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Enhancement on the wettability of lithium battery separator toward nonaqueous electrolytes

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ABSTRACT

Wettability of separator toward nonaqueous electrolyte can significantly affect cell performance of lithium battery. This work systemically studied the factors that affect wettability of commonly used polyolefin separator toward nonaqueous electrolyte, including solvent components, lithium salt types and their concentrations. Various wetting additives were examined. Pluronic surfactants of polyoxyethylene and polyoxypropylene triblock copolymers are reported as wetting additives to enhance the separator wettability toward electrolyte. Moreover, water was innovatively used as a wetting additive to improve separator wettability toward electrolyte. After a trace amount of H_2O (200 ppm) was added into the electrolyte of 1 M $LiPF_6$/PC, the electrolyte uptake in the polyolefin separator was significantly improved by more than three times. Based on the cell performance of Li|$LiFePO_4$ cells, it was concluded that introduction of the wetting additive H_2O was helpful to improve discharge capacities and rate capability along with excellent cycling stability.

1. Introduction

Lithium-ion batteries (LIBs) have achieved significant success in consumer electronic devices and have been regarded as one of the most promising power sources to drive hybrid or pure electric vehicles [1,2]. However, there are still many challenges on LIBs technologies. Higher safety, higher energy, higher power but lower costs are strongly needed for those batteries in electric vehicles. Especially, fast charging rate is important to shrink the charging time. Diffusion of lithium ions between electrode materials is usually regarded as the main factor that restricts the fast chargeability and rate capability of LIBs. Until now, many efforts have been made to enhance lithium ion diffusion coefficients in electrode materials [3–7]. Seldom attentions have been paid to the separator and electrolyte system. For commercial production of the LIBs, wettability of separator toward nonaqueous electrolytes has great impact on cell performance, including energy density, power density, cycle life and safety [8,9].

In a LIB, the separator should wet easily in the electrolyte, which facilitates the process of electrolyte filling in battery assembly [9]. Fig. 1 visually describes the impact of different wettability of the separator toward electrolyte on lithium ion transportation. Good electrolyte permeation in the separator provides the paths for Li^+ ion migration. When the wettability of separator toward electrolyte is poor, the pores in the separator are not completely filled with the liquid electrolyte and thus a high resistance will result from the blocked paths for Li^+ ion transportation [10]. Usually poor wettability is attributed to the large difference in polarity between the non-polar polyolefin separators and the polar organic liquid electrolytes [11]. Previously we reported a polar Al_2O_3 inorganic membrane with the excellent electrolyte retention and it as the separator exhibited higher discharge capacity, and rate capability, and better low-temperature performance than the commercial polymer separator in graphite|$LiFePO_4$ cells [12]. Extensive efforts have been made to manufacture polar separators by ceramic [13–15] or polymer [16–18] coating on conventional polyolefin separators. Those ceramic (Al_2O_3 or SiO_2) and polymer (poly(ethylene-oxide) or polydopamine) coating can obviously enhance the separator wettability toward nonaqueous electrolyte by the strong interaction between the oxygen-containing groups in the coated surface of separators and the carbonate solvents of electrolytes. Basically, main efforts on separator have been devoted to solve the wetting issue, even though there is a quite high threshold on the manufacture technology of the separators. However, the wetting issue still exists for the modified separators in some special electrolyte systems designed for some special purpose, e.g. super-concentrated electrolytes for suppressing lithium dendrite growth on

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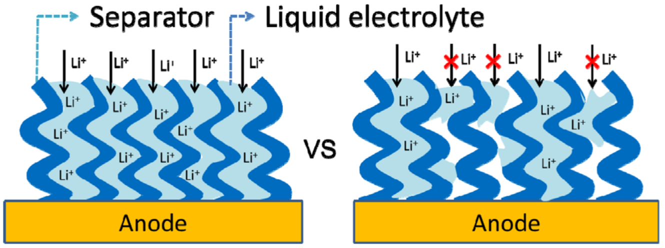

Fig. 1. Schematic illustration of the impacts of separator wettability toward electrolyte on lithium ion transportation. The left picture represents good separator wettability, but the right one represents poor separator wettability toward electrolyte.

lithium metal anode [19]. The separator wettability toward those electrolyte systems must be improved in terms of electrolyte systems.

In our previous experience on the electrolyte studies, solvent components, lithium salt types and concentrations have more or less impact on separator wettability. In commonly used carbonate-based electrolyte systems, the wettability of polyolefin separator is quite different when some carbonate solvents are replaced partly by their homologues (ethylene carbonate (EC) by propylene carbonate (PC), dimethyl carbonate (DMC) by diethyl carbonate (DEC)). However, to our best knowledge, few systemic studies aim to improve the separator wettability toward electrolytes by reformulating electrolyte systems. Moreover, it is widely accepted that use of electrolyte additives is one of the most economic and effective methods for the improvement of lithium-ion battery [20]. But the functional electrolyte additives for enhancing the separator wettability were seldom reported. In this study, we systemically investigated key factors those affect the separator wettability toward electrolyte in the LIBs. As an economic and effective way, introduction of wetting additives including organic or inorganic reagents into the electrolyte system can significantly enhance the wettability of commonly used polyolefin separators. The enhanced separator wettability toward nonaqueous electrolyte is beneficial for the electrochemical performance of Li|$LiFePO_4$ batteries.

2. Experimental

2.1. Preparation of electrolytes

All of the electrolyte solvents (EC, PC, DMC and DEC) and lithium salts ($LiPF_6$, $LiClO_4$, lithium bis (trifluoromethanesulphonyl) imide (LiTFSI) and lithium bis(oxalate) borate (LiBOB)) were purchased from Zhangjiagang Guotai Huarong Chemical New Materials Co., Ltd and used as received. The additives of SiO_2 powders with the size of 7 nm and Pluronic surfactants of polyoxyethylene and polyoxypropylene triblock copolymers (F127 and P123) were purchased from Sigma Aldrich. All electrolytes used in this study were prepared in an argon-filled glove box (MBraun) with the oxygen and moisture level less than 0.1 ppm.

2.2. Characterizations of separator wettability

Contact angle was used to characterize the wetting capacity of a liquid drop on the surface of solid substrates. The contact angles between separator and electrolyte were tested on a goniometer (DSA10-Mk2, KRUSS Gmbh Germany). Considering microporous properties of the separators in LIBs, electrolyte uptake experiments were also used to evaluate separator's wettability toward electrolytes. The separator used is polyethylene (PE) (Celgard 2730). For the electrolyte uptake experiment, polymer separators were pouched into discs (Φ16 mm), the separator discs were immersed in electrolytes for 2 h, and excessive electrolyte on the separator were adsorbed using filter paper. The electrolyte uptake was calculated using the following equation:

$$\text{Electrolyte uptake} = \frac{M - M_0}{M_0} \times 100\% \qquad (1)$$

where M_0 and M represent the weights of the seperator discs before and after adsorbing electrolyte. The final electrolyte uptake values were presented as the average over five parallel tests. The electrolyte viscosity was measured by Rotary rheometer (Bohlin Gemini HR Nano, Malvern) equipped with a 5 cm geometry.

2.3. Electrochemical performance measurements

The influence of separator wettability toward electrolytes on electrochemical performance was investigated by using CR2032 coin-type cells. The cathode were prepared by coating the mixed slurry of $LiFePO_4$, acetylene black, and polyvinylidene fluoride (PVDF) (84:8:8, by wt.) in N-meth-yl-2-pyrrolidinone (NMP) onto a high-purity aluminum foil. After drying and pressing, the received laminate was punched into discs (Φ14 mm) as the electrode for assembling coin cells. The mass loading of the cathode was controlled at ~2.5 mg cm^{-2}. Microporous polyethylene (PE) membrane was used as separator. Lithium foil was used as the counter electrode and reference electrode for the Li|$LiFePO_4$ cell assembly. Electrochemical impedance spectrum (EIS) measurements of the Li|$LiFePO_4$ cells were performed on a CHI 660e electrochemical workstation with an applied 10 mV sinusoidal perturbation in the frequency range from 0.01 to 100 kHz at room temperature. The rate performance test was carried out between 2.0 and 4.1 V at different current densities ranging from 0.1 to 10 C on an Arbin BT2000 battery cycler. The cycling performance was carried between 2.0 and 4.1 V at 2 C on the cycler, and all the cells were initially cycled twice between 2.0 and 4.1 V at a current rate of 0.1 C for activation.

3. Results and discussion

3.1. Factors influencing electrolyte wettability toward separator

3.1.1. Solvents

Four solvent systems, EC/DMC (1:1 w/w), EC/DEC (1:1 w/w), PC, and PC/DMC (1:1 w/w) were used to investigate the solvent effect on separator wettability toward electrolyte. The former two are the typical EC-based electrolytes for LIBs and the latter two are the representatives of the PC-based electrolytes for secondary lithium batteries. Different from EC with high melting point (36 °C), PC can be used as the only solvent in the electrolyte. The physical properties of these carbonate solvents are listed in **Table 1** [21]. To mimic real operating environment, $LiPF_6$ is added in each solvent system to form 1 mol L^{-1} (1M) target electrolyte solutions. Fig. 2 shows the electrolyte uptake of separators with respect to electrolytes of 1 M $LiPF_6$ in various solvents. It shows that the electrolyte uptake of the separator immersed in 1 M $LiPF_6$/PC is the smallest, only 30%. Based on Table 1, PC has the highest viscosity and dielectric constant amongst four solvents. Electrolytes with high viscosity usually lead to high surface tension, which is tightly related to the wettability of separator [22]. The spreading parameter S is a useful parameter for gauging wetting. $S = \gamma_{SG} - (\gamma_{SL} + \gamma_{LG})$, where γ_{SG}, γ_{SL}, and γ_{LG} are solid–gas, solid–liquid and liquid–gas surface tensions, respectively. When $S > 0$, liquid will totally wet to solid (complete wetting). When $S < 0$, partial wetting occur. Therefore, the high surface tension of the electrolyte will reduce the wettability of separator. High dielectric constant means high polarity so that the electrolyte of 1 M $LiPF_6$/PC is not facile to spread on