) 150 kGy irradiated separator and (e) 200 kGy irradiated separator.

separator are about 140, 137, 138 and 136 °C and melting integrity temperatures of those are 158, 154, 160 and 166 °C, respectively. The temperature differences between shut-down and melting integrity are about 18, 16.5, 22 and 30.5 °C, respectively. It is well-known that one of methods to improve safety feature of the Li ion batteries is to increase the temperature gap between shut-down and melting integrity of the separator [14]. Therefore, authors believe that thermal resistance of the PE separator is increased drastically by gamma ray irradiation.

DSC and thermal shrinkage tests were performed using the non-irradiated and irradiated separators to understand the reason of this improvement on thermal property of separators. Fig. 5 shows DSC results of various separators. It is known that the PE separator melts at 138 °C (Fig. 5(a)). In cases of irradiated separators, the melting temperature is slightly increased by increasing of gamma ray irradiation dose as shown in Fig. 5. These results are relatively well matched with the results of DSC. Fig. 6(a) and (b) shows results of the thermal shrinkage of separators after storage at 120 and 150 °C for 1 h, respectively. Dimensional change of the non-irradiated and irradiated separators was calculated from Eq. (1). After storage at 120 °C for 1 h, the dimension of non-irradiated separator initial dimension is reduced by about 24% from the original size while the

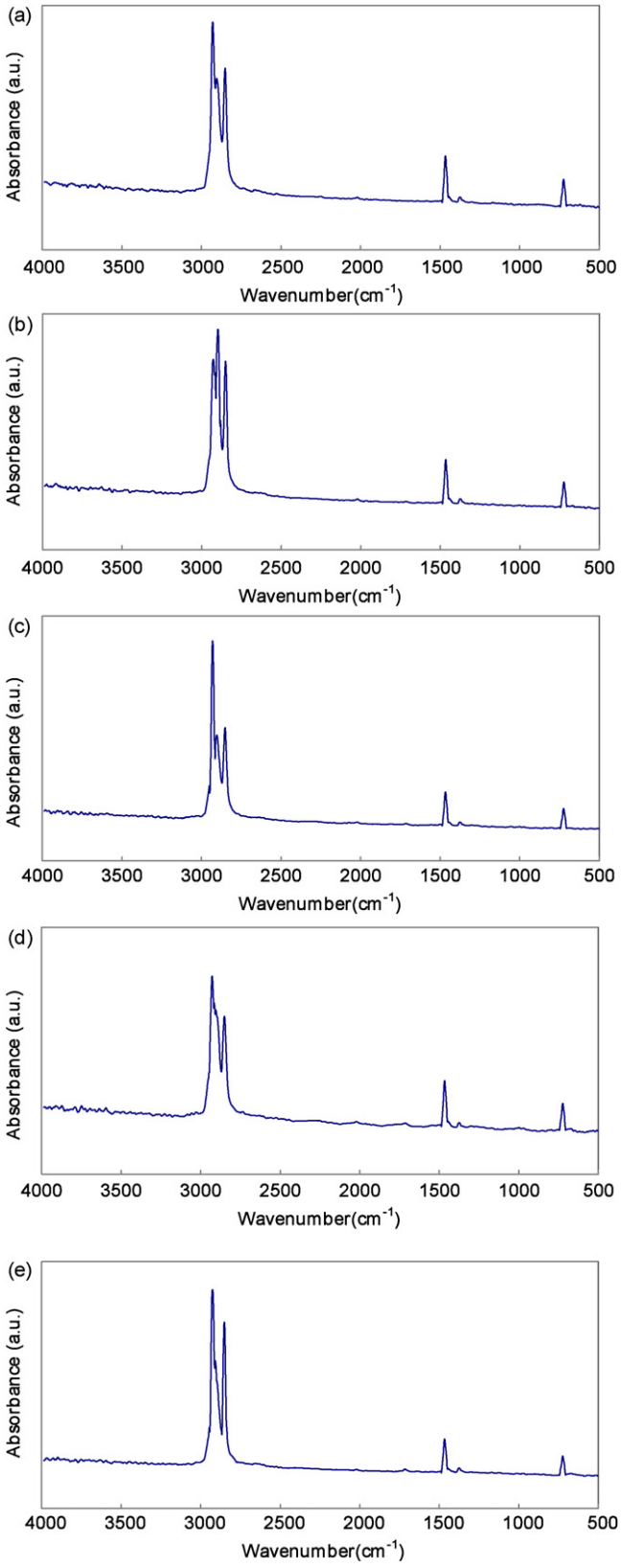

Fig. 2. FTIR spectra of (a) non-irradiated separator, (b) 50 kGy irradiated separator, (c) 100 kGy irradiated separator, (d) 150 kGy irradiated separator and (e) 200 kGy irradiated separator.

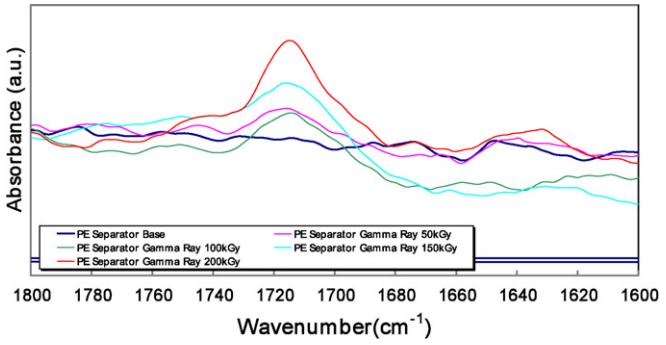

Fig. 3. FTIR spectra of the non-irradiated and irradiated separator at range from 1600 cm^{-1} to 1800 cm^{-1}.

ones of irradiated separators are reduced much less. It is observed that the reduced rate for 50, 100, 150 and 200 kGy gamma ray irradiated separators is 16, 12, 6 and 5%, respectively. After storage at 150 °C for 1 h, it is clearly observed that reduction of initial dimension is drastically decreased with increasing of gamma ray irradiation dose as shown in Fig. 6(b). These results give a good explanation for the reason of the temperature increase between shut-down and melting integrity by gamma ray irradiation. It has been reported that thermal shrinkage of separator was dramatically improved due to the cross-linking of the separator when separator is treated by electron beam irradiation [11]. Therefore, the improvement of thermal shrinkage might be attributed to the cross-linking of PE separators and thermal resistivity of them can be increased by gamma ray irradiation.

2032 coin type full cells were assembled with different separators to investigate electrochemical properties of the non-irradiated and irradiated separator. Graphite and $LiCoO_2$ were used as an anode and a cathode, respectively. Cells were discharged at 0.2, 0.5, 1, 2 and 3 rates to evaluate the effect of different separators on rate property. Fig. 7 shows the discharge curve at those rates. At those rates, a cell consisted of the irradiated separators has good capacity retention except 200 kGy gamma ray irradiation in comparison with a cell consisted of the non-irradiated separator. The change of ionic conductivities was measured to verify the reason of improvement in rated discharge properties by increasing of gamma ray irradiation dose because the rated discharge properties are largely dependent on ionic conductivity. In Fig. 8, the ionic conductivities change as a function of gamma ray irradiation dose. It is observed that the ionic conductivity is increased from 50 to 150 kGy dose of gamma ray irradiation then decreased from 150 to 200 kGy. The highest ionic conductivity is achieved at 150 kGy dose of gamma ray irradiation while the lowest ionic conductivity is obtained at 200 kGy dose of gamma ray irradiation. The ionic conductivity is strongly dependant on the pathway of ion transport. As shown early in Table 1, gurley number is not influenced by increasing of gamma ray irradiation dose. It can be speculated that the increase of the ionic conductivity is not resulted from the change of pathway of ion transport but from the change of molecular structure. These results are well matched to the results of the rated discharge properties. Therefore, it can be concluded that the rated discharge property is improved because of the molecular structural change of the PE separator by the gamma ray irradiation, especially 150 kGy dose.

Cycle life test was performed at room temperature. Cells were cycled electrochemically between 3.0 V and 4.2 V with CC–CV (constant current followed by constant voltage) condition. 0.5-C rate was applied during CC condition and voltage of 4.2 V was kept until the current decayed to 1% of a cell capacity during followed CV condition. Fig. 9 shows cycle performance of cells used in different separators. There is not much difference in cycle life of cells having the irradiated separator and the non-irradiated separator. This

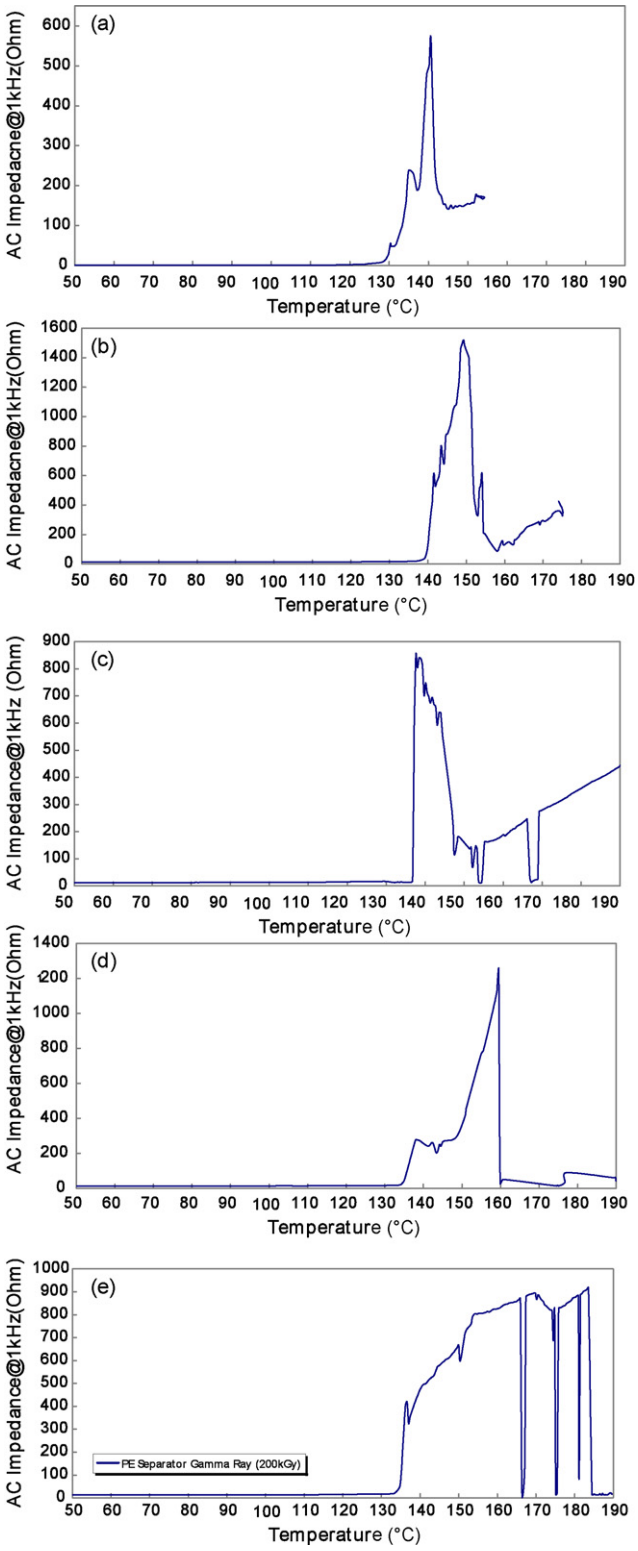

Fig. 4. Internal impedance at 1 kHz as a function of temperature: (a) non-irradiated separator, (b) 50 kGy irradiated separator, (c) 100 kGy irradiated separator, (d) 150 kGy irradiated separator and (e) 200 kGy irradiated separator.

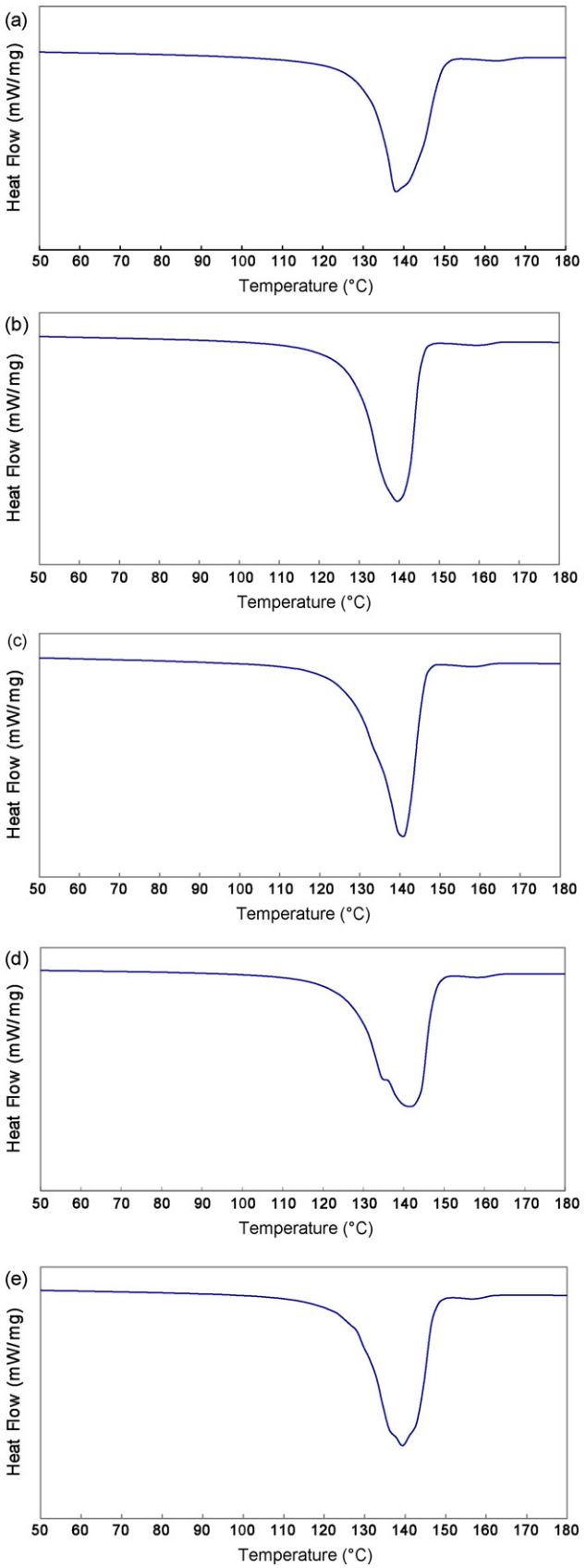

Fig. 5. DSC of (a) non-irradiated separator, (b) 50 kGy irradiated separator, (c) 100 kGy irradiated separator, (d) 150 kGy irradiated separator and (e) 200 kGy irradiated separator.

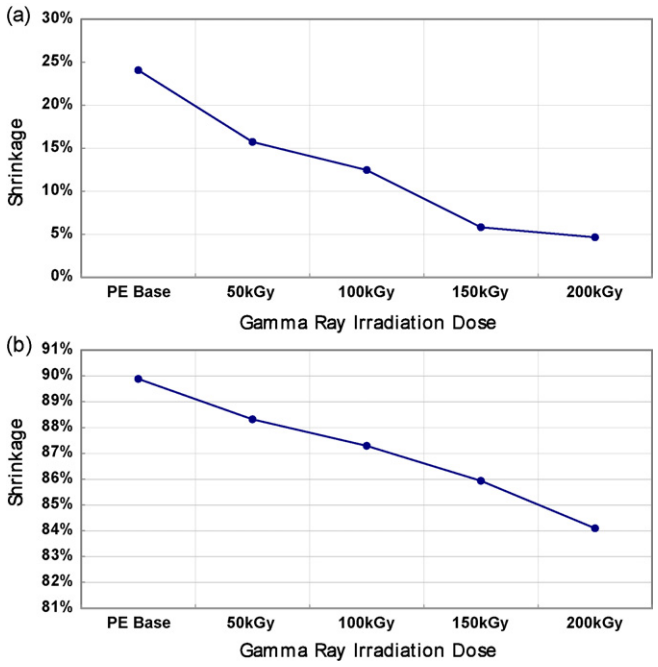

Fig. 6. Reduction of dimension of the non-irradiated and irradiated separator after storage at (a) 120 °C for 1 h and (b) 150 °C for 1 h.

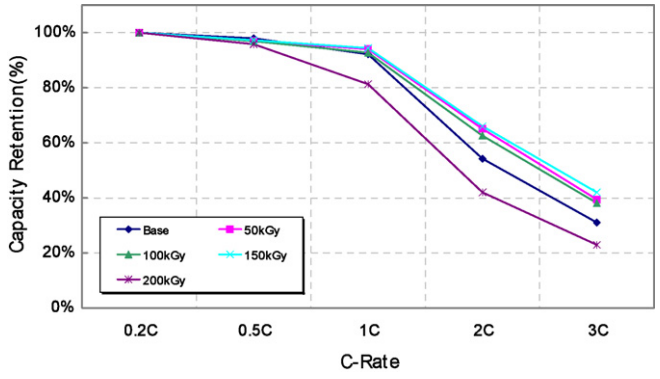

Fig. 7. Capacity retention of the non-irradiated and irradiated separators at 0.2, 0.5, 1, 2, 3 and 5 C rates.

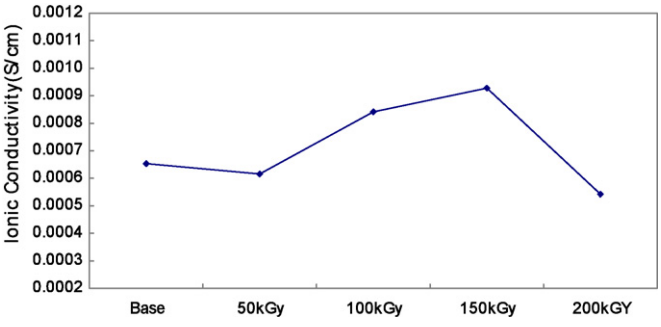

Fig. 8. Ionic conductivity of the non-irradiated separator and irradiated separators.

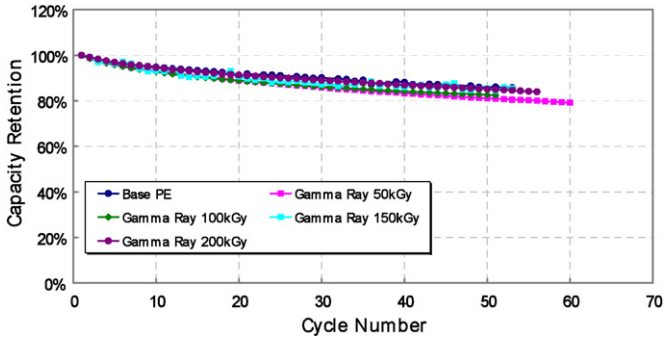

Fig. 9. Cycle performance of the non-irradiated and irradiated separator.

result implies that gamma ray irradiation on the separator does not induce negative effects on cycle property which is one of the most important properties of Li ion batteries.

4. Conclusions

Thermal resistance of separators is one of the most important properties which affects to the safety feature of Li ion batteries. This property of the PE separator is improved drastically by gamma ray irradiation without trade-off of electrochemical properties such as rated capacity and cycle performance. Especially, the temperature difference between shut-down and melting integrity of the irradiated separators is increased about two times in comparison with that of the non-irradiated separator. The reason of this improvement is attributed to cross-linking of the PE separator. It can be expected that safety properties such as overcharge and nail penetration for Li ion batteries might be improved by using a gamma ray irradiated separator. The discharge properties of cells at various rates are also improved by using gamma ray irradiated separators. From present results, it can be concluded that the separator irradiated by gamma ray without overdosed irradiation is a good candidate for the separator of high energy and high power Li ion batteries because it has a good thermal property at high temperature without any adverse effect on the electrochemical performance of Li ion cells.

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