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Review

Surface-Modified Membrane as A Separator for Lithium-Ion Polymer Battery

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Abstract: This paper describes the fabrication of novel modified polyethylene (PE) membranes using plasma technology to create high-performance and cost-effective separator membranes for practical applications in lithium-ion polymer batteries. The modified PE membrane via plasma modification process plays a critical role in improving wettability and electrolyte retention, interfacial adhesion between separators and electrodes, and cycle performance of lithium-ion polymer batteries. This paper suggests that the performance of lithium-ion polymer batteries can be greatly enhanced by the plasma modification of commercial separators with proper functional materials for targeted application.

Keywords: battery; membrane; plasma; separator; surface modification

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1. Introduction

As there is a growing demand for high-performance rechargeable batteries used in portable electronic equipment, mobile products, and communication devices, the lithium-based batteries as a power source are of great scientific interest. Among many types of rechargeable batteries, the lithium-ion polymer battery (LIPB) has potential to be used in a broad range of industries, because it can be produced in a variety of forms, thus making it possible to fabricate readily portable batteries in the required shapes for various electronic applications [1].

In LIPB, the separator placed between the cathode and the anode is one of critical components. Its primary function is to effectively transport ionic charge carriers between two electrodes as an efficient ionic conductor as well as to prevent the electric contact between them as a good electric insulator [1–3]. The separators must be chemically or electrochemically stable and have mechanical strength sufficiently enough to sustain the battery-assembly processes because the separator has a significant effect on the manufacturing process and the performance of LIPB [3–5]. Commercially available polyolefin separators have good mechanical and thermal properties and effectively prevent thermal runaway caused by the electrical short-circuits or rapid overcharging. However, these separators do not readily absorb the electrolyte solvents with high dielectric constants, such as ethylene carbonate (EC), propylene carbonate (PC), and γ-butyrolactone (GBL), because of their hydrophobic surfaces with low surface energy, and they have poor ability to retain the electrolyte solutions [6,7]. In addition, the solvent leakage from the interfaces between the electrodes or the opposite sides of current collectors often causes the deterioration of the cycle life of LIPB [8].

To overcome these drawbacks of conventional polyolefin separators, much research has been undertaken to develop alternative separators that are compatible with polar liquid electrolytes and stable with electrode materials [9–12]. A number of efforts have been made to achieve high-performance polyolefin separators by coating them with the gel polymer electrolyte (GPE) to improve compatibility with various electrolyte solutions as well as the electrochemical properties of LIPB [13–15]. Although these surface-modified polyolefin separators exhibit good mechanical and thermal properties as well as the degree of compatibility with electrolyte solutions, they still have several disadvantages, such as complex multi-step processes and relatively expensive modification of the surface of hydrophobic polyolefin separators with adequate hydrophilic monomers to increase the surface energy enough to absorb the electrolyte solutions. Among the numerous methods of surface modification of polyolefin separators, the radiation process is one of the most promising methods due to the rapid formation of active sites for initiating the reaction through the polymer matrix and the uniformity of polymers over the entire specimen [16]. The plasma process is a preferred and convenient technique when considering a large scale production or commercialization of the membrane. However, to date, studies on the surface modification of polyolefin separators using the plasma technology have rarely been investigated.

This paper focuses on the enhancement of the cycle performance of LIPB with the benefit of plasma technology. We begin with a brief summary of the research activities of the surface modification of polyolefin membranes and their structural and physical properties. Subsequent sections discuss the fabrication of novel modified PE membranes by means of the plasma-induced coating process. We expect that this study will help in preliminary evaluation and understanding of the plasma-modified PE membrane as a separator for LIPB and its possible realization. This paper suggests that the modified PE membrane via plasma treatment holds great potential to be utilized as a high-performance cost-effective separator for LIPB. Finally, we conclude this review with personal perspectives on future directions in the fundamental research as well as potential applications using plasma-induced coating technology.

2. Fabrication of Separator for LIPB

2.1. General Features

The separator is a critical component in LIPB, and its primary function is to facilitate ionic transport between the electrodes as well as to prevent the electric contact of two electrodes. However, the presence of the separator in LIPB induced the electrical resistance and limited space inside the battery to satisfy the need for slimming and safety, which significantly influences the battery performance. Therefore, the fabrication of high-performance separators plays an important role in controlling the overall performance of LIPB, including high power or energy density, long cycle life, and excellent safety. A number of factors influencing the performance of LIPB must be considered in achieving high-performance separators for the battery applications. Among a wide variety of properties for the separators, the following criteria are required to fabricate the separators for LIPB [1–5]: (a) electronic insulator, (b) minimal electric resistance ($<2\ \Omega\text{cm}^2$), (c) dimensional stability (shrinkage: <5%), (d) mechanical strength enough to allow the assembly process (tensile strength: $>1500\ \text{kg/cm}^2$), (e) chemical stability against degradation by electrolyte or electrode reactants (should be stable for long cycle life), (f) effective prevention of the migration of particles or soluble species between the electrodes, (g) good wettability in electrolyte solution (should be wet completely in liquid electrolytes), and (h) uniform thickness and pore distribution (thickness: <25 μm; pore size: <1 μm; porosity: ~40%). Because the exhaustive description of all separator membranes for LIPB is beyond of the scope of this paper, readers are referred to excellent review papers [4,5] on the general features of porous membranes as the separators for LIPB and various fabrication processes as well as the relationships between structure and properties of separator membranes.

Most of microporous membranes currently used in LIPB is based on polyolefin resins, including polyethylene (PE), polypropylene (PP) and their blends or multilayer forms such as PE-PP and PP-PE-PP [17–21]. Usually, a microporous polymer membrane as a separator for LIPB can be fabricated by dry and wet processes, including the extrusion step to make thin films and the orientation steps to impart porosity and increase mechanical strength [22,23]. The separators made by dry process show a distinct slit-pore and straight microstructure, while those made by wet process exhibit interconnected spherical or elliptical pores [4,5]. The dry process for polymers with high crystallinity consists of the following steps [24–27]: (a) the extruding step (polyolefin resins are melt-extruded into a uniaxially oriented film), (b) the annealing step (to improve the size and lamellar crystallites), and (c) the stretching step (*i.e.*, annealed films are deformed along the machine direction by three sequential processes of cold stretching to create the pore structure, hot stretching to increase the size of pores, and relaxation to reduce internal stresses within the films). Consequently, the porosity of microporous membranes depends on morphology of films, annealing conditions and stretching ratios [4,5]. The wet process for both crystalline and amorphous polymers can be performed as follows [28–32]: (a) the mixing of hydrocarbon liquid and other additives with polyolefin resins and heating, (b) the extrusion of the heated solution into a sheet, orientating the sheet uniaxially or biaxially, and (c) the extraction of the liquid with a volatile solvent to form the microporous structure [22,33]. For semi-crystalline polymers, the stretching step can be performed before/after the extraction step to achieve high porosity and large pore size [34]. The characteristics of commercial polyolefin-based microporous membranes used in LIPB are summarized in Table 1. Celgard separators are single layer of PE or PP and their trilayer structures, while Asahi and Tonen separators are single layer of PE manufactured via the wet process. However, commercially available polyolefin separators cannot satisfy the enhanced battery characteristics and stability accompanied by the need for sliming various electronic devices required in the practical industrial fields. In addition, they cannot be wetted easily organic electrolyte solutions with high dielectric constant usually used in LIPB, and have poor ability in conserving the electrolytes during the repeated cycling process. Further, they have a shortcoming since it causes a phenomenon of leaking organic electrolyte solutions between electrodes or separators, thereby lowering the cycle life performance of LIPB. Accordingly, the physical properties of polyolefin separators must be improved in order to be applied as the separators for high performance and safety LIPB.

Table 1. Physical properties of commercial polyolefin membranes as the separators for LIPB. Adapted with permission from Reference [4]. © 2004 American Chemical Society.

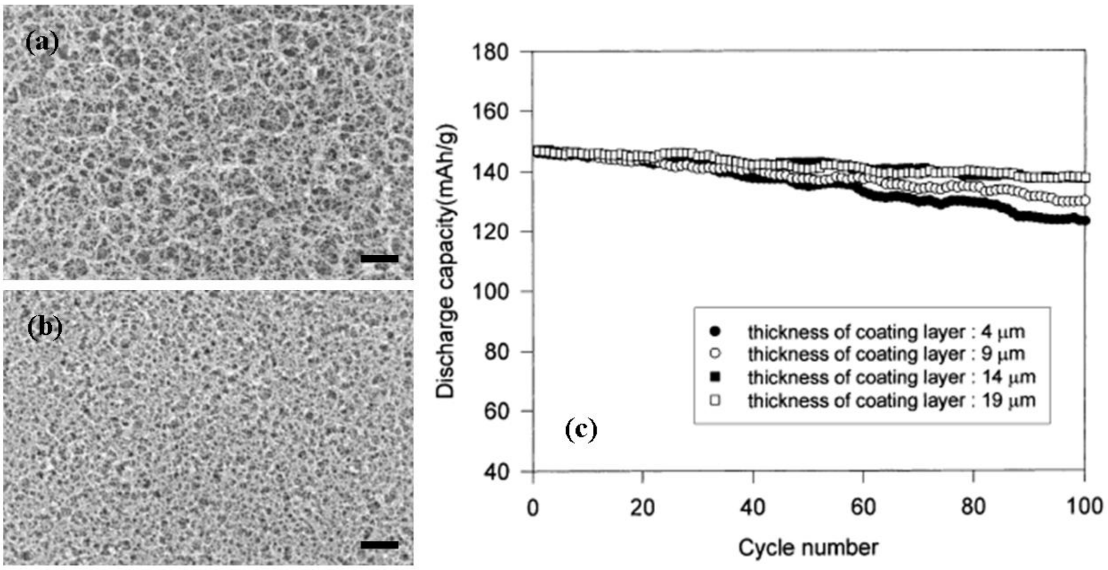
	Commercially available separator membranes				
Characteristics	**Celgard 2730**	**Celgard 2400**	**Celgard 2325**	**Asahi Hipore**	**Tonen Setela**
Structure	single layer	single layer	trilayer	single layer	single layer
Material	PE	PP	PP-PE-PP	PE	PE
Thickness (μm)	20	25	20	25	25
Ionic resistivity (Ω/cm)	2.23	2.55	1.85	2.66	2.56
Porosity (%)	~43	~40	~42	~40	~41
Melting temperature (^{o}C)	~135	~165	135/165	~138	~137

2.2. Surface Modification of Separators for LIPB

Surface modification of polyolefin membranes is necessary to make them hydrophilic, because of their inherent hydrophobic properties, leading to poor wettability and electrolyte retention against electrolyte solutions containing polar solvents [6]. The modification has been performed by treating the separator with a wetting agent or grafting hydrophilic functional groups onto the surface and pores of the separators [35–41]. The use of a surfactant generally improves wettability, but it is unable to increase electrolyte retention. Taskier [35] combined a surfactant and a hydrophilic cellulose acetate together to treat polyolefin membranes for enhancing the electrolyte retention and wettability. In general, the treatment of porous membranes using the surfactants makes the membranes hydrophilic temporarily since the surfactants are subjected to washing away by liquid electrolytes upon the repeated cycling or storage. For this reason, the permanent grafting of hydrophilic functional groups is highly desirable for the surface modification of polyolefin membranes. The porous polyolefin membranes can be modified chemically via sulfonation, fluorination, and graft-polymerization. For graft-polymerization initiated by UV-irradiation, the monomers polymerize and graft onto the surface of polyolefin membranes in the presence of a photo-initiator used to increase the sensitivity of polymers to UV-irradiation. In the case of the continuous UV-induced grafting process developed by Senyarich and Viaud [37], porous polyolefin membrane was first passed through the solution bath containing the monomers and photo-initiator, and then the wetted membrane was moved into the UV-chamber where the UV-induced graft polymerization was initiated by UV-irradiation. The uptake and retention of liquid electrolytes was also influenced by the degree of grafting and the type of monomers.

The interfacial adhesion between separators and electrodes is a critical factor in determining the long-term performance of LIPB. Even a small failure at the interface can cause significantly uneven current distributions because of high contact resistance in the failure areas, leading to the formation of dendritic lithium on the negative electrode and the increase in the battery impedance. For improving the interfacial adhesion, a thin polymer layer such as poly(ethylene oxide) (PEO) and poly(vinylene fluoride) (PVDF) can be gelled by liquid electrolytes to coat the surfaces of polyolefin membranes [14,42–44]. In these methods, GPE formed upon gelling with liquid electrolytes serves as the adhesives to bond the separator and electrodes, which increases the uptake and retention of liquid electrolytes. The surface polymer coating of microporous membranes has been performed by dipping or spraying, in which a heating step should be required for promoting the formation of GPE in practical fabrication process. However, these methods have a negative effect on the performance of separators for LIPB, because structurally dense polymer layers may block the penetration of liquid electrolytes into the pores of microporous membranes. Therefore, polymer layers with porous structures are highly desirable for facilitating the electrolyte filling process.

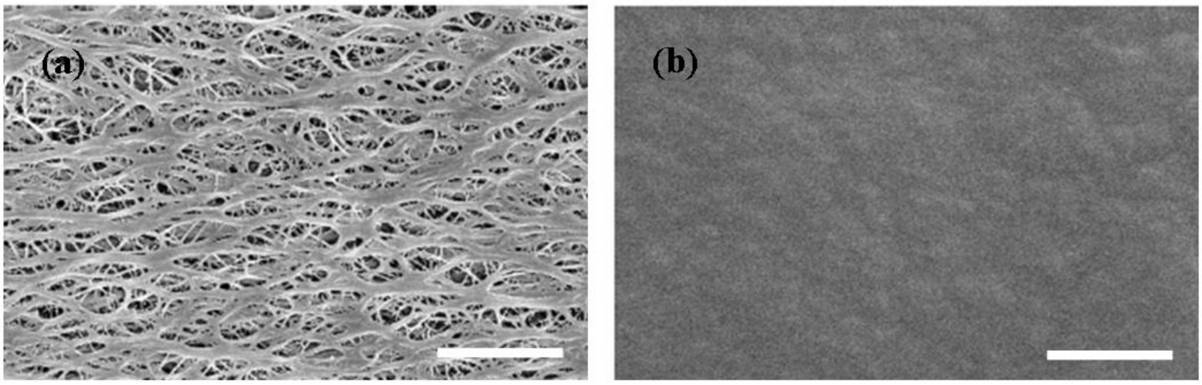
Figure 1. SEM images of polymer-coated PE separators prepared with (a) 1 wt% and (b) 3 wt% of polymer concentrations (scale bar: 5 μm). (c) Discharge capacity of LIPB cells fabricated with the modified PE separators of different gel layer thickness with the cycle number. Adapted with permission from Reference [45]. © 2004 Elsevier Ltd.



The dip coating and phase inversion methods have been proposed to form the microporous polymer layer [45]. The PE membranes were coated with the gellable acrylonitrile (AN)–methyl methacrylate (MMA) copolymer, and then were immersed in the water-bath to induce the phase inversion, leading to the formation of polymer layers with highly microporous structure via phase inversion method. The pore size of the polymer-coated PE separator decreases with increasing the polymer concentration of dipping solution (Figure 1), and the presence of micropores on their surface can lead to the efficient uptake of liquid electrolytes when it is soaked in the electrolyte solutions. The cycling performance of LIPB cells depends on the thickness of gel layer as shown in Figure 1(c). The AN-MMA copolymer coated on both sides of PE separators can adapt to encapsulate the electrolyte solutions in the porous membranes and can further assist in adhering to the separator. Consequently, the LIPB cells fabricated with surface-modified PE separators show stable capacity retention and excellent rate performance, resulting from the strong bonding between separators and electrodes. Kim *et al.* [46] also reported that the presence of hydrophilic SiO_2 as an inorganic filler in the polymer coating layers significantly reduced the contact angle of liquid electrolytes and enhanced their wetting to the separator. The LIPB cells fabricated with the modified separator exhibit excellent capacity retention and rate performance due to the improved interfacial characteristics.

Microporous polyolefin membranes can be also employed as dimensional supports to improve the mechanical strength of GPE. The impregnation of GPE into the pores of membranes has been performed mostly through dipping method [15,47,48] and *in situ* polymerization [13,49]. In the dipping method, GPE can be easily impregnated into the small pores of membrane at elevated temperature, and the impregnation of GPE can be conducted by applying the solution of GPE in aprotic solvents onto the microporous membrane, followed by the evaporation of solvents to obtain the GPE-impregnated membrane. Kim *et al.* [48] reported the fabrication of LIPB using highly porous membrane filled with solvent-free polymer electrolytes, in which the polymer electrolytes was prepared by penetrating highly conductive polymer electrolytes into the pores of PE separators, which are characterized by highly porous structure with a nominal thickness of 18 m and porosity of ~50%. The pores of PE separators filled with polymer electrolytes become fully covered by polymer electrolytes (Figure 2). The sticky polymer electrolyte plays an effective role of an ionic conduction inside of the separator and can assist in the enhancement of the interfacial adhesion between separators and electrodes. For *in situ* polymerization, Abraham *et al.* [13] reported the impregnation of GPE by UV-irradiation of microporous membranes soaked with electrolyte solutions. The GPE-impregnated membrane offers better protection against internal short circuit than GPE alone, resulting in more stable capacity retention of the prepared cells.

Figure 2. SEM images of (a) PE and (b) PE separators filled with polymer electrolyte (scale bar: 5 μm). Reproduced with permission from Reference [48]. © 2006 Elsevier Ltd.



2.3. Plasma Treatment Techniques

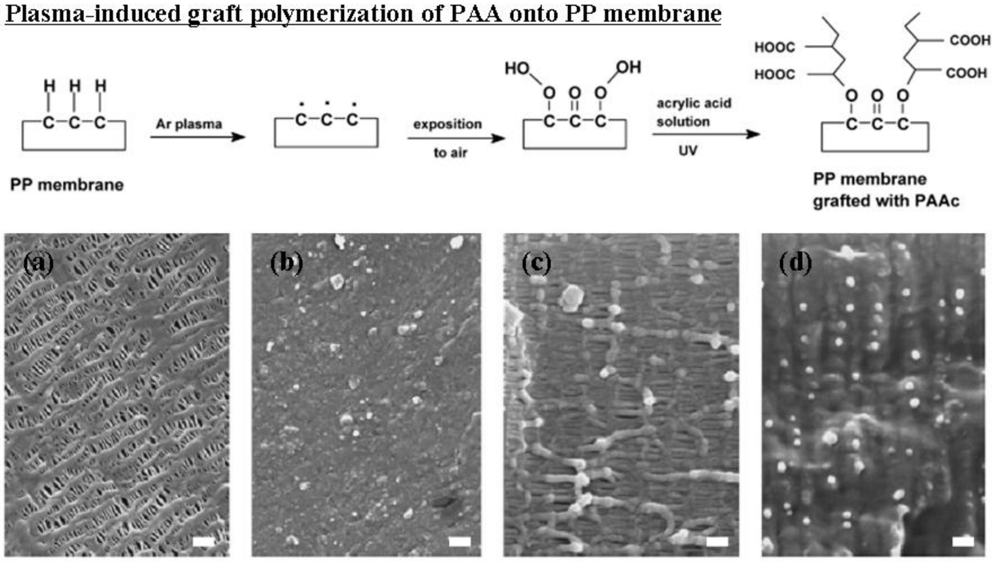
Plasma treatment methods have been developed to modify polymer surfaces for enhanced adhesion, wettability, printability, dye-uptake, *etc.*, and the plasma process modifies the surfaces on only several molecular levels, thus allowing the surface functionalization of polymers without sacrificing their appearance and bulk properties [50]. Plasma is a chemical process and its chemistry determines on polymers. Among several plasma processes, cold gas plasma treatments are used in processing of them. Cold gas plasma generally has very low temperature (300~600 K) and particle density of 10^{10}~10^{12} no./cm^3, suitable for modifying polymer materials [51]. Exposing gases to sufficient electromagnetic power dissociate them, creating a chemically reactive gas that modifies the exposed surfaces. At the atomic level, plasma consists of ions, electrons, and various neutral species at different energy levels. One of the excited species is the free radical, which can directly react with the surface of polymers, leading to remarkable modification to their chemical structures and properties. The generated ions and electrons collide with the atoms of surfaces, and transfer energy to form more radicals, ions, and atoms. The general reactions induced via cold gas plasma, depending on the substrate, gas chemistry, reactor design, and operating parameter, are as follows [50–52]: (a) cleaning to remove organic contamination from the surfaces, (b) ablation or etching of materials form the surface of polymer to remove a weak boundary layer and increase the surface roughness and area, (c) crosslinking of near-surface molecules, to cohesively strengthen the surface layers, (d) activation by creating reactive sites, grafting of chemical moieties and functional groups to modify the chemical structures of polymer surfaces, and (e) polymerized deposition of thin polymeric films on the surface. Various gases used for plasma reactions are presented in Table 2.

Table 2. Various gases used for plasma reactions.

Plasma reactions	Gas
Cleaning	Oxygen
Ablation / Etching	Argon, Helium, Oxygen
Crosslinking	Oxygen-free noble gases such as argon and helium
Activation	Ammonia, Argon, Helium, Nitrogen, Tetrafluoromethane
Polymerization	Fluoro-monomers (Hexafluoroethylene, Perfluoroallylbenzene, Pentafluorostyrene, *etc.*) Acrylic-monomers (Acrylic acid, Acrylonitrile, Alkyl acrylates, *etc.*)

As oxygen gas plasma breaks the C-C bonds of polymers, volatile monomers or oligomers ablate at shorter molecules, and they are cleaned with the exhaust. After cleaning, the plasma begins ablating the top layer of polymers. Amorphous and crystalline regions will be removed at different rates, producing the surface topology with a view to increasing the mechanical adhesion. On the contrary, noble gases such as argon and helium generate the free radicals on the surface and they react with adjoining radicals of molecules to form the crosslinks. This process increases the strength, the temperature resistance, and the solvent resistance of the surface of polymers. Unlike ablation and crosslinking, a certain gas or mixture of gas generates the free radicals on the surface and then react with radicals of functional molecules in the plasma by covalent bonding. In particular, oxygen and tetrafluoromethane gas plasma do oxidative reaction and form polar groups such as carboxyl, hydroxyl, and hydroperoxyl on the molecules. This oxidation increases the surface energy and enhances the hydrophilicity and the wettability of polymers. If use with substances such as fluoro-monomers and acrylic-monomers, the polymerization will take place. This process provides the permanent coating of thin films on the surface of polymers. In general, fluoro-monomer gas plasma provides a low surface energy and hydrophobic surfaces, while acrylic-monomer gas plasma induces permanent hydrophilicity and wettability without mixing of other gases.

Figure 3. (Top) Schematic drawing of surface modification of microporous PP membranes via plasma-induced graft polymerization of PAA onto PP membrane. (Bottom) SEM images of surfaces [(a) and (b)] and cross-sections [(c) and (d)] of PP [(a) and (c)] and surface-modified PP membrane (b) and (d)] (Scale bar: 1 μm). Adapted with permission from Reference [56]. © 2007 Elsevier Ltd.



Recently, a number of efforts have been made up to develop the performance of separators by means of the plasma treatment technique, because it is very efficient techniques to modify the surface properties of polymer membranes without producing impurities or sacrificing their properties. Kubota [53] treated PP separator films with nitrogen gas plasma to create polymeric radicals for utilizing the graft polymerization-initiating sites, followed by the immersion with acrylic monomer solution and polymerization at 65 °C, and the resultant separators showed the increased ionic conductivity. For nikel-metal secondary battery, Tsukiashi *et al.* [54] modified PP non-woven fabric separators by means of the technique of gas plasma treatment using several gases such as oxygen, nitrogen, and argon to increase their surface hydrophilicity and they reported that the modified PP non-woven separators with the contact angle below 100^{o} showed the increased capacity retention. Ciszewski *et al.* [55,56] reported the plasma-induced graft polymerization of poly(acrylic acid) (PAA) under UV irradiation using commercial PP microporous membranes for nickel–cadmium (Ni-Cd) battery. In their approach, depicted schematically in Figure 3, PP membranes were modified by argon plasma treatment to create grafting sites, followed UV irradiation to covalently-bond acrylic acid to the surface of PP membranes. SEM images clearly revealed the changes of the surfaces of modified PP membranes occurred during plasma-induced graft polymerization of PAA onto PP membranes: the holes that observed on the surface of unmodified PP membranes disappear and they are covered the layer of PAA deposited on the surface of modified PP membranes. They suggested that hydrophobic surfaces of PP membranes changed into hydrophilic via this plasma-induced graft polymerization process and the surface-modified PP membrane as a separator for Ni–Cd cells showed good mechanical properties and very low electrolytic area resistance. Choi *et al.* [57] reported that the electrospun PVDF nanofibers treated with ethylene plasma provided the web surface with low melting PE layer, in which polymerized-PE layer acted as a shutter by melting at elevated temperature, thus contributing to the battery safety. More recently, Kim *et al.* [58] reported the fabrication of the plasma-modified PE membrane as a separator for LIPB, in which the surface of microporous PE membranes was modified with acrylonitrile via the plasma-induced coating process and the LIPB cells fabricated with the modified PE separators showed the enhanced cycling life and rate performance. In the following section, the modification of microporous PE membranes via the plasma-induced coating technique and the effect of the modified PE membranes on the cycle performance of LIPB were discussed in detail. We suggest that the performance of LIPB can be greatly enhanced by the plasma modification of commercial separator membranes with proper materials for targeted application.

3. Plasma-Modified PE Membrane as A Separator for LIPB

3.1. General Fabrication

To create high-performance and cost-effective separator membranes for practical applications in LIPB, we fabricated a novel modified PE membrane by coating the plasma-induced acrylonitrile onto the surface of PE membranes via plasma technology. Acrylonitrile was chosen as a polymeric coating material for the surface of PE membranes because of its chemical stability and ability to be easily wetted by electrolyte solutions for use in LIPB [59,60]. The system consists of the reactor equipped with the inner electrodes to which an alternating voltage was applied at a frequency of 13.56 MHz, an RF power supply with an impedance matching network, and a vacuum pump. Commercially available PE membranes were dipped in acrylonitrile solution, and subsequently, the dipped membranes were placed between the electrodes in the reactor where the plasma-induced coating was initiated by the plasma generation. Prior to starting up the plasma treatment, plasma reactor was evacuated, and argon gas was introduced into the reactor at a flow rate of 400 sccm using unit mass flow controller. Then, the vacuum pressure of the plasma reactor was maintained at a constant value of 10^{-3} Torr. The electrical power of the plasma was supplied by an RF power operating at 300 W and the treatment time was 10 min (for the detailed procedures, see ref. [58]).

To estimate the cycle performance of the LIPB cell, the cathode was prepared by coating the slurry consisting of 96% lithium cobalt oxide, 2% acetylene black, and 2% PVDF binder dissolved in a *N*-methyl pyrrolidone solvent onto aluminum foils. The graphite anode was prepared by coating the slurry of 94% graphite and 6% PVDF binder onto copper foils. The LIPB cell was assembled in the form of the aluminum pouch by sandwiching the unmodified or modified membranes between cathode and anode. After assembling the cell, polymer precursor solutions consisting of urethane acrylate and hexyl acrylate dissolved in the mixture of EC, ethyl methyl carbonate (EMC), and dimethyl carbonate (DEC) (EC:EMC:DEC = 3:2:5, by volume) containing 1.3 M lithium hexafluorophosphate ($LiPF_6$), were injected into the aluminum pouch, then was vacuum-sealed, followed by thermal curing to produce the cross-linked GPE (for the detailed procedures, see ref. [58]). The prepared LIPB cell was cycled once at 0.2 C rate to improve the wetting of GPE and to form stable solid electrolyte interphase layers on the electrode surface.

3.2. Surface Properties

XPS analysis was performed to clarify the surface elemental composition for PE membranes. All binding energies were referenced to C_{1s} neutral carbon peak at 284.6 eV. XPS spectrum of PE membrane exhibited the presence of only carbon, corresponding to C_{1s} core level. However, the modified PE membrane exhibited intense and narrow peak at 532.5 eV and very weak intensity peak centered at 400.5 eV, corresponding to O_{1s} and N_{1s} core levels, respectively, as well as C_{1s} core level for PE membrane as shown in Figure 4(a). XPS spectra of C_{1s} core level for the modified PE membrane can be decomposed into five contributions appearing at 284.6, 285.5, 286.2, 287.6, and 289.1 eV (Figure 4b). These observed peaks were assigned to C–C/C–H, C–O, C–N, C=O, and –COO groups formed on the surface of the modified PE membrane originating from PE membrane and AN. The –CH and $–CH_2$ (of pristine PE), oxidized (–C=O, –COO, –COC–), and –C=C– groups were reported to present in Ar plasma treated high density polyethylene [61]. The percentage contributions of C_{1s} components of the modified PE membrane are shown in Table 3. After the plasma-induced coating process, the contribution of the C–N groups in the XPS spectra of C_{1s} core level for the modified PE membrane was 7.55%, which was attributed to the presence of plasma-induced acrylonitrile (PiAN) in the modified PE membrane. This result demonstrates that the PiAN was effectively induced onto the surface of the modified PE membranes via plasma treatment.

Figure 4. (a) XPS spectra and (b) high resolution spectra of C_{1s} core level for the modified PE membranes. The inset of (a) shows N_{1S} core level spectra of the modified PE membranes. Reproduced with permission from Reference [58]. © 2009 Elsevier Ltd.

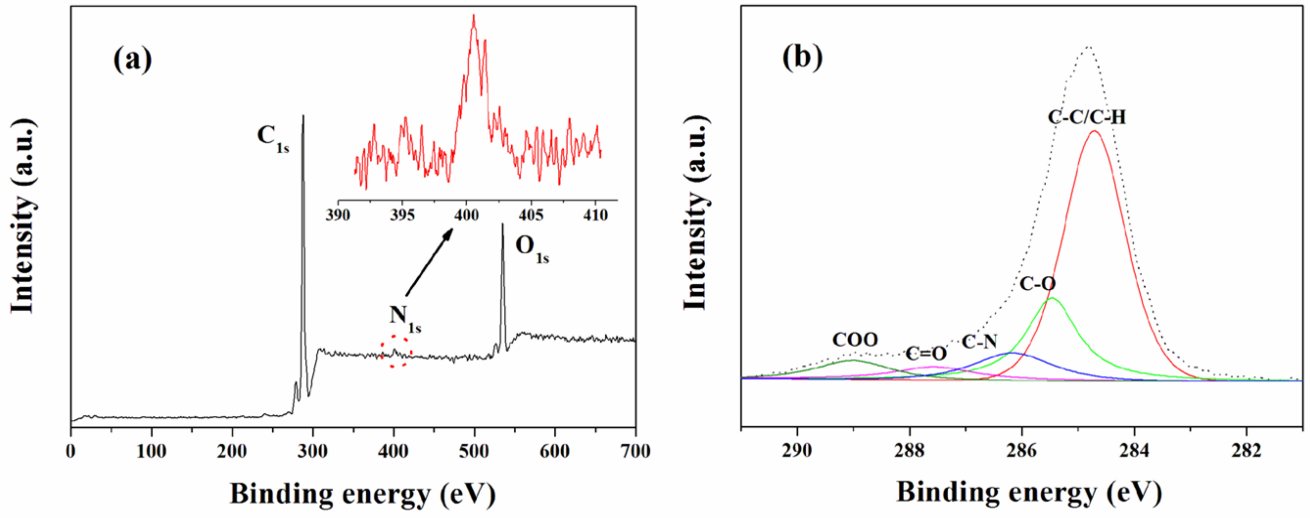
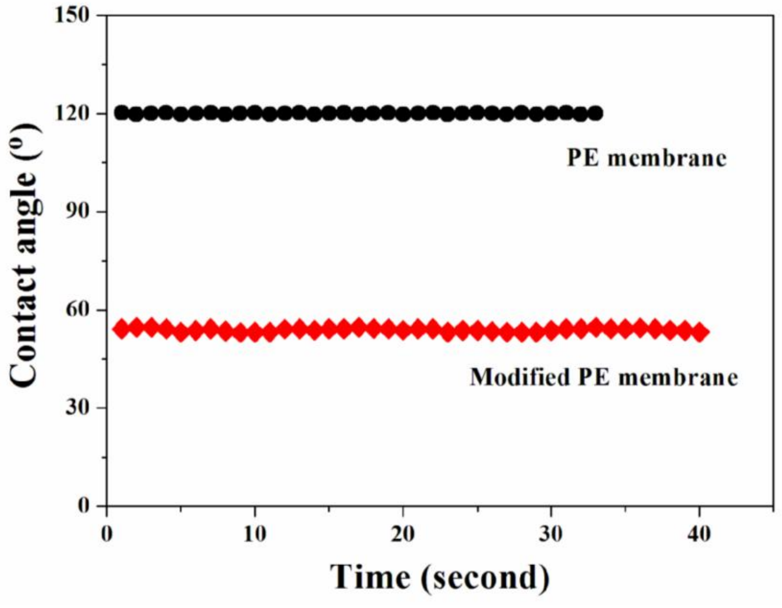


Table 3. XPS analysis of PE and the modified PE membranes. Reproduced with permission from Reference [58]. © 2009 Elsevier Ltd.

Materials	Functional groups (%)				
	C–C/C–H	C–O	C–N	C=O	C–O–O
PE membrane	98.37	1.16	-	0.26	0.21
Modified PE membrane	63.77	17.54	7.55	5.00	6.14

The contact angle measurements of PE and the modified PE membranes were conducted to clarify the effect of PiAN on the surface property of the membrane. The water contact angle was determined by means of the sessile drop method, and the water droplet was limited to about 0.5 μl to prevent gravitational distortion of its spherical profile. The surface energies of the membranes were calculated by measuring the contact angles of two testing liquids: water and diiodomethane on the surface of the membranes at room temperature. For LIPB, the wettability of the separator plays a critical role in the cell performance because the separator with good wettability can effectively retain the electrolyte solutions and facilitates the electrolytes to diffuse well into the LIPB cell assembly [1–5]. As shown in Figure 5, the contact angle of modified PE membranes significantly decreased, implying that the modified PE membrane has better wettability as compared to PE membrane. This result demonstrates that the surface energy of the modified PE membrane increased by the presence of PiAN on the membrane surfaces effectively induced via plasma treatment. Thus, it is expected that the presence of PiAN on the surface of the modified PE membranes makes it possible for them to have high surface energy to be wetted more sufficiently in the electrolyte solution as compared to PE membrane.

Figure 5. Water contact angles of PE and the modified PE membranes. Reproduced with permission from Reference [58]. © 2009 Elsevier Ltd.



The surface energy and its polar component of PE and the modified PE membranes can be estimated from the Qwens–Wendt equation modified by Fowkes and Kinloch [62–65]:

$$(1+\cos\theta)\gamma_{LV} = 2\sqrt{\left(\gamma_{LV}^{d}\cdot\gamma_{S}^{d}\right)} + 2\sqrt{\left(\gamma_{LV}^{p}\cdot\gamma_{S}^{p}\right)} \tag{1}$$

$$\gamma_S = \gamma_S^d + \gamma_S^p \tag{2}$$

where θ is the observed contact angle; γ_{LV} and γ_S are the surface free energy of testing liquid and a polymer, respectively, and the superscript *d* and *p* refer to the dispersive and polar components of surface energy, respectively. The preferred values of the surface energy and its components for two testing liquids used are as follows: $\gamma_L = 72.8$, $\gamma_L{}^d = 21.8$, and $\gamma_L{}^p = 51.0$ mJ/m^2 for water and $\gamma_L = 50.8$, $\gamma_L{}^d = 50.4$, and $\gamma_L{}^p = 0.4$ mJ/m^2 for diiodomethane [66]. As shown in Table 4, the modified PE membrane exhibited higher values of γ_S, $\gamma_S{}^p$, and X_p than those of PE membrane. This result indicated that the presence of the PiAN effectively induced via plasma-induced coating process increased the fraction of polar component in the surface energy of the modified PE membrane, resulting in the enhanced polarity and higher surface energy of the modified PE membrane. It should be noted that the increased polar component in the surface energy of the modified PE membrane can favor the enhancement of the interfacial adhesion between the membrane and the electrodes, thus contributing to the improvement in the cycle performance of LIPB.

Table 4. The surface energy and polarity of PE and the modified PE membranes. Reproduced with permission from Reference [58]. © 2009 Elsevier Ltd.

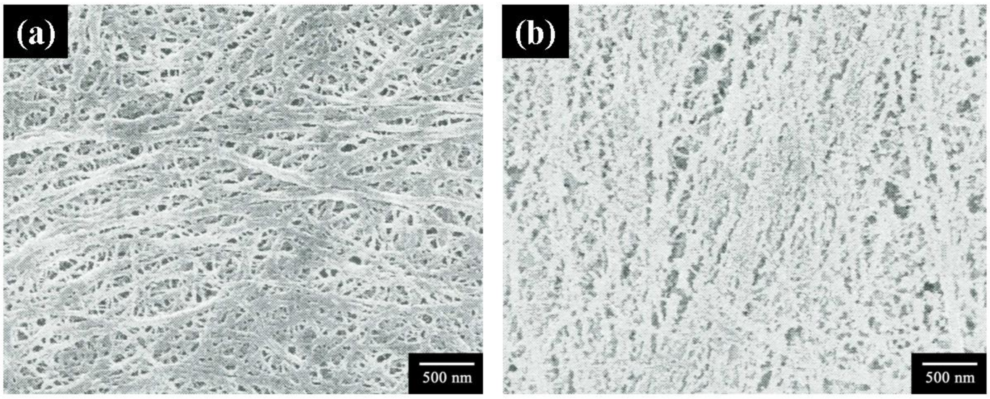
Materials	**γ_s**	**$\gamma_s{}^d$**	**$\gamma_s{}^p$**	**X_p [a]**
PE membrane	30.3	28.9	1.4	0.05
Modified PE membrane	56.6	40.8	15.8	0.28

[a] The polarity, $X_p = \gamma_p/\gamma$

3.3. Morphology

SEM images of the surfaces for PE and the modified PE membranes are shown in Figure 6. The PE membranes had highly porous structures with uniform pore sizes of approximately 200 nm. According to the supplier's specification, PE membranes exhibit a pore structure with the thickness of 23 μm and the porosity of ~40%. After the plasma-induced coating process, the modified PE membranes exhibited rough surfaces and expanded pore structure relative to PE membranes. The surfaces of the modified PE membrane appeared to be porous structures with some dense or coated layers, suggesting that some pores or surfaces for the modified PE membranes may be partially covered by PiAN. In addition, PiAN covered in both top and bottom sides of the surface of the modified PE membranes can be observed, implying that PiAN were introduced simultaneously into both sides of the surface of the modified PE membrane via the plasma-induced coating process. In general, the presence of pores on the membrane can lead to the efficient uptake of electrolyte solutions. Although both membranes were easily wetted in a few seconds in contact with electrolyte solutions, the modified PE membranes exhibited better wettability than PE membrane. This result was in good agreement with much lower contact angle and higher surface energy of the modified PE membranes as compared to PE membranes.

Figure 6. SEM micrographs of (a) PE and (b) the modified PE membranes. Reproduced with permission from Reference [58]. © 2009 Elsevier Ltd.



3.4. Ionic Conductivity and Adhesion

For polymer electrolyte-based systems, the ionic conduction is mainly provided by the electrolyte solution [67,68], and the variation of ionic conductivity is related to polymer morphology and microstructure of membranes for the retention of electrolyte solutions [1–3]. The ionic conductivity of the modified PE membranes at room temperature was higher than that of PE membranes (Table 5). In general, non-polar polyethylene separators exhibited poor wettability and electrolyte retention with electrolyte solutions containing polar solvents, due to their inherent hydrophobic properties. For PE membranes, it was difficult to be completely wetted by organic solvents with high dielectric constant due to its hydrophobic surface with low surface energy, leading to lower ionic conductivity. However, the modified PE membranes exhibited better electrolyte retention as compared to PE membranes due to its good compatibility between PiAN and carbonate-based electrolyte solutions, resulting from the fact that electrolyte solutions were well-retained in the porous membrane by polymer-solvent interactions [69]. Thus, the modified PE membranes exhibited high ionic conductivity due to the enhanced wettability and electrolyte retention, resulting from the presence of PiAN induced onto the surface of the modified PE membrane by the plasma treatment.

Table 5. Ionic conductivity and peel test results for PE and the modified PE membranes. Reproduced with permission from Reference [58]. © 2009 Elsevier Ltd.

Materials	**Ionic conductivity (mS/cm)** [a]	**Average load (N)** [b]	**Peel strength (N/m)** [b]
PE membrane	0.8	0.44	19.1
Modified PE membrane	1.4	0.52	22.6

[a] In 1.3 M $LiPF_6$ and EC:EMC:DEC (3:2:5 by volume)

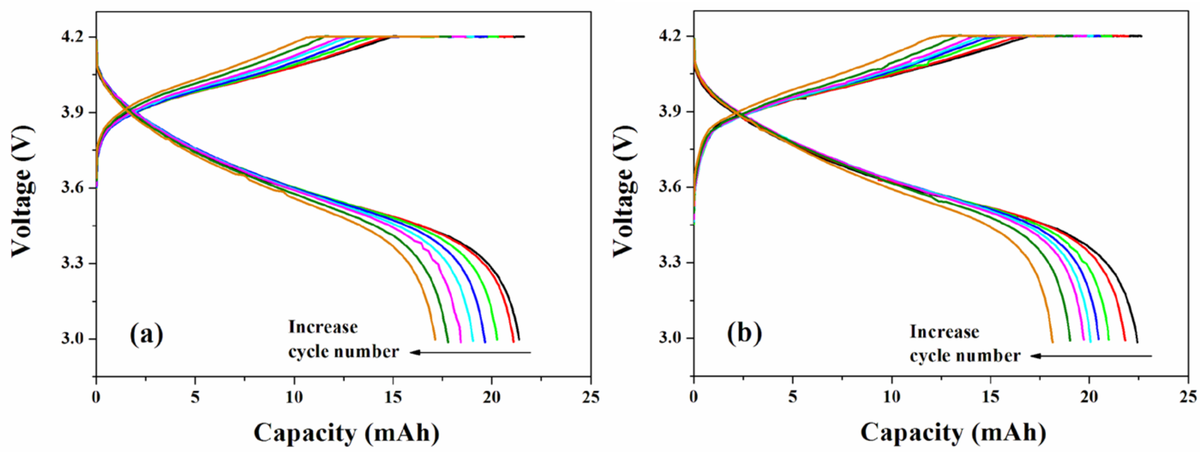
[b] By T-peel testing according to the ASTM D1876 standard

The peel testing of PE and the modified PE membranes was performed to clarify the effect of PiAN induced onto the surface of PE membranes via plasma-induced coating process on the interfacial adhesion between electrodes and separators. As shown in Table 5, the average peel strength of the test cell based on the modified PE membranes was increased to 22.6 N/m by up to 18% compared to the reference cell with PE membranes. This result suggested that the adhesion between the separator and the electrodes was improved by the presence of PiAN effectively induced onto the surface of the modified PE membranes via plasma-induced coating process.

3.5. Cycle Performance of LIPB Cell

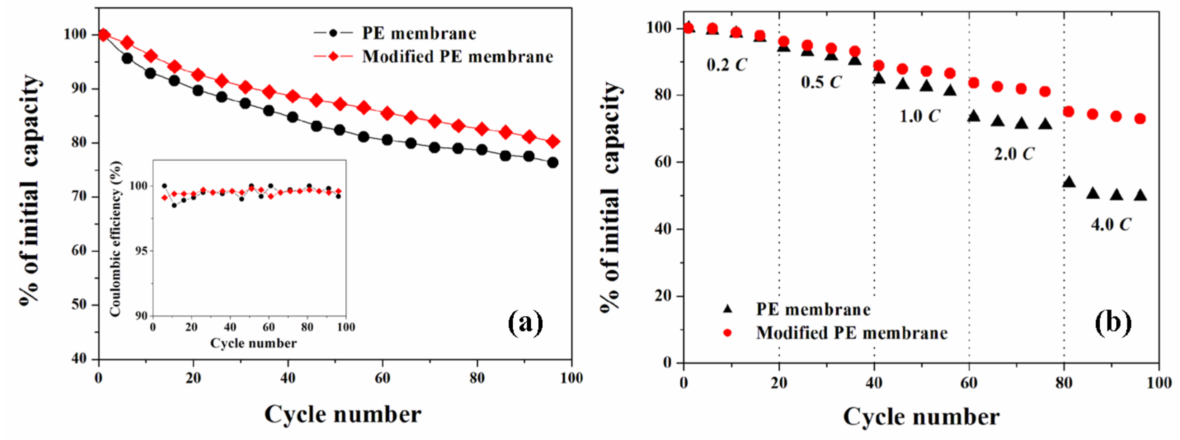
The LIPB cells fabricated with PE or the modified PE membranes were subjected to charge-discharge tests after preconditioning with cut-off voltages of 4.2 V for the upper limit and 3.0 V for the lower limit at 1 C rate using a TOSCAT-300U instrument (Toyo System Co.). The charge-discharge profiles of the fabricated LIPB cells with the cycle number are shown in Figure 7. The small voltage drop in passing from charge to discharge observed in the charge-discharge profiles indicated the lower resistance of the LIPB cells. As the cycle number increased, the voltage and capacity decreased, which was attributed to the high polarization resulting from the increased internal resistance of the cell and the decrease in the diffusivity of lithium ion in the electrodes [1–5]. As shown in Figure 7, the discharge capacity of the LIPB cells fabricated with the modified PE membranes was higher than that of the cells with PE membranes. The plasma-induced coating process can enhance the interfacial adhesion between the electrodes and the separator, which lowered interfacial resistance of the cell, resulting in higher cycle performance of the LIPB cells fabricated with the modified PE membrane.

Figure 7. Charge-discharge profiles of the LIPB cells fabricated with (a) PE and (b) modified PE membranes as a function of cycle number. Reproduced with permission from Reference [58]. © 2009 Elsevier Ltd.



The discharge capacities of the LIPB cells fabricated with PE or the modified PE membranes with the cycle number are shown in Figure 8(a), and the inset of Figure 8(a) shows the coulombic efficiency of the LIPB cells with the cycle number. In general, the coulombic efficiency can be defined as the ratio of the discharge capacity to charge capacity. The relatively low coulombic efficiency of PE and the modified PE membranes during the initial cycling was attributed to the formation of solid electrolyte interphase layers on the surface of the graphite electrode [70–72], providing the good stability to the graphite anode toward the electrolyte reduction during lithium intercalation-deintercalation. Coulombic efficiency of the LIPB cells fabricated with PE and the modified PE membranes gradually approached to unit value (>99.5%). The discharge capacity of the LIPB cells was slowly decreased with increasing the cycle number, which was attributed to the deterioration of the interfacial contact of electrodes and the physical changes in the active materials for electrodes [1–5], leading to the gradual increase in the internal resistance of the LIPB cells during the repeated charge-discharge cycling. After 96th cycles, the LIPB cells fabricated with the modified PE membrane retained 80.3% of the initial discharge capacity, while that with PE membrane showed 76.4% of that. Higher discharge capacity of the LIPB cells fabricated with the modified PE membrane may be attributed to the enhanced wettability and the reduced interfacial resistance [46]. This result suggests that PiAN effectively induced on the surface of the modified PE membranes play a critical role in determining the cycle performance of the LIPB cells and that stable cycle performance can be obtained by modifying the surface of PE membrane with the plasma-induced coating process.

Figure 8. (a) Discharge capacity of the LIPB cells fabricated with PE or modified PE membranes as a function of cycle number. The inset shows the variations of the Coulombic efficiency of the corresponding LIPB cells with the cycle number. (b) Rate capability of the LIPB cells fabricated with PE or the modified PE membranes as a function of cycle numbers. Adapted and reproduced with permission from Reference [58]. © 2009 Elsevier Ltd.



The rate capabilities of the LIPB cells fabricated with PE or the modified PE membranes with the cycle number are shown in Figure 8(b). The LIPB cells fabricated with PE or the modified PE membranes exhibited the capacity retentions of 90.3 and 93.1%, respectively, at 0.5 C rate, and then decreased with further increasing the current rate. The LIPB cells fabricated with the modified PE membranes showed higher capacity retention than in the case of PE membrane. As compared to PE membrane, better rate capability of the LIPB cells fabricated with the modified PE membrane resulted from the enhanced interfacial adhesion between electrodes and separator as well as better wettability and electrolyte retention. This result demonstrates that good cycle performance of the LIPB cells can be obtained by using a novel modified PE membrane with effective plasma-induced coating process, suggesting that the modified PE membrane is expected to be a promising polymer membrane as a high-performance and cost-effective separator for rechargeable LIPB.

4. Concluding Remarks

In LIPB, the separator is a critical component, and its primary function is to facilitate ionic transport between the electrodes as well as to prevent the electric contact of the electrodes. This paper describes the fabrication of a novel modified PE membrane via plasma-induced coating process to create high-performance and cost-effective separator membranes for practical applications in the rechargeable LIPB. The enhanced interfacial adhesion and cycle performance of the LIPB cells fabricated with modified PE membranes by means of plasma-induced coating process are observed. The surface modification of PE membranes via plasma-induced coating process plays a critical role in determining the performance of the resultant LIPB cells. The plasma-modified PE membranes exhibited the increased ionic conductivity, the good wettability, and the enhanced interfacial adhesion between the electrodes and the separators. Consequently, the LIPB cells fabricated with modified PE membranes exhibit better cycle performance as compared to unmodified PE membranes. This paper suggests that the performance of LIPB can be greatly enhanced by the plasma modification of commercially available separator with proper materials for targeted application. Future development of microporous polymer membranes as separators for advanced LIPB will be performed by balancing high performance of separators against their safety and manufacturing cost.

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