Short communication

Enhancement of electrochemical and thermal properties of polyethylene separators coated with polyvinylidene fluoride–hexafluoropropylene co-polymer for Li-ion batteries

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A R T I C L E   I N F O

A B S T R A C T

The physical effects of a polyethylene (PE) surface on the electrochemical and thermal properties of a PE separator coated with polyvinylidene fluoride (PVDF)–12 wt% hexafluoropropylene (HFP) co-polymer have been investigated for use in lithium ion batteries. To change the surface property of the PE separator, it is treated using gamma ray irradiation. In comparison with the non-irradiated separator, the irradiated separator shows strong affinity for polar solvents due to the carbonyl band formed during gamma ray irradiation. And the PVDF–12 wt%HFP co-polymer is coated on the both sides of the non-irradiated and irradiated separators using a dip-coating process. It is clearly observed that the ionic conductivity of the irradiated separator coated with PVDF–12 wt%HFP is higher than that of the non-irradiated separator coated with the same one. Based on the activation energy calculation, the ionic conductivity is found to strongly depend on the characteristics of the interfaces between them. In addition, rate discharge property and thermal stability of the irradiated separator coated with PVDF–12 wt%HFP are much better than those of the non-irradiated one. The improvement of the thermal stability could be attributed to cross-linking of the support PE separator using gamma ray irradiation.

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1. Introduction

Separators are one of the key components of Li-ion batteries. The main function of separators is to allow transport of ionic charge carriers and prevent electrical short circuits between a cathode and an anode. In order to select a separator for Li-ion batteries, several factors must be considered. For instance, the separators should have lower ionic resistance, robust mechanical and dimensional stability, sufficient physical strength to sustain battery assembly processes, and durable chemical resistance against electrode and electrolyte [1]. Polyolefin separators, such as polyethylene (PE) and polypropylene (PP), are the most commercially used separators for Li-ion batteries because their properties are generally satisfactory. However, they have poor liquid electrolyte retention and do not absorb electrolytes with high dielectric constants, such as cyclic carbonates, owing to their hydrophobic surface with low surface energy [2,3]. On the other hand, gel polymer electrolytes are composed of a liquid electrolyte and a polymer matrix. Therefore, the gel polymer electrolytes take advantage of both increased ionic conductivity of the liquid electrolyte as well as safety of the polymer matrix. However, gel polymer electrolytes have poor mechanical properties because they have been softened by the liquid electrolyte uptake of the polymer matrix. This drawback might cause problems during the cell assembly processes, such as winding tension and internal shorts.

Recently, much research effort has been devoted to enhancing the mechanical properties of separators for application in Li-ion batteries. Among these investigations, most are based on gel polymer electrolyte surface coating. The surface coating of a polyolefin or non-woven fabric separator provides mechanical support [4–7]. The simple fabrication process [8] and strong mechanical properties [5,9] of separators coated with gel polymer are very attractive features for use in Li-ion batteries. However, since the gel polymer electrolyte has a much lower ionic conductivity than conventional liquid electrolytes [7,8] and the polymer coating process produces new interfaces between the support separators and coating materials, the composite separators generally show low ionic conductivity. The poor ionic conductivity adversely influences cell performance, especially at high current densities. Therefore, to enhance the ionic conductivity of the separator coated with gel polymer electrolyte, the interfacial resistance between the support separator and gel polymer electrolyte needs to be reduced. Some researchers have investigated the ionic conductivity and cell performance of the separators coated with various gel polymer

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Table 1
Basic properties of the polyethylene separator.

Items	Measured value
Thickness (μm)	16
Porosity (%)	44–47
Membrane tensile strength (kgf cm^{-2})	
MD	1210–1510
TD	600–860
Membrane tensile elongation (%)	
MD	20–70
TD	70–130

electrolytes, but the interface was not seriously considered [5,7,9]. Thus, we have focused on the influence of the interfacial resistance to the ionic conductivity of separators coated with gel polymer electrolytes.

In this study, PE and polyvinylidene fluoride (PVDF)–12 wt% hexafluoropropylene (HFP) co-polymer were used as the support separator and gel polymer electrolyte, respectively. In order to modify the interface properties between them, gamma ray irradiation was used to treat the support PE separator before the gel polymer electrolyte coating. The main purpose of this work is to improve the ionic conductivity and cell performance of a separator coated with a gel polymer electrolyte by modifying the interface between the support separator and the gel polymer electrolyte.

2. Experimental

The polyethylene (PE) membrane was procured from Asahi Kasei Chemicals, and its basic properties are given in Table 1. The PE separator was modified using gamma ray irradiation to reduce the interfacial resistance between the support separator and the gel polymer electrolyte. A gamma ray irradiator with a ^{60}Co source was used. The PE separator was irradiated using gamma rays at a dose rate of 10 kGy h^{-1} and the applied radiation dose was 150 kGy. The PVDF–12 wt%HFP co-polymer (molecular weight = 470,000) was used as a gel polymer electrolyte. To coat the PVDF–12 wt%HFP co-polymer on the non-irradiated and irradiated PE separators, 2 g of PVDF–12 wt%HFP co-polymer was dissolved in 80 mL of acetone at room temperature. The non-irradiated and irradiated PE separators were dipped in the coating solution and dried at a relative humidity of 35% using a humidity-control system.

The molecular structure of the PE separator after the gamma ray irradiation was characterized by Fourier transform infrared spectroscopy (FT-IR, Bruker VERTEX 70) in a wave number range of 400–4000 cm^{-1} under ambient conditions. The morphology and microstructure of the non-irradiated and irradiated PE separators coated with PVDF–12 wt%HFP were examined using a field emission scanning electron microscope (FE-SEM, JEOL JSM-7000F) after Pt coating.

The electrolyte uptake was obtained by measuring the weight of separators with a certain area before and after liquid electrolyte soaking for 1 h and then calculated using Eq. (1):

$$\text{Electrolyte uptake} \ \ (\%) = \frac{W_f - W_i}{W_i} \times 100 \tag{1}$$

where W_i and W_f are the weight of the PE separators coated with PVDF–12 wt%HFP before and after soaking, respectively. The Gurley number of the PE separators coated with PVDF–12 wt%HFP was measured using a Gurley-type densometer (Toyoseiki). The ionic conductivities of the separators were measured by AC impedance analysis using a Solatron 1280C over a frequency range from 20,000 to 0.1 Hz with an amplitude of 10 mV. In the determination of the ionic conductivity, the non-irradiated and irradiated PE separators coated with PVDF–12 wt%HFP were sandwiched between two lithium metal electrodes and soaked in a liquid electrolyte in
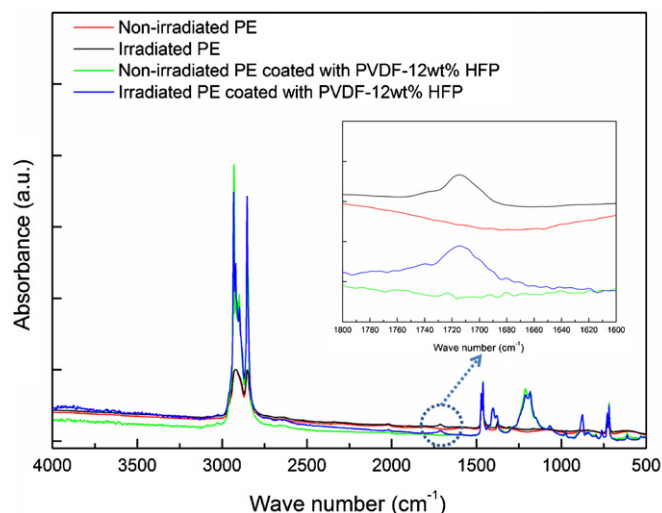

Fig. 1. FT-IR spectra of non-irradiated PE separator, irradiated PE separator, non-irradiated PE separator coated with PVDF–12 wt%HFP, and irradiated PE separator coated with PVDF–12 wt%HFP. Inset graph shows the enlarged spectra for the wave numbers 1600–1800 cm^{-1}.

2032 coin type cells. 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 the electrolyte resistance obtained from the AC impedance test. The activation energy was obtained by measuring the ionic conductivities of the separators at different temperatures (30, 40 and 50 °C). The activation energy was calculated using the Arrhenius equation as follows:

$$\sigma = A \exp\left(\frac{-Q_a}{RT}\right) \tag{2}$$

where σ is the ionic conductivity, A is the pre-exponential factor, R is the gas constant ($R = 8.314$ J K^{-1} mol^{-1}) and T is the temperature (K). The separator areas (5 cm $W \times 5$ cm L) were measured before and after oven storage at 120 °C for 1 h to analyze the thermal shrinkage properties. The shrinkage of the separators was calculated using Eq. (3):

$$\text{Shrinkage} \ \ (\%) = \frac{A_i - A_f}{A_i} \times 100 \tag{3}$$

where A_i and A_f are the initial and final areas of the separator, respectively.

The 2032 coin-type cells were assembled by sandwiching the separator between a LiCoO$_2$ cathode and a graphite anode. The cells were filled with a liquid electrolyte, which was 1 M LiPF$_6$ in ethylene carbonate (EC)/ethyl methyl carbonate (EMC) (3:7 in volume, PANAX ETEC) with a 3 wt% vinylene carbonate (VC) additive. The cathode consisted of LiCoO$_2$ (95 wt%), PVDF binder (3%), and Super-P (2%) as the conducting agent and the anode comprised graphite (97.5 wt%), CMC (1%), and SBR (1.5%). The capacities per unit area for the cathode and anode were 4.0 ± 0.1 mAh cm^{-2} and 4.2 ± 0.1 mAh cm^{-2}, respectively. Rate discharge tests were performed for 3.0–4.2 V at the C rates of 0.2 C, 0.5 C, 1 C, 2 C, and 3 C. Cycle life performance was examined under the constant current mode at 0.5 C rate from 3.0 to 4.2 V using a cycle tester (Maccor 8500).

3. Results and discussion

The molecular structure changes of the non-irradiated and irradiated PE separators were investigated by FT-IR spectroscopy. Fig. 1 shows the FT-IR spectra of the separators before and after gamma ray irradiation. Typical PE separator characteristic bands appeared at 2850–3000 cm^{-1} and 1465 cm^{-1}, which correspond to the C–H

stretching vibrations and C–H bending vibrations, respectively [10]. However, in Fig. 1(inset graph), it was observed that significant changes at 1720 cm^{-1} occurred after gamma ray irradiation, which is related to the carbonyl formation [11]. The mechanism for the carbonyl group formation could be explained by oxygen reacting with free radicals produced in the polyethylene matrix during gamma ray irradiation under atmospheric conditions [12,13]. In addition, the carbonyl band was still observed in the irradiated separator coated with PVDF–12 wt%HFP, which suggests that it exists on the interface following the coating process. The carbonyl formation is expected to play an important role in improving the electrolyte wettability. The effect of the carbonyl formation on the affinity towards polar solvents was studied by performing an electrolyte uptake test on the non-irradiated PE, irradiated PE, non-irradiated PE, and irradiated PE coated with PVDF–12 wt%HFP. The results are shown in Fig. 2. The electrolyte uptake of the irradiated separator was 91% while that of the non-irradiated separator was 72%. In addition, irradiated PE coated with PVDF–12 wt%HFP has higher electrolyte uptake than non-irradiated PE coated with PVDF–12 wt%HFP. The uptake results imply that improvement of the affinity with polar solvents could be attributed to carbonyl formation during gamma ray irradiation.

Fig. 3 shows the microstructure of the non-irradiated PE, irradiated PE, non-irradiated PE coated with PVDF–12 wt%HFP, and irradiated PE coated with PVDF–12 wt%HFP, respectively. As shown in Fig. 3(a) and (b), the microstructures of the PE separator before and after irradiation were almost the same. In Fig. 3(c) and (d), microporous structures with pore sizes ranging from 6 to 8 μm were formed in the coated PVDF–12 wt%HFP co-polymer layer regardless of irradiation. It is well known that the microporous structure of the PVDF–HFP co-polymer is formed through phase inversion [14,15]. Fig. 4 demonstrates the ionic
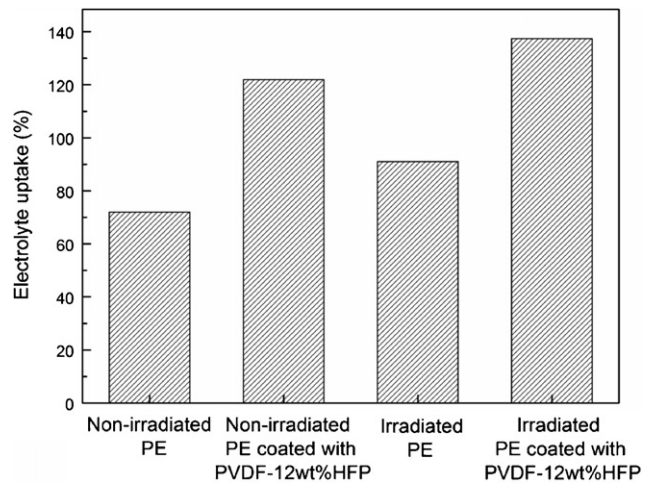

Fig. 2. Electrolyte uptake of the non-irradiated and irradiated PE separators.

conductivities of the non-irradiated and irradiated separators coated with PVDF–12 wt%HFP. It was expected that the ionic conductivities of the non-irradiated and irradiated separators coated with PVDF–12 wt%HFP would be similar because of the microporous structure similarity. However, ionic conductivity of the irradiated separator coated with PVDF–12 wt%HFP was higher than that of the non-irradiated PE separator coated with PVDF–12 wt%HFP even though the non-irradiated and irradiated PE separators were coated under the same conditions and had similar microporous structures after dip-coating. Therefore, it is expected that the physical properties of the separator surface affect
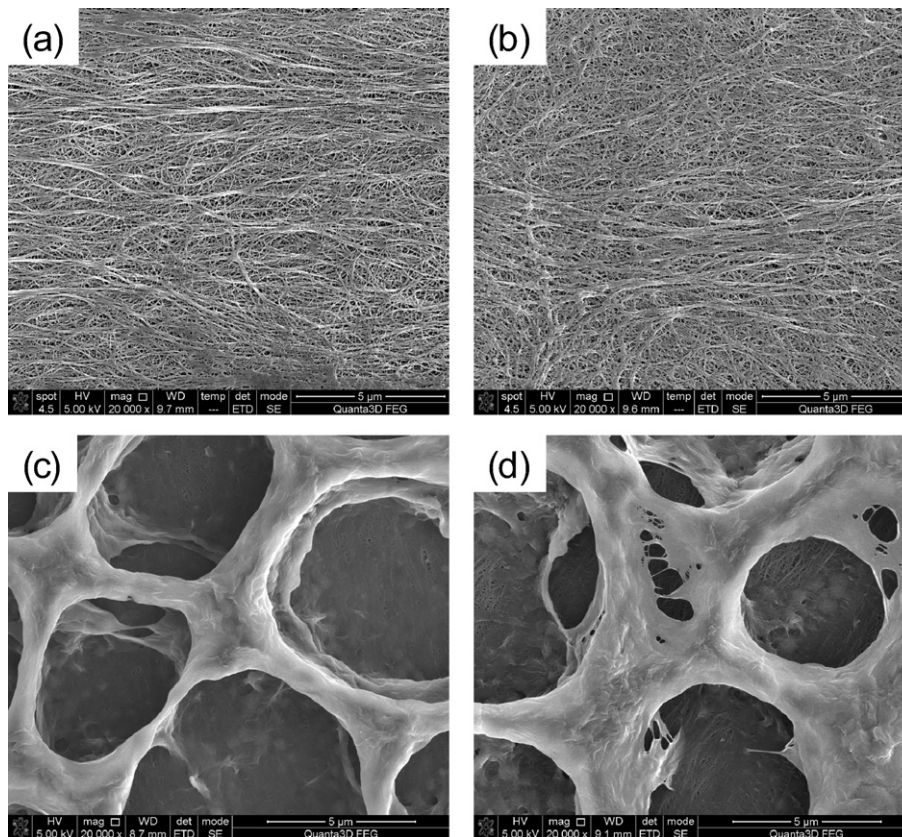

Fig. 3. Microstructure of (a) the non-irradiated PE separator, (b) the irradiated PE separator, (c) the non-irradiated PE coated with PVDF–12 wt%HFP co-polymer and (d) the irradiated PE coated with PVDF–12 wt%HFP co-polymer.
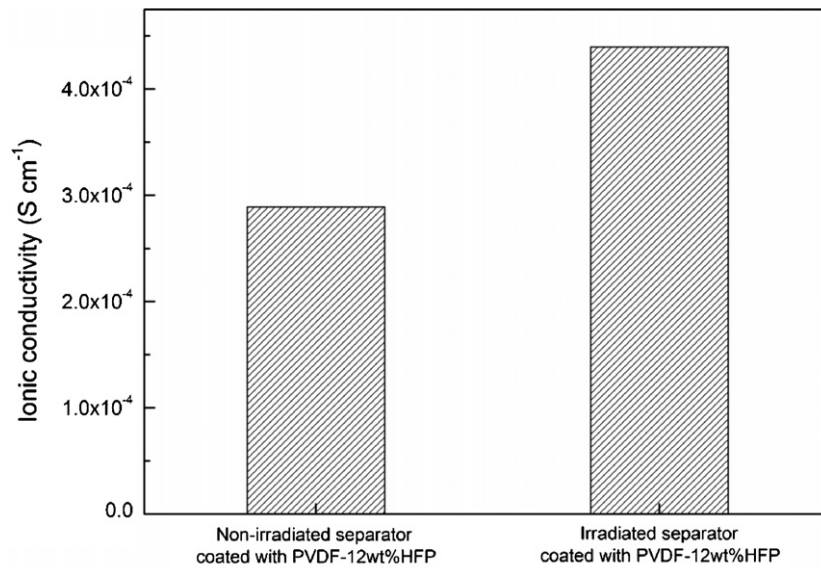
Fig. 4. Ionic conductivities of the non-irradiated and irradiated PE separators coated with PVDF–12 wt%HFP co-polymer.

the interface characteristics between the support PE separator and PVDF–12 wt%HFP co-polymer.

To investigate the physical and interface relationship, the activation energy corresponding to mobility of lithium ions through the interface formed between the support PE separator and PVDF–12 wt%HFP was calculated. It was necessary to measure the ionic conductivities of the separators at various temperatures (T) to obtain the activation energy. The ionic conductivities of all the separators were plotted against T^{-1} according to $\ln(1/T) = A\exp(-Q_a/RT)$ in Fig. 5. The activation energies of the separators were determined from the slopes in Fig. 5. From the Arrhenius relationship, the activation energies for the non-irradiated and irradiated PE separators were found to be $11.1 \pm 1.1\,kJ\,mol^{-1}$ and $10.2 \pm 1.1\,kJ\,mol^{-1}$, respectively. In addition, the activation energies of the non-irradiated and irradiated PE separators coated with PVDF–12 wt%HFP were found to be $26.3 \pm 2.6\,kJ\,mol^{-1}$ and $16.8 \pm 1.7\,kJ\,mol^{-1}$, respectively. The activation energies of the composite separators reflect the Li-ion mobility through the bulk of the PE and coated co-polymer as well as the interfaces between both materials [16]. The

activation energy of the irradiated composite separator was significantly lower than that of the non-irradiated one. When the mobility of lithium ions through the PVDF–12 wt%HFP co-polymer was considered constant, it should be noted that the mobility of lithium ions through the interfaces between the irradiated PE separator and PVDF–12 wt%HFP co-polymer is much higher than that between the non-irradiated separator and PVDF–12 wt%HFP co-polymer. The results indicate that the hydrophilic PVDF–12 wt%HFP co-polymer may be more compatible with the irradiated PE separator because the carbonyl formed using gamma ray irradiation could make the surface of the PE separator more hydrophilic.

Fig. 6 shows the discharge capacity retention of the coin-type full cells employing the non-irradiated PE, irradiated PE, non-irradiated PE coated with PVDF–12 wt%HFP co-polymer, and irradiated PE coated with PVDF–12 wt%HFP co-polymer at different current rates (0.2, 0.5, 1, 2, and 3 C). The non-irradiated and irradiated PE coated PVDF–12 wt%HFP showed lower rate capability than the separators without the PVDF–12 wt%HFP coating owing to the increase of thickness by the PVDF–12 wt%HFP coating [17], which is somewhat inevitable to enhance mechanical and thermal stabilities of
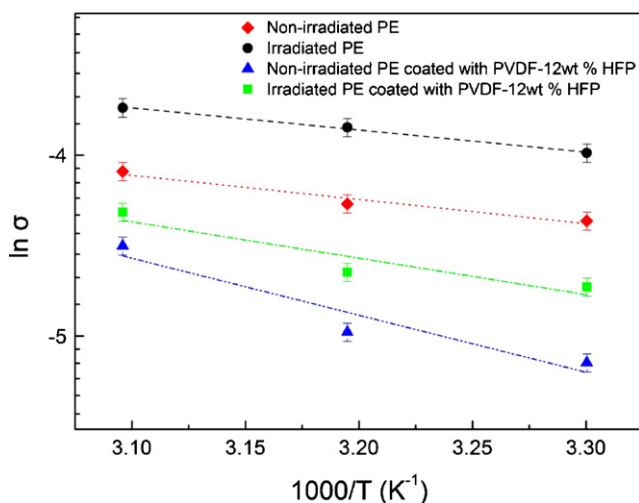

Fig. 5. Arrhenius plot for the activation energy calculation related to the mobility of lithium ions.
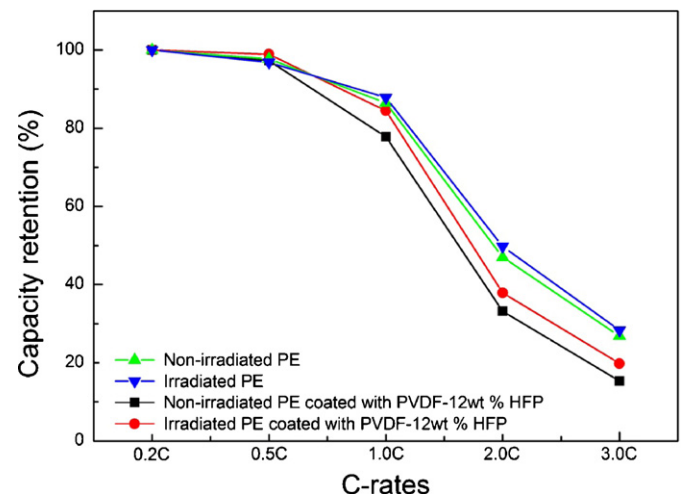

Fig. 6. Capacity retention at a range of 0.2–3 C rates of the non-irradiated PE, irradiated PE, non-irradiated PE coated with PVDF–12 wt%HFP co-polymer, and irradiated PE coated with PVDF–12 wt%HFP co-polymer.

Fig. 7. Cycle performance of the non-irradiated PE, irradiated PE, non-irradiated PE coated with PVDF–12 wt%HFP co-polymer, and irradiated PE coated with PVDF–12 wt%HFP co-polymer.
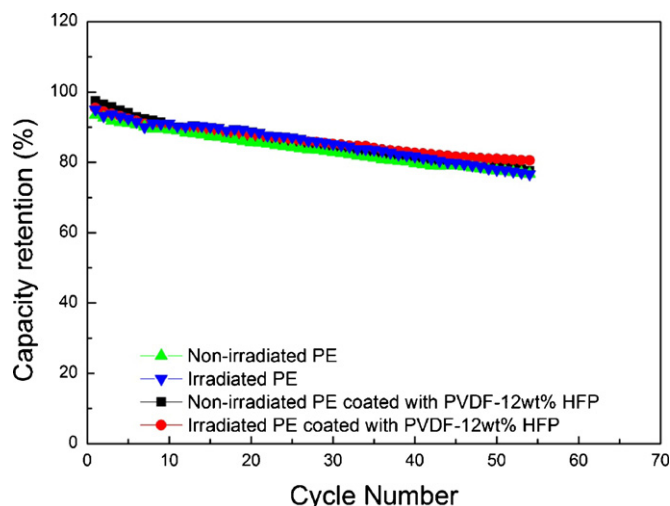
the separators. To verify the effect of gamma ray irradiation on the composite separators, the rate capability of the non-irradiated and irradiated PE coated with PVDF–12 wt%HFP should be compared. The irradiated separator coated with PVDF–12 wt%HFP exhibits higher capacity retention than the non-irradiated separator coated with PVDF–12 wt%HFP. This difference could be ascribed to a reduction in interfacial resistance between the irradiated separator and PVDF–12 wt%HFP co-polymer. The cycle life test of the coin type full cells assembled with the non-irradiated PE, irradiated PE, non-irradiated PE coated with PVDF–12 wt%HFP co-polymer, and irradiated PE coated with PVDF–12 wt%HFP co-polymer was carried out at room temperature. Fig. 7 presents the cycling stability of the cells with the above separators. The stability results show that there is not much difference in the cycle life of the cells having separators with and without PVDF–12 wt%HFP co-polymer coating. This result reveals that the change of surface properties using gamma ray irradiation does not lead to any degradation on cycle performance even after the co-polymer coating.

The thermal stability of the non-irradiated and irradiated separators coated with PVDF–12 wt%HFP was evaluated using oven

storage at 120 °C for 1 h. Thermal shrinkage was calculated from Eq. (3) described in Section 2 and the result is plotted in Fig. 8. It is observed that the thermal shrinkage ratio of the non-irradiated separator coated with PVDF–12 wt%HFP was 23.0% while that of the irradiated separator coated with PVDF–12 wt%HFP was 2.3%. This result implies that an irradiated separator coated with PVDF–12 wt%HFP is much more stable at high temperatures than a non-irradiated separator coated with PVDF–12 wt%HFP. Thermal properties of PE and PP are reported to be greatly improved by cross-linking using gamma ray or electron beam irradiation [18,19]. Therefore, the thermal stability improvement of the irradiated separator coated with PVDF–12 wt%HFP could be attributed to cross-linking of the support PE separator induced by gamma ray irradiation.

4. Conclusions

Gamma ray irradiation was used for the modification of the interface between the support PE separator and the coated material. Electrolyte uptake of the gamma ray irradiated PE separator was dramatically improved due to the carbonyl formation which was not apparent in the non-irradiated PE separator. The ionic conductivity of the irradiated separator coated with PVDF–12 wt%HFP increased compared to the non-irradiated separator coated with PVDF–12 wt%HFP. Based on activation energy calculation corresponding to the mobility of lithium ions, it was found that the characteristic of the interface was closely related to the physical surface property of the support PE separator. In addition, the ionic conductivity through the entire composite separator was found to strongly depend on the characteristics of the interface formed between them. The PVDF–12 wt%HFP could be more compatible with an irradiated PE separator because the carbonyl formation may provide a more hydrophilic PE separator surface. The thermal stability of the irradiated separator coated with PVDF–12 wt%HFP was better than that of the non-irradiated one, which could be ascribed to cross-linking of the support PE separator induced by gamma ray irradiation.

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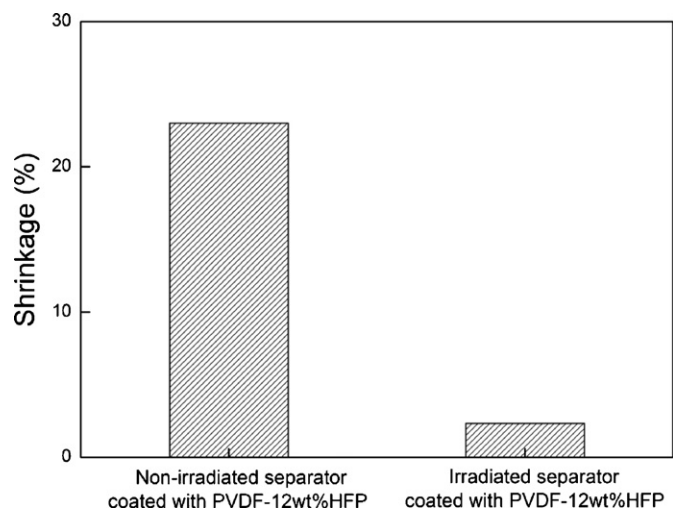[19] I. Krupa, A.S. Luyt, Polym. Degrad. Stabil. 71 (2001) 361.

Fig. 8. Thermal shrinkage of the non-irradiated and irradiated PE separators coated with PVDF–12 wt%HFP after storage at 120 °C for 1 h.