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Surface-modified polyethylene separator via oxygen plasma treatment for lithium ion battery

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ABSTRACT

The separator is an important component in lithium ion batteries (LIBs). However, commercial separators such as polyethylene (PE) and polypropylene (PP) are in urgent need to be modified to improve the surface properties to meet requirements for high performance LIBs. In this study, oxygen plasma has been applied to modify the surface of PE separating membrane with functional groups, which has greatly improved the electrolyte wettability and retention of PE separators. The cells with plasma-treated PE separators showed improved charge–discharge capability with lower interfacial resistance and stable cycling performance. This result demonstrates a high potential of the plasma-treated PE separator in LIBs.

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Introduction

A secondary battery can be discharged and charged a large number of times unlike the primary battery. Secondary batteries include many kinds of batteries, such as a nickel–cadmium battery, nickel–metal hybrid battery, lithium ion batteries (LIBs), redox flow battery, lithium/sodium sulfur batteries (Li–S/Na–S), and so on, among which LIBs are the most popular rechargeable batteries for portable electronics such as mobile products, communication devices, and electronic equipment. Recently, the importance and demands of LIBs has been remarkably increased, because LIBs have high energy density, excellent cycle life, and relatively low self-discharge property [1,2].

The separator is placed between the negative and positive electrodes in the battery. It plays a key role in LIB, not only does it control the lithium ions that pass through its inner channel, but also it prevents the physical contact of the cathode and anode while serving as the electrolyte reservoir to allow the transport of ionic charge carriers [3–5]. Polyolefin separators, such as polypropylene (PP) and polyethylene (PE), have been used widely for LIBs. Polyolefin separators have superior mechanical and

chemical stabilities, and also effectively prevent electrical short-circuits or overcharging by keeping the cathode and anode apart. However, they have hydrophobic surface with low surface energy, and thus have poor wetting/retaining ability to the electrolyte solutions [6]. Therefore, the development of polyolefin separators with good wettability is one of the most urgent challenges for high performance LIBs. To overcome these drawbacks, various methods including inorganic particle coating [7–12], polymer coating [13], physical/chemical vapor deposition [14], and grafting hydrophilic polymer [15–18] have been employed to improve the wettability of the polyolefin separators. Even though the modification of hydrophobic polyolefin separators with suitable hydrophilic monomers to impart enough hydrophilicity to readily absorb the electrolyte solution is one of the best methods, they still have the drawbacks such as complex multi-steps and relatively high expense.

Plasma treatment is an energy-saving, pollution-free, and dry process for surface modification. Plasma treatment has several advantages over other competitive techniques, such as environmental safety, and uniformity, reproducibility, and selective modification without a serious loss of bulk properties. In particular, the oxygen plasma treatment could generate a significant amount of hydrophilic oxygen-containing functional groups (C=O, C–OH, COOH) on the polymer surfaces [15]. The hydrophilicity and wettability of the separators are increased by the oxidation reaction. In this study, the oxygen plasma treatment was employed

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to selectively modify the surface of commercial PE separator and its effect on mechanical and electrochemical properties was investigated in detail.

Experimental

Materials

Commercialized PE separator (thickness, 9 μm) made by wet process was kindly supplied from Celgard Co. (Korea). The electrolyte solution of 1 M lithium hexafluorophosphate (LiPF_6) dissolved in the mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (EC:DMC = 1:1, by volume), was purchased from Leechem Co. (Korea). Anhydrous 1-butanol (99.8% purity) was purchased from Sigma-Aldrich Co. (USA). Lithium metal (thickness, 300 μm) was purchased from Cyprus Foote Mineral Co. (USA).

Plasma treatment process

PE separator was surface-modified by oxygen plasma treatment. Surface treatment equipment with RF plasma source (PLASMART MINIPLASMA-station) was used to modify the surface of the PE separator. Oxygen plasma treatment of the PE separator was carried out for various time durations in a chamber (26 cm \times 26 cm \times 10 cm) connected to a two-stage rotary pump via a liquid nitrogen cold trap (base pressure of 4×10^{-8} mbar). A PE separator was placed in the center of the chamber, followed by evacuation to base pressure. The experimental power input from RF generator was 50 W and the treatment time varied from 0 to 10 min. The gas flow rate was 100 sccm (standard cm^3/min). Schematic oxygen plasma treatment for the PE separator is presented in Fig. 1. The original PE separator was denoted as "untreated". The separator samples treated with oxygen plasma for 1, 3, 5, and 10 min were referred to 1 min, 3 min, 5 min, and 10 min, respectively.

Physical and structural characterization of modified separator

In order to examine the chemical structure of oxygen plasma-treated PE separators, X-ray photoelectron spectroscopy (XPS) was performed on a Thermo Scientific MultiLab 2000 system using Al $K\alpha$ source (1486.6 eV). All binding energies were referenced to the C_{1s} neutral carbon peak at 284.5 eV. The untreated and oxygen plasma-treated PE separators were characterized by attenuated total reflectance infrared spectroscopy (ATR-IR, ALPHA-P, Diamond crystal) in wavenumber range of 3500–500 cm^{-1} and a maximum resolution of 0.9 cm^{-1} at room temperature.

The contact angle (CA) measurement of the untreated and modified PE separators (1, 3, 5, and 10 min) was carried out by using a contact angle measurement (DSA100, Kruss) to verify the effect of the oxygen plasma treatment on the wettability of the electrolyte. The CA was determined by means of sessile drop method, using two different testing liquids: distilled water and the electrolyte liquid (1 M lithium hexafluorophosphate (LiPF_6) dissolved in the mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (EC:DMC = 1:1, by volume)). The

CA measurement was carried out at room temperature and the droplet amount was limited to about 10 μl .

The etching rate of the treated PE samples during exposure to oxygen plasma treatment was determined by weighing equal sized separators (5 cm \times 5 cm) before and after plasma treatment, by the following equation:

$$\text{Weight loss (mg/cm}^2\text{)} = \frac{W_0 - W}{S} \quad (1)$$

where W_0 and W indicate the weight of the separators before and after plasma treatment, respectively, and S indicates the surface area of separator.

The electrolyte uptake of separators was determined by soaking the separators in the electrolyte solution. The weight of the separators was taken after removing the electrolyte remaining on the surface of separators with filter paper and the electrolyte uptake was calculated using the equation:

$$\text{Electrolyte uptake} = \frac{W - W_0}{W_0} \times 100 \quad (2)$$

where W_0 and W are the weight of the dry and wet separators.

The porosity was determined from the uptake value after immersing separators in 1-butanol for 30 min, and calculated with the following Eq. (3):

$$\text{Porosity} = \frac{m_b/P_b}{(m_b/P_b) + (m_s/P_s)} \times 100 \quad (3)$$

where m_s and m_b are the mass of the separators and 1-butanol, respectively, and P_s and P_b are the density of the separator and 1-butanol, respectively. The mechanical strength of separators was measured on a tensile tester (Instron-4467) at room temperature with 50 N capacity load cell and stretching rate of 500 mm/min. The dimension of test specimens was 10 \times 100 mm.

Cell assembly and electrochemical characterizations

The electrochemical stability of the separators was determined by linear sweep voltammetry (LSV) of Li/separator with liquid electrolyte (LE)/stainless steel (SS) cells at a scan rate of 1 mV/s over the range of 2.5–5.5 V at 25 $^\circ\text{C}$. The interfacial resistance between the separator and lithium metal electrode was measured by electrochemical impedance spectroscopy (EIS) over the frequency range 100 mHz to 2 MHz at an amplitude of 20 mV at room temperature with the Li/separator with LE/Li cells, the schematic of which is given in Fig. 8. For further electrochemical testing, coin cells were fabricated by placing a separator with LE between lithium metal anode and in-house prepared carbon coated lithium iron phosphate (LiFePO_4) cathode. LiFePO_4 cathode was prepared by casting the slurry of the synthesized LiFePO_4 powder, conductive Super-P (SP) carbon, and poly(vinylidene fluoride) (PVDF) binder at a weight ratio of 80:10:10 in N-methyl-2-pyrrolidone (NMP) onto an Al foil, dried at 60 $^\circ\text{C}$ for 12 h, and thereafter at 80 $^\circ\text{C}$ for 24 h under vacuum to get the electrode of ~ 22 μm thickness and the active material loading of 3.18 mg/ cm^2 . The electrochemical performances of the Li/separator with LE/ LiFePO_4 cells were performed in an automatic galvanostatic charge-discharge unit, WBCS3000 battery cyler (WonA Tech.

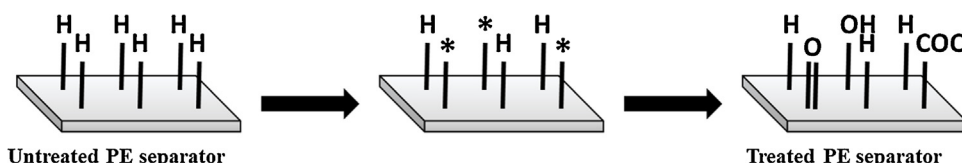


Fig. 1. Schematic representation of surface modification of the PE separator via oxygen plasma treatment.

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