

Modification of Lithium Ion Battery Separators by Electron Beam Radiation Induced Grafting of Glycidyl Methacrylate onto Porous PP Film

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In order to modify porous polypropylene (PP) film which is used as separator of lithium ion battery, monomers glycidyl methacrylate (GMA) with epoxy groups were grafted onto porous PP film by electron beam induced pre-irradiation technology. Firstly, the influences of reaction conditions such as concentration of monomer, absorbed dose and temperature on grafting yield were carried out. Secondly, the prepared graft copolymers PP-g-GMA were assembled to Lithium ion battery to make clear the influence of modification of PP film on the property of Lithium ion batteries. The performance test of Lithium ion battery showed that battery assembled with the grafted PP of grafting yield 68.4% exhibited higher capacity and better cycling performance. Grafted PP with different grafting yield was characterized by FTIR and differential scanning calorimetry technique. All results further confirmed modification of porous PP film. The research provided a facile and effective way for introducing poly glycidyl methacrylate (PGMA) chains onto PP film. Compared to the original PP separators, the grafting of PGMA chains onto PP improved the affinity between the grafted PP and liquid electrolyte, which benefited the increase of separators performances.

Keywords: Porous polypropylene film, Glycidyl methacrylate, Electron beam induced grafting, Lithium ion battery separator

1. INTRODUCTION

A rapid increase has been found in the lithium ion battery market for portable power for electronic products, for example, laptops, hybrid electric vehicles and electric vehicles. Separators are important component of lithium ion battery. Micro-porous films made of polyolefins are widely used

as separators for lithium ion battery because of their proper electrochemical and chemical performances [1-2]. Although polypropylene separators have excellent stability, they are not able to be completely wetted by electrolyte because of their hydrophobic nature [3-5]. The decrease in performance may be due to leakage of the electrolyte solution from between electrodes. Therefore, the modification of polyolefin separators is necessary to increase their adsorbability to electrolyte [6-7].

As for modification of polyolefin, radiation-induced graft method is better than other grafting methods, such as using light and chemical initiator [8-9], because the high absorbed dose produced by radiation can form many radicals [10-11]. This method has been used for the production of battery separator [12-14]. Preparation of a separator can be carried by using various monomers [15]. Monomers with carboxyl groups or sulfonic groups are appropriate for the modification of the separators which are used in aqueous electrolyte batteries [16-18], while monomers with ester groups are appropriate for separators which are used in non-aqueous electrolyte batteries [19-20].

Radiation-induced graft includes simultaneous method and pre-irradiation method. Simultaneous graft method has a limitation resulting from the formation of homopolymer, because monomers are irradiated together with polymer backbone [21-22]. Therefore, in this paper we adopted electron beam induced pre-irradiation grafting method for the preparation of composite separator with PGMA graft chains. Gwon et al [24] and other groups [25-27] have studied the grafting of PMMA or PGMA chains onto polyolefin for hydrophilicity and antifouling properties. In comparison, the method used in our research has advantage of low-cost and good safety. Considering the comprehensive application of PP separators in lithium ion battery and the necessary of improving their affinity to liquid electrolyte, our work offers a simple and efficient ways for introducing PGMA graft chains onto PP separators.

2. EXPERIMENTAL

2.1. Materials

A commercial porous PP film, with pore diameter 40-100 nm and thickness 12 μm , was supplied by Shenzhen Zhimeida new energy Co., Ltd. Glycidyl methacrylate (GMA) was purchased from Aldrich and used directly. The liquid electrolyte (1.0M LiPF_6 DMC/EC=1:1) was produced by Zhangjiagang Guotai-huarong New Chemical Materials Co., Ltd. Other chemicals, such as ammonium ferrous sulfate and N, N-dimethylformamide (DMF) were analytical-reagent grade, and used without purification.

2.2. Equipments

A 2 MeV electron accelerator (GJ-2), located at Shanghai Applied Radiation Institute, was used to irradiate PP film. The original PP and grafted PP were characterized by FTIR spectroscopy (IRAffinity-1, Shimadzu) respectively. The samples thermal properties were carried out by using a differential scanning calorimeter (DSC200PC, Netzsch). The charge and discharge cycling test of Li-ion cells assembled with modified PP were conducted by battery test equipment (LAND-CT2001A).

2.3. Preparation of GMA-g-PP separators

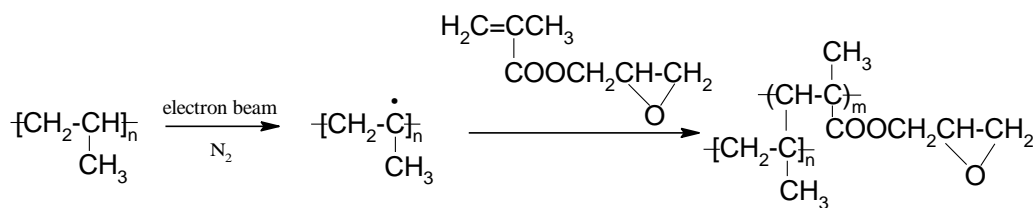


Figure 1. Preparation of GMA-g-PP separators by pre-irradiation grafting method

Figure 1 shows the synthesis process of GMA-g-PP separators by electron beam induced grafting of GMA onto porous PP film. The porous PP films were sealed inside polyethylene bags containing high purity N_2 . The sealed PP was irradiated by an dynamitron accelerator with current of 1 mA. The grafting process was performed in a tube where solvent DMF and monomer GMA were firstly added. After bubbling with N_2 for 15 minutes, pre-irradiated PP was immersed in the Pyrex tube. The mixture solution was bubbled with N_2 for 5 minutes, and then the Pyrex tube was sealed. The grafting reaction was carried out in a water bath at constant temperature. After the reaction, the grafted PP was removed, and washed throughout with a mixture of methanol and tetrahydrofuran (1:1) to eliminate homopolymer or unreacted monomer which were adhere on the surface of the PP. Thereafter, the grated PP was dried in a vacuum oven at $60^\circ C$ until a constant weight was got. The grafting yield could be calculated using the formula (1):

$$\text{Grafting yield (\%)} = \frac{W_g - W_o}{W_o} \times 100 \quad (1)$$

Where W_o and W_g are the weights of original PP and GMA-g-PP, respectively.

The dried film was moved into a glove box and immersed in the electrolyte solution, 1 M $LiPF_6$ in EC/DMC, for 15 min to absorb enough electrolyte solution. To study the difference between original PP and grafted PP in Li-ion battery cell property, we assembled button type batteries using grafted PP and original PP with an area of 0.78 cm^2 . Using Land battery test equipment, the charge and discharge cycling test of the Li-ion cells were galvanostatically investigated. All tests of the cells were conducted in the dry box filled with Ar.

3. RESULTS AND DISCUSSION

3.1. The influence of monomer concentration on grafting yield at different absorbed dose

Both absorbed dose and monomer concentration are very important factors which obviously affect grafting yield.

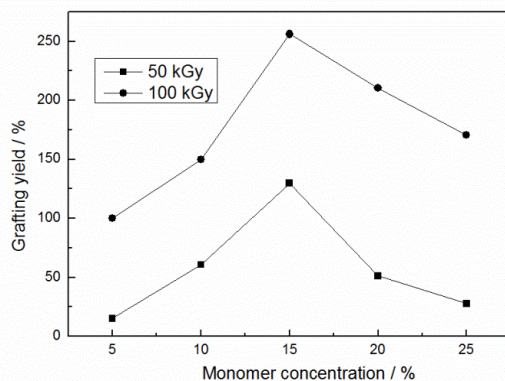


Fig. 2

Figure 2. The effect of monomer concentration on grafting yield at different absorbed doses

Figure 2, shows that the grafting yield increases quickly with the monomer concentration within the scope of 5-15%, then decreases with increasing monomer concentration. The grafting reaction depends mainly on the monomers available to the trapped radicals within porous PP. Higher is monomer concentration, and more GMA is available to the PP substrate. With further increase of monomer concentration, monomers tend to homopolymerize, which reduces the diffusion rate of monomers, and the reaction probability between trapped radicals with monomers decreases. As a result, the grafting yield decreases when monomer concentration is higher than 15%. At the same monomer concentration, the higher is irradiation dose, higher grafting yield is achieved. This is due to the participation of more radicals in the grafting reaction.

3.2. The influence of reaction temperature on grafting yield

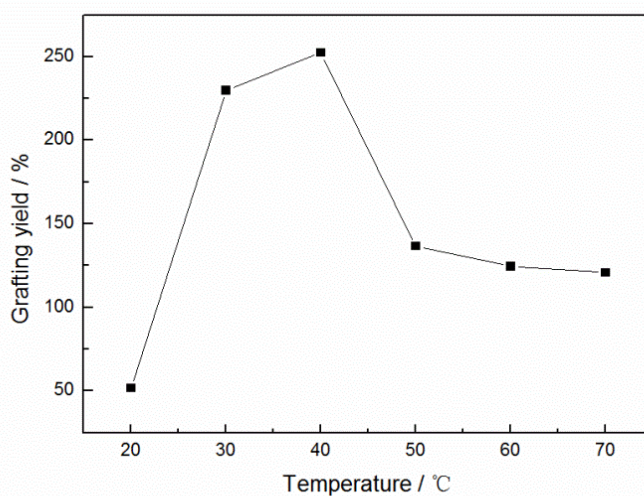


Fig. 3

Figure 3. The effect of reaction temperature on grafting yield

Figure 3 shows the relationship between grafting yield and grafting temperatures with 100 kGy absorbed dose. The grafting yield increases with temperatures when temperatures are below 40 °C. It may be explained by the fact that decay rate of trapped radicals formed by electron beam radiation is slow at low reaction temperature, so rate of monomer diffusion regulated and controlled the grafting rate. At higher temperature more monomers can react with radicals, so highest grafting yields were obtained at 40 °C. The grafting yield decreases obviously over 40 °C, which can be due to the fast decay rate of the trapped radicals at high temperature. So, the grafting reaction is dominated by decaying rate of the trapped radicals and the monomer diffusion rate. Higher temperature can accelerate diffusion rate of monomer, at the same time which also increase the decay rate of the trapped radicals [28].

3.3. FTIR characterization

The structure of the original PP, graft copolymer GMA-g-PP was analyzed by FTIR. Comparing the spectra (a) with (b) in Figure 4, there are some new absorption peaks in spectra (b), one peak at 1732 cm⁻¹ stands for the C=O groups, and another peak at 902 cm⁻¹ corresponds to the absorption of epoxy groups. The characteristic absorption peaks at 1143 cm⁻¹ and 1254 cm⁻¹ are attributed to the symmetric stretching and asymmetric stretching vibration of C-O-C in grafted GMA respectively. For original PP, there is only asymmetric stretching vibration of C-H in PP. All the evidences clearly indicate PGMA chains are grafted onto the original PP.

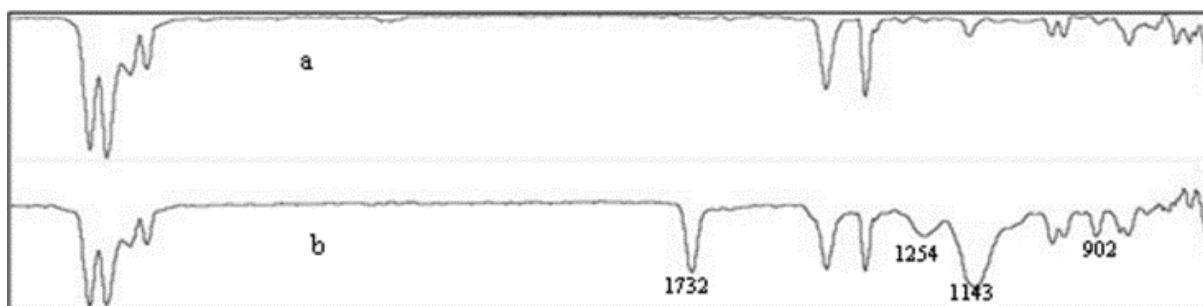


Fig. 4

Figure 4. FTIR spectrum of original PP (a) and graft copolymer GMA-g-PP with grafting yield 68.4% (b)

3.4. DSC thermograms

The changes of crystallinity and thermal behavior caused by grafting, were tested by differential scanning calorimeter. All samples were loaded into the system at 20 °C orderly, and thermograms were ran under N₂ atmosphere in temperature range of 20-200 °C with a heating rate of 20 °C/min. The melting heat (ΔH_m) for all samples was calculated from the area under the thermograms curves. Crystallinity of the grafted PP was calculated by the following formula:

$$\text{Crystallinity (\%)} = \frac{\Delta H_m}{\Delta H_{100}} \times 100 \quad (2)$$

ΔH_{100} is the melting heat of PP with 100% crystallinity, which equals 207.1 J/g. Figure 5, presents the DSC curves of the original PP (1), 13.8% GMA-g-PP (2), 30.1% GMA-g-PP (3), 68.4% GMA-g-PP (4). For all samples, although the shape of the thermograms remains almost identical, intensity of peaks decreases with the increase of the grafting yield. ΔH_m of all samples is obtained from the area under the thermograms curves. From curves (1) to (4), the values of ΔH_m were 114.4, 67.6, 60.8 and 45.6 J/g, respectively.

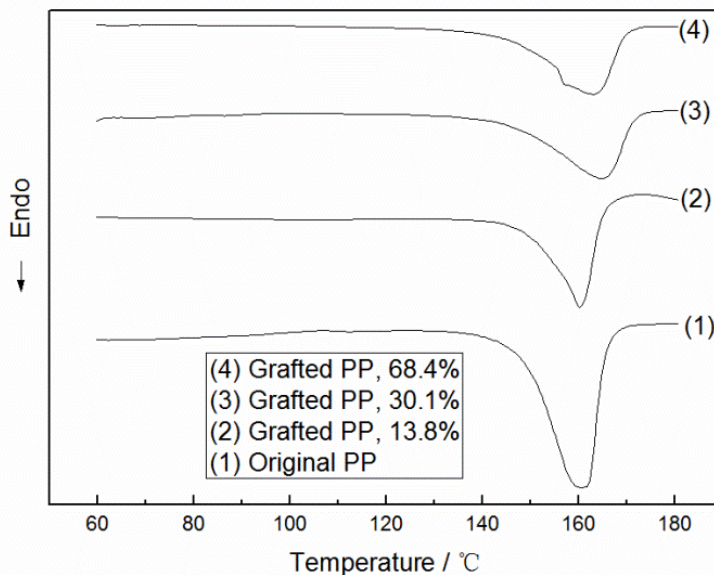


Fig. 5

Figure 5. DSC curves of original PP and grafted PP with different grafting yield

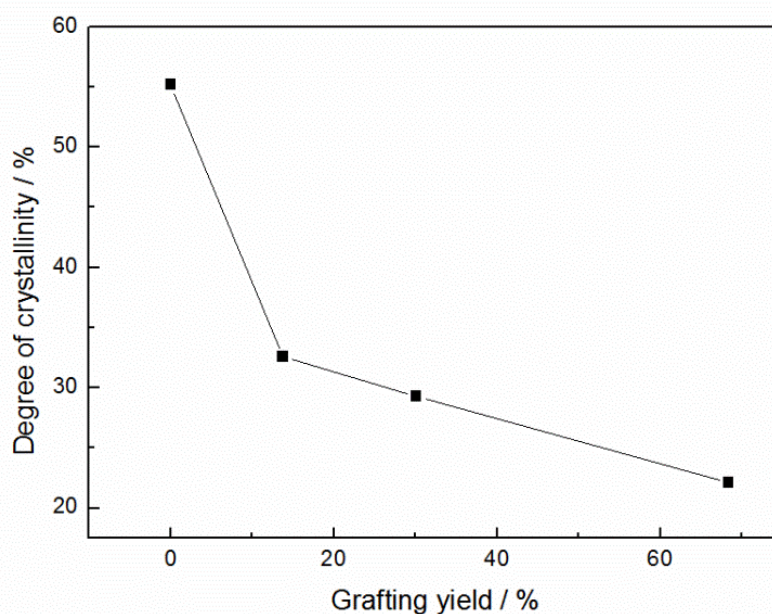


Fig. 6

Figure 6. The influence of grafting yield on degree of crystallinity

Figure 6 shows the relationship between degree of crystallinity of grafted PP obtained by Eq.(2) and grafting yield. Degree of crystallinity obviously reduced with increasing grafting yield. The grafting reaction occurred by the combination of amorphous poly glycidyl methacrylate chains in non-crystalline region of the original PP. Grafted polyglycidyl methacrylate chains hence gave rise to dilution effect on the intrinsic crystallinity of un-grafted PP, so ΔH_m and degree of crystallinity of grafted PP decreased with increasing grafting yield. The reduction of crystallinity and introduction of hydrophilic groups onto PP separator can obviously increase its absorbability towards liquid electrolyte and improve the separator property.

3.5. Morphology

Figure 7 showed the SEM pictures of original PP separator and PP separators modified by grafting of GMA with different grafting yield. The SEM images of original PP separator (Figure 7(a)) exhibited a net structure with a lot of pores which were distributed on the surface of original PP. Figure 7(b) indicated the formation of microporous structures on the surface of grafted PP. Comparing Figure 7(b) with Figure 7(a), it could be seen obviously that the surface of grafted PP separator became rougher. These result revealed that hydrophilic GMA was grafted onto surface of PP separator.

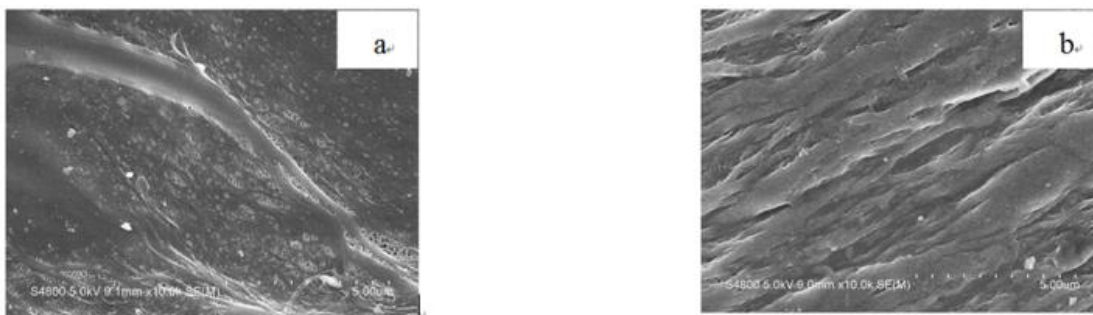


Fig. 7

Figure 7. Typical SEM micrographs of the original PP separator (a) and grafted PP separator with grafting yield 68.4% (b)

3.6. Thermal stability

Figure 8 demonstrated TGA curves of original PP (A), 30.1% GMA-g-PP (B) and 68.4% GMA-g-PP (C). An obvious change was observed for the thermal behavior of GMA-g-PP. In Figure 8 (B) and 8 (C), loss in weight was found at three different temperature regions. The first loss in weight at range of 30-140°C could be explained by the loss of water absorbed on the surface of PP. The second loss in weight at range of 240-350°C was due to loss of carbonyl groups or epoxy groups in graft copolymer. The third loss in weight which began at 350°C was attributed to the degradation of main chains of PP. For original PP, weight loss was only found at one temperature region beginning at 280°C and ending at 440°C, which was due to the degradation of PP. Compared Figure 8 (B) with 8

(C), the higher is grafting yield, the higher is residual weight. The results clearly indicate that graft chain including epoxy groups provides catalytic impetus to the charring.

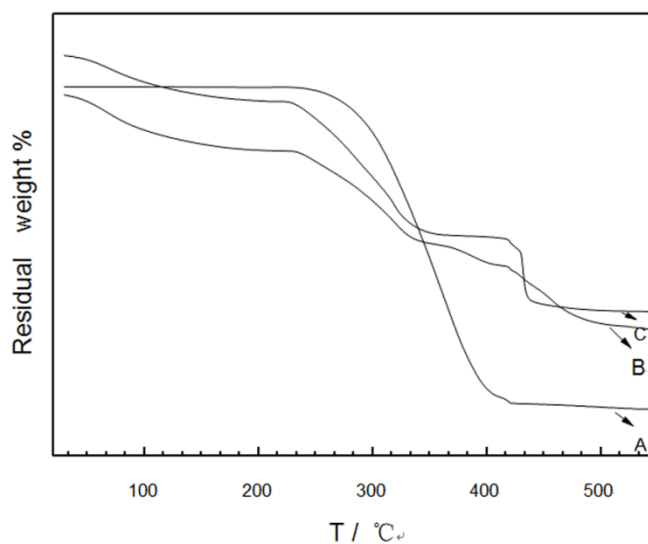


Fig. 8

Figure 8. Thermogravimetric curves of the original PP separator (A), grafted PP separators with grafting yield 30.1% (B) and 68.4% (C)

3.7. Liquid electrolyte uptake

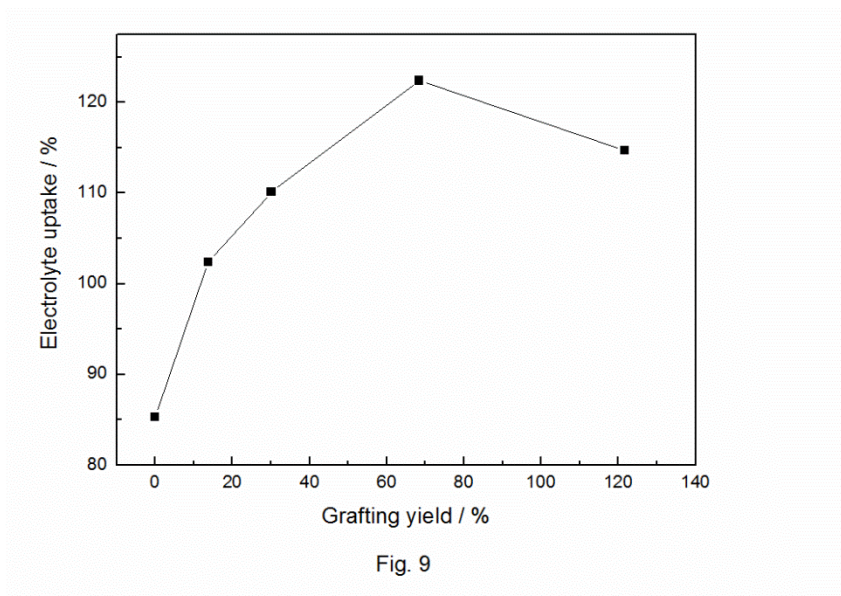


Fig. 9

Figure 9. The effect of grafting yield on liquid electrolyte uptake

Figure 9 shows the influence of grafting yield on electrolyte uptake which was measured at room temperature. Electrolyte uptake increased with an increase of grafting yield up to 68.4%, beyond which it decreased. At low grafting yield, the grafted PP could absorb much electrolyte because the

surface of PP functionalized by GMA had better absorbability towards liquid electrolyte than original PP separator. However, the decrease in electrolyte uptake at high grafting yield can be attribute to that the grafted layer became more compact, that impeded the swelling of grafted layer and hindered the diffusion of electrolyte inside of grafted layer [29].

3.8. Electrochemical property

In order to assess the electrochemical property of Li-ion cell, using grafted PP with different grafting yield and original PP separator, we assembled Li/PPs/LiCoO₂ cells. Figure 10 exhibits the relationship between discharge capacity and cycle numbers for the Li/PPs/LiCoO₂ cells be undergone to 30 cycles when original PP and grafted PP were served as separator respectively.

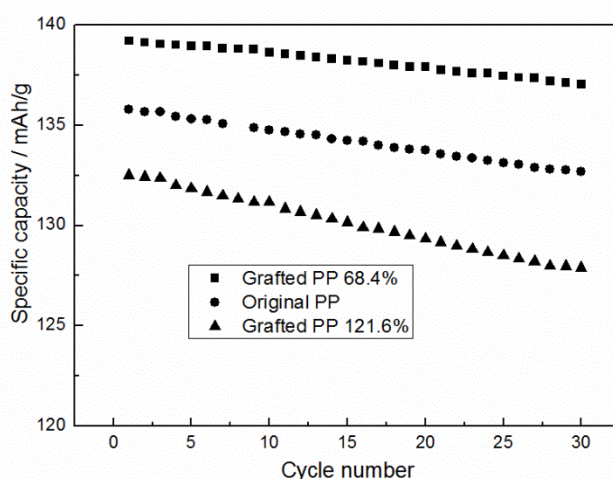


Fig. 10

Figure 10. The charge and discharge capacities of cell assembled with original PP separator and GMA-g-PP as a function of the cycle numbers

For all separators the initial specific capacities of testing cells were between 132.5 and 139.2 mAh/g. All cells assembled with original PP and GMA-g-PP separators indicated that the discharge specific capacities during a cycle decreased gradually because of the Jahn-Teller distortion of the cathode materials [30-31]. When cycling at 25 °C, all of cells showed relatively stable charge/discharge properties and had little capacity decay. After 30 cycles, the best cycling performance and the minimum decay in the capacity was found for the testing cell assembled with grafted PP with grafting yield 68.4%. The testing cell with original PP and grafted PP having grafting yield 121.6% showed discharge capacity fading of 2.33% and 3.47% at 30th cycle respectively. The testing cell with grafted separator having grafting yield 68.4% showed a discharge capacity decay of 1.56% at the 30th cycle. It can be concluded that the capacity retention of grafted PP with grafting yield 68.4% was much better than that of original PP and grafted PP with grafting yield 121.6%, and which showed discharge capacity decreased at high grafting yield. This different property generally attributes to absorptivity of electrolyte solution into the PP separators. The results are also consistent with the above results of

liquid electrolyte uptake. The grafted PP with grafting yield of 68.4% showed a better absorbability to a liquid electrolyte than original PP separator and grafted PP with grafting yield of 121.6%.

4. CONCLUSIONS

In practical application, Electron beam induced pre-irradiation grafting technique has been paid much attention because less homopolymer is formed than simultaneous grafting technique and the grafting can be conducted away from radiation sources at any time. Therefore, in this paper GMA-g-PP separators were successfully prepared by electron beam induced radiation. When PP was irradiated at 50 kGy or 100 kGy, the maximum grafting yield was obtained at concentration of GMA 15%. Grafting yield increased with increase of temperature until the maximal grafting yield 249.6% was attained at temperature 40°C, and then the combination of monomer radicals with increasing temperature resulted in lower graft yield.

The FT-IR test showed that GMA was covalently bound to original PP separator. Formation of microporous structures on the surface of grafted PP were observed by introduction of graft copolymer PGMA because the hydrophilic PGMA caused phase inversion during the grafting reaction. TGA results indicated carbonyl groups and epoxy groups were successfully grafted onto the PP separator. The degree of crystallinity decreased as grafting yield increased. The reduction of crystallinity can obviously improve the compatibility between liquid electrolyte and separator and enhance separator performance.

Most especially, the introduction of carbonyl groups and epoxy groups onto PP separator by pre-irradiation method offered a novel and convenient way for increasing hydrophilicity of commercial Li-ion battery separator. Electrolyte uptake increased with an increasing grafting yield up to 68.4% above which it decreased because grafted chains on the surface of grafted PP become denser at higher grafting yield. Li/PPs/LiCoO₂ cells fabricated by grafted PP separators with grafting yield 68.4% showed the best cycle performance. Meanwhile, GMA is one of multifunctional monomers which have easily modified epoxy groups. Considering the utilization of GMA-g-PP copolymer in other fields such as waste water treatment, adsorption of metallic ions and so on, the results of this study provided an effective approach for introducing reactive epoxy groups onto surfaces of polymers.

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