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Surface modification of polypropylene battery separator by direct fluorination with different gas components

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ABSTRACT

Improvement in hydrophilicity of polypropylene (PP) separator and its stability is essential for enhancing the comprehensive performance of battery. In this study, the PP separators were surface modified by direct fluorination with F_2/N_2 and $F_2/O_2/N_2$ gas atmosphere. The alkali absorption ratios (AARs) of these two kinds of fluorinated separators are 302.7% and 418.4%, respectively, which is about nine and twelve times than that of the virgin PP separator. At the same time, the AARs of the fluorinated separators stored for 90 days at ambient temperature in air environment still remain. The surface energy of PP separators is increased from 37.8 mN/m to 47.7 mN/m and 48.9 mN/m determined by contact angle measurement after direct fluorination. X-ray photoelectron spectroscopy (XPS) and attenuated total reflection infrared spectroscopy (ATR-FTIR) results indicate that polar groups, such as $-\mathrm{C}{=}\mathrm{O(OH)}$ and $-\mathrm{C}-\mathrm{F}_x$, are introduced into the polymeric structures of the two fluorinated separator surfaces. Larger quantity of polar groups, especially $-\mathrm{C}{=}\mathrm{O(OH)}$, are introduced on separator surface by the $F_2/O_2/N_2$ modified route, which results in the difference of the AARs and behavior of alkali absorption. Scanning electron microscope (SEM) demonstrates that the size and shape of micropores of PP separators remain almost unchanged after direct fluorination.

1. Introduction

Due to good mechanical properties and excellent chemical stability as well as a high safety to shut down when an unusually large amount of heat is generated, polypropylene (PP) microporous membrane has been widely used as battery separator material, which can ensure the security of battery in daily use [1–3]. However, because of its non-polar and hydrophobic surface resulting in poor compatibility with liquid electrolytes and low ionic conductivity, the battery capacity and cycle-life are seriously affected [4,5]. It is an urgent issue that how to improve wettability of PP separator and its stability to accommodate and retain liquid electrolytes. The capacity of absorption and retention of liquid electrolytes is generally estimated by alkali absorption ratio (AAR) [6,7].

Currently, a variety of modification methods have been focused to overcome the problem, such as corona treatment [8,9], sulfonation treatment [10,11], radiation-induced grafting treatment [12–14], plasma treatment [15–17], etc. Gineste et al. [12] investigated that radiation induced grafting of acrylic acid and diethyleneglycol dimethacrylate monomers onto the surface of the monolayer PP microporous membrane and influence of grafted monomer content on the hydrophilicity was investigated. Liu et al. [16] discussed the surface modification of PP non-woven fabric for battery separator carried out by low-temperature plasma treatment technology, which contributed to hydrophilic polar groups that resulted in an increase in surface energy and alkali absorption. However, radiation-induced grafting leads to increased expansion of battery separator and reduced permeability while plasma treatment deteriorates stability of the resultant hydrophilic separator.

Compared with conventional chemical and physical methods, direct fluorination is a gas-phase chemical reaction of gaseous F_2 and its mixtures with a polymer surface, which is an effective chemical method to modify and control physicochemical surface properties of polymers. Because F_2 possesses strong electronegativity and high chemical reaction capability, when in contact with F_2, polar groups, such as $-\mathrm{C}-\mathrm{F}$ covalent bond, etc., are introduced onto the polymer surface by free-radical substitution reaction [18–20].

In this study, two different gas atmosphere for direct fluorination were used. The fluorine–nitrogen or fluorine–oxygen–nitrogen mixture were employed to modify surface of PP separator. The effect of fluorination modification routes on AAR was observed. The correlation between AAR and chemical structure of PP separator has been studied by X-ray photoelectron spectroscopy (XPS) and attenuated total reflectance infrared spectroscopy (ATR-FTIR) to reveal the reasons for produced activation effect and influence of different gas component fluorination. In addition, contact angles, surface

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energy and scanning electron microscope (SEM) were utilized to characterize the surface polarity and morphology of PP separator before and after direct fluorination.

2. Experimental

2.1. Materials

Polypropylene (PP) microporous membrane for battery separator with the thickness of 30 μm and porosity of 32% was obtained from Shenzhen Xingyuan Material Technology Co., Ltd. The PP separator possesses elliptical micropores, which are arranged in the same direction shown in the following figure. Major of the ellipse ranges from 0.06 to 0.45 μm, and minor axes of the ellipse ranges from 0 to 0.18 μm. The F_2/N_2 (10 vol% for F_2) mixed gases was supplied by China Nuclear Honghua Specialty Gases Co., Ltd. Potassium hydroxide, the analytical grade, was purchased from Chongqing East Sichuan Chemical Co., Ltd. (Chongqing, China).

2.2. Experimental methods

2.2.1. Material purifying

Prior to direct fluorination, the samples were placed in acetone and ultrasonicated to remove oil stain and other impurities on the surface. Later samples were washed with ethanol and dried in a vacuum oven at 40 °C for 12 h.

2.2.2. Direct fluorination treatment

The treatment of samples by direct fluorination in a closed stainless steel reactor was carried out at room temperature. Samples were divided into two groups, and the direct fluorination process was described as follows. Route one: the air in the closed reactor was removed and replaced by nitrogen for three cycles, and then F_2/N_2 (10 vol% for F_2) mixture gas was passed into the chamber at room temperature for 10 min, and the mixture gases pressure was controlled at 10 kPa. After the completion of reaction, the gas in the reactor was pumped out. The treated sample was taken out from the reactor, which was denoted as F-PP. Route two: prior to passing F_2/N_2 gases into chamber, O_2 at 5 kPa was purged into the reactor. The other operations were the same as route one, the obtained sample was denoted as FO-PP. The virgin sample was denoted as U-PP.

2.3. AAR determination

The AAR of the battery separator was determinated according to Chinese SJ/T10171.7-91 for AAR of alkaline battery separator. First, the mass fraction of 40% analytical grade potassium hydroxide solution was prepared. Samples of size 40 mm × 40 mm were left in 40% KOH solution for 4hr. The samples were taken out from the alkali solution, and weighed after 30 ± 2s on electronic balance, which could weigh up to 0.0001 g (each AAR value was the average of more than five successful measurements). The AAR (%) was calculated using the following equation:

$$\mathrm{AAR}\,(\%) = \frac{G_2 - G_1}{G_1} \times 100$$

where G_1 and G_2 are the mass of the sample before and after immersion in the alkali solution, respectively.

2.4. Characterization

Contact angles analysis were carried out on the Germany Krüss 100 type surface tension meter with deionized water and diiodomethane at room temperature, then surface energy was calculated according to a conventional method [21]. XPS measurement was performed on a Kratos ASAM 800 spectrometer (Kratos Analytical Ltd., U.K.) with nonmonochromatic Al K_α (1486.6 eV) X-ray source (a voltage of 15 kV, a wattage of 250 W) radiation, and the vacuum chamber pressure was controlled at a range of 10^{-6}–10^{-7} Pa. Attenuated total reflection infrared spectroscopy (ATR-FTIR) was operated on the Nicolet 560 infrared spectrometer employing attenuated total reflection mode for observing the chemical changes on the samples. Scanning electron microscope (SEM) was operated with FEI Inspect F (FEI company, USA) at 20 kV and the magnification was set at 40,000×.

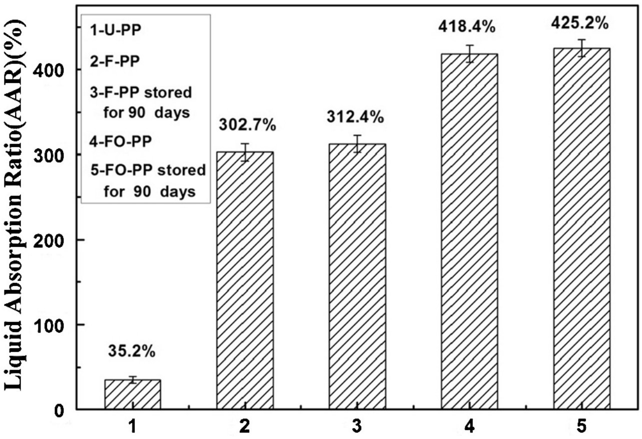

Fig. 1. The AARs of PP separator before and after direct fluorination.

3. Results and discussion

3.1. AARs

The AARs of PP separators before and after direct fluorination are shown in Fig. 1. The AAR of the U-PP is only 35.2% for its non-polar hydrophobic structure, while that of F-PP and FO-PP are increased to 302.7% and 418.4%, respectively, which are greatly enhanced through the two kinds of gas atomsphere direct fluorination routes. Besides, the AAR of FO-PP is about 38.2% more than that of F-PP, which indicates that the direct fluorination with oxygen employed is more efficient in improving the AAR. After storage for 90 days at ambient temperature in air environment, the AARs of both modified separators are 312.4% and 425.2%, respectively, which provides evidence that the fluorinated separators have excellent storage stability.

The relevant literatures show that the liquid electrolyte absorption capacity of PP microporous membrane and its stability are closely related to the surface morphology and chemical structure [12,16,22].

3.2. The contact angles and surface energy

The photographs of static contact angle of U-PP, F-PP and FO-PP with deionized water are presented in Fig. 2. As shown in Fig. 2, contact angles of F-PP and FO-PP with deionized water are significantly reduced, decreasing from 110° to 79.4° and 49.7°, respectively, compared with that of U-PP. It can be found that the hydrophilicity of the fluorinated PP separators is increased. Besides, the PP separator modified by direct fluorination with oxygen has a smaller contact angle. The surface energy of U-PP, F-PP and FO-PP is tabulated in Table 1. The surface energy of PP separator is significantly improved by two different direct fluorination routes, which is enhanced from 37.8 mN/m to 47.7 mN/m and 48.9 mN/m, respectively. Polar component (γ_s^p) of F-PP and FO-PP is increased