

## Thin-film type Li-ion battery, using a polyethylene separator grafted with glycidyl methacrylate

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### Abstract

For the improvement of organic electrolyte holding ability, the hydrophobic surface of a porous polyethylene (PE)-membrane separator was modified by grafting a hydrophilic monomer, glycidyl methacrylate (GMA), PE-g-GMA, by using electron beam technology, and applied to a thin film type Li-ion battery to elucidate the effect of a surface modification of a PE membrane separator on the cyclic life of Li-ion batteries. The Li-ion battery using the PE-g-GMA membrane separator showed a better cycle life than that of the unmodified PE membrane separator, indicating that the surface hydrophilicity of the PE membrane separator improved the electrolyte holding capability between the electrodes in the Li-ion cell and prevented the electrolyte leakage.

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### 1. Introduction

The secondary Li-ion batteries have been paid attention to wide-range applications of power source for the portable electronics, electric vehicle, and electric storage reservoir [1–13]. The Li-ion battery cells are consisted of anode, cathode and separator membrane, and the optimum combination of each component is very important to achieve the best performance of the Li-ion battery [1,2]. To our knowledge, the studies on the separator membranes have been poor even though a polyethylene (PE) separator membrane is commercially used in the Li-ion batteries. As a matter of fact, the separator membranes are considered to be a key component material in a Li-ion battery because it affects an electrolyte filling process in the battery manufacturing process as well as the battery performance, e.g., cycle life [2]. One of the disadvantages of the PE separator membrane that is based on polyolefin is its

hydrophobic surface with low surface energy because it is difficult to absorb and hold the organic solvents with high dielectric constant, such as ethylene carbonate (EC), propylene carbonate (PC), etc. between a positive and a negative electrode in a battery cell. The decrease in cycle life may be due to the electrolyte solvent leakage from between electrodes to near tab, or the opposite side of the current collectors.

To overcome these disadvantages, the surface of hydrophobic PE membrane has to be modified with adequate hydrophilic monomer to increase its surface energy to absorb electrolyte solvents. For the effective surface modification of PE-based separator membrane, radiation-induced graft polymerization is superior to other grafting techniques, such as those, using plasma, light, and chemicals, because the high density of the electron beams can create a large amount of radicals of arbitrary shapes and qualities of the polymer uniformity over the entire sample [14]. This technique has been commercialized for the production of the ion-exchange membranes as a battery separator and hydrophilized hollow-fiber membrane for microfiltration of protein solutions [14].

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In this work, we prepared the grafted PE membrane with the hydrophilic monomer, glycidyl methacrylate (GMA), PE-g-GMA, by using electron beam technology, and applied it to a thin film type Li-ion battery to elucidate the effect of the PE membrane on the cyclic life of Li-ion batteries.

## 2. Experimental

The reagent grade glycidyl methacrylate (GMA) was used without further purification. Deionized water and reagent grade methanol were used as solvents.

Details concerning the EB irradiation and grafting are given elsewhere [14]. In short, the EB irradiation was performed with 1 MeV electron accelerator and electric current of 5 mA at 50 °C under a nitrogen atmosphere. The PE membrane samples were irradiated to a dose of 30 Mrad on a cooling plate kept at 25 °C in an argon atmosphere. After intermittent storage in liquid nitrogen, the irradiated PE membrane was immersed to a glass ampoule, containing 20 wt.% GMA monomer that was previously degassed with bubbling nitrogen gas. After the GMA was grafted onto the electron-beam irradiated PE in the liquid phase for 10 min at 50 °C, the PE membrane separator (hereafter referred as PE-g-GMA) was washed in a solution mixture of water and methanol and dried in a vacuum oven at room temperature. The degree of grafting is the percentage increase in weight to graft GMA into the PE separator membrane. The dried membrane was transferred into a glove box and soaked in the electrolyte solution, 1 M LiPF<sub>6</sub> in EC/DMC (1:1 by volume, Samsung Cheil Industries, battery grade), for 10 min to wet the membrane. To investigate the difference between grafted PE and unmodified PE in the Li-ion battery cell performance, we fabricated thin film type batteries of an MCMB/PE-g-GMA/LiCoO<sub>2</sub> and a MCMB/PE/LiCoO<sub>2</sub> with an area of 1 cm × 1 cm. The cells were then enclosed in a metallized plastic bag and vacuum-sealed. All assemblies of the cells were carried out in the dry box filled with argon gas. The charge and discharge cycling tests of the Li-ion cells were galvanostatically conducted, using Toyo battery test equipment (TOSCAT-3000U).

## 3. Results and discussion

The infrared spectra of PE-g-GMA and PE separator membranes are shown in Fig. 1. It is observed in Fig. 1 that the C=O peak of GMA in the PE-g-GMA, which is shown in Fig. 2, is present at 1700 cm<sup>-1</sup>. This means that the surface of PE separator membrane was modified successfully with GMA. This result is consistent with the fact that there was an increase in weight fraction to approximately 0.2 wt.% in the PE-g-GMA separator after the grafting reaction.

In order to investigate the wetting ability of electrolyte solvents on the PE-g-GMA separator membrane, 1 M LiPF<sub>6</sub> in EC/DMC was poured on the surface of separators. Fig. 3 shows their photographs obtained by optical microscope. It

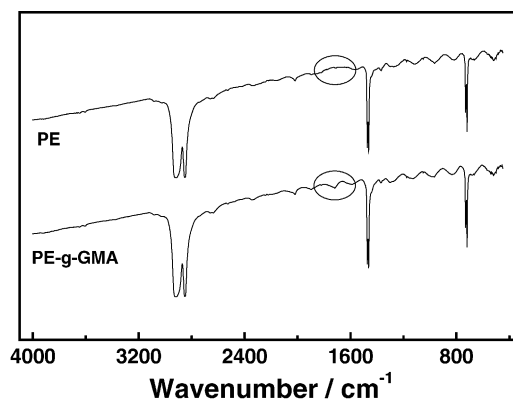


Fig. 1. Infrared spectra of PE-g-GMA and PE separator membranes.

is clearly observed from a drop-like electrolyte shape on the unmodified PE surface in Fig. 3(a) that the electrolyte solvent is not capable of wetting the unmodified PE separator membrane completely. However, the electrolyte solvent is capable of wetting the PE-g-GMA film as seen in Fig. 3(b), which means that the PE-g-GMA separator membrane has a high surface energy to be wetted sufficiently. The contact angles of the unmodified PE and the PE-g-GMA were measured to be approximately 70° and 5°, respectively, indicating that the surface energy of PE separator can be greatly increased with grafting with polar GMAs.

Li-ion cell with PE-g-GMA separator membrane was subjected to the charge discharge tests after preconditioning with cut-off voltages of 4.2 V for the upper limit and 2.8 V for the lower limit at C/5 rate. The cells contained the optimum electrolyte solution of 2.43 ml/g of cathode material to evaluate the membrane surface modification effect. If a cell has over the optimum amount, it would be difficult to evaluate solvent holding effect of the surface treatment of membrane because of the excess amount of an electrolyte. The typical

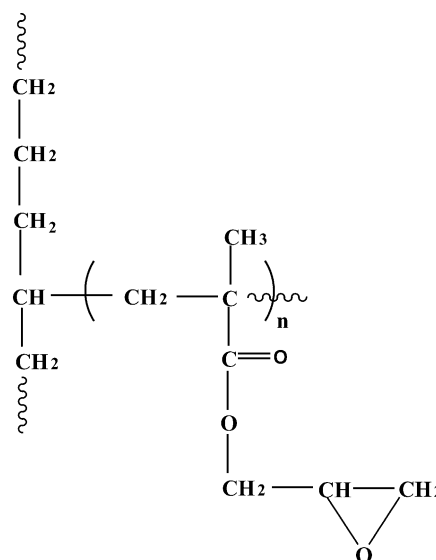


Fig. 2. Chemical structure of PE-g-GMA.

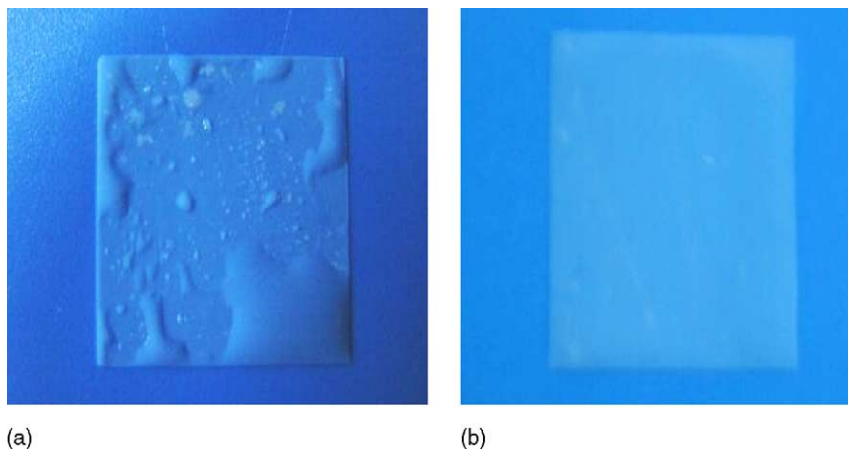


Fig. 3. Photographs ( $\times 1$ ) of PE-g-GMA, (a) and unmodified PE and (b) separator membranes obtained by optical microscope. 1 M LiPF<sub>6</sub> in EC/DMC was poured on the surfaces of the separators.

charge/discharge curves were clearly observed as shown in Fig. 4. This cell initially delivered a discharge capacity of over 145 mAh/g based on the LiCoO<sub>2</sub> material in the cathode. The coulombic efficiency, which is defined as the ratio of the discharge capacity to charge capacity, approached to unit value.

In order to investigate the effect of the surface property of the separator membrane on the cycle life of the Li-ion cell, the repeated charge/discharge cycles were observed at C/2 rate and shown in Fig. 5. It is interesting that the cell with the PE-g-GMA membrane gave a higher discharge capacity than that of the cell with the PE membrane at C/2. This means that the cell with the PE membrane, need more amount of electrolyte solution to give full capacity. Also, it is clearly observed from Fig. 5 that the cycle life of the Li-ion cell, using PE-g-GMA is much better than that of using the unmodified PE separator membrane. It may be known that the cyclic life of the Li-ion battery cell is somehow dependant on battery cell type, such as a thin film type, cylindrical shape, etc. The low cyclic life of the test cell with the PE membrane may be originated from the thin film type shape packed in vacuum in which the

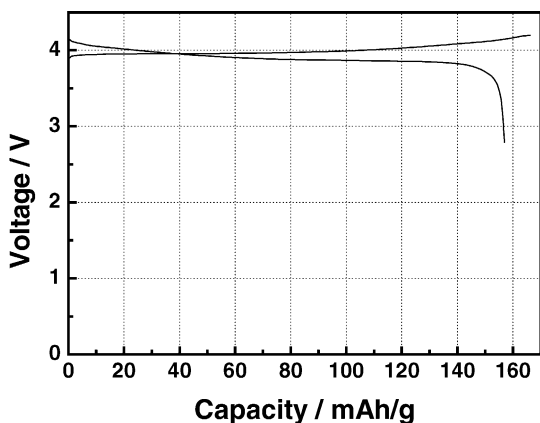


Fig. 4. Charge–discharge profiles of a thin film type Li-ion battery with PE-g-GMA separator.

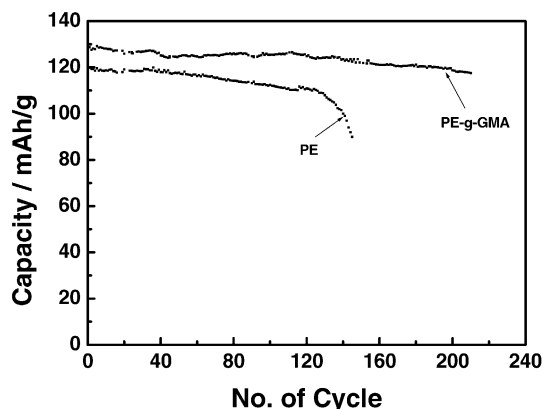


Fig. 5. Cycling performance of Li-ion batteries, using PE-g-GMA and PE separator membranes.

electrolyte solvent leakage may be easy due to the vacuum state in the cell, compared to a rectangular or a cylindrical shape packed in metal container. Thus, this result suggests that the longer life of the cell with the surface modified PE-g-GMA separator membrane is due to a higher surface energy of the membrane to prevent solvent leakage from between the electrodes.

#### 4. Conclusion

We have prepared the surface modified PE-g-GMA separator membrane with the grafting reaction of GMA by using the EB technology to improve the wetting ability of electrolyte solvents and applied it to a thin film type Li-ion battery. The Li-ion battery, using the PE-g-GMA separator, showed a much better cycle life than that of the unmodified PE membrane separator, indicating that the increased hydrophilicity of PE membrane separator improved the electrolyte holding capability between the electrodes in the Li-ion cell to prevent electrolyte leakage.

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