Tannic acid/polyethyleneimine-decorated polypropylene separators for Li-Ion batteries and the role of the interfaces between separator and electrolyte

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ABSTRACT

Surface chemistry of the separator plays an important role in the performance of the lithium ion battery separator, which not only influence the wettability with the electrolyte, but also the lithium ion migration through the separator. Here we developed a simple method to modify the polypropylene separator with tannic acid (TA) and polyethyleneimine (PEI). A thin and uniform TA/PEI layer was formed onto the surfaces of the separator through a simple assembly process without destroyed the micro-structure. The modified PP separator showed excellent wettability, high ambient ionic conductivity (0.95 mS cm^{-1}) and lithium-ion transference number (0.44), indicating that the TA/PEI layer played a role in the lithium ions migration. The possible mechanism of the surface promoting lithium ion migration was discussed in this paper. The battery performances of the modified separator were also conducted. As a result, cells with the TA/PEI-coated PP separator displayed superior cycle stability and rate capability.

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1. Introduction

Lithium-ion batteries (LIBs) are widely used in portable electronics, electric vehicles, aerospace and energy storage systems due to their high energy density, long cycle life and high operational voltage [1–3]. Generally, a LIB is composed of four fundamental components: negative electrode (anode), positive electrode (cathode), electrolyte, and separator [4]. Although separators are not involved in the electrochemical reactions in a lithium-ion battery, they play an important role to physically isolate the positive and negative electrodes while allow the rapid migration of lithium ions during the charge and discharge processes [5]. Therefore, the separator directly affects the safety and power performance of a battery. Among a variety of separators developed so far, polyolefin-based microporous separators (polyethylene (PE), polypropylene (PP) and laminates of polyethylene and polypropylene (PP/PE/PP)) remain dominance in commercial LIBs on account of their excellent mechanical properties, good electrochemical stability, proper low

cost and thermal shutdown properties [6,7]. However, these polyolefin separators still suffer from some drawbacks. Their intrinsically poor wettability in traditional liquid electrolyte leads to low electrolyte uptake and retention, which impair the cycle life and rate capability of LIBs [8,9]. Furthermore, the low ionic conductivity and lithium ion transference number of the separators also fail to achieve the demands of high-performance LIBs for the emerging fields.

Many efforts have been made to modify these polyolefin separators. Surface coating with inorganic nanoparticles [10–13] and polymers [14,15] is applied in routine. Grafting hydrophilic monomers [16–18] also have also attracted a lot of interest. Researchers generally suggest that the increase in wettability and electrolyte uptake are the major causes of the improvement in separator's performance. Therefore, most of the modifications have focused on increasing the hydrophilicity of the separator and paid less attention to the mobility behavior of ions. In fact, these modifications not only change the wettability, but also the surface chemistry of the separator. Recent studies have indicated that the interfaces between the separator and electrolyte have effects on the lithium ions migration through the separator [18,19]. Notably, Polyolefin-based membranes have a very high specific surface area (BET:

$42 \, m^2 \, g^{-1}$). Thus, the role of the interfaces cannot be ignored.

In this paper, we developed a facile surface modification by using tannic/polyethyleneimine as the binary coating precursors to form an ultrathin layer on polypropylene separator. Tannic acid (TA), a plant polyphenol, is abundant in the nature and widely applied due to its nontoxicity and low cost. Similar to dopamine, the TA also possesses great binding affinity to different substrates. With multiple phenolic hydroxyl groups, TA can self-polymerize in an alkalescence aqueous solution and form a hydrophilic coating on the surface of the membrane [20]. However, this reaction is time-consuming. Lee et al. [21] pointed out that phenolic groups and amino groups were the two crucial points for the formation of the covalent bonds in PDA network. Inspired by this thought, we chose the polyethyleneimine (PEI) as the co-modifier. PEI, the analogue of polyoxyethylene (PEO), is also known as a lithium ion conductor [22–25] because nitrogen atoms can facilitate ion pair dissociation and promote the ion conductivity.

To avoid the effect of the porosity decrease on the ionic conductivity, the coating layer should be as thin as better. Layer-by-layer self-assembly is a good idea due to its ability to control over the thickness of TA/PEI multilayer at molecular level. The hydrogen bonding interaction between TA/PEI can achieve fast assembly and the presence of covalent bonds can improve the stability of the TA/PEI coatings. The modified membranes became more hydrophilic and showed excellent wettability toward the liquid electrolyte. The ionic conductivity and lithium-ion transference number were also improved significantly, indicating that the surface chemistry plays an important role in lithium ion migration through the separators. The possible mechanism was discussed in this paper. Additionally, cells with the modified separators showed improved battery performance.

2. Experimental

2.1. Materials

Tannic acid (TA, MW = 1701.23 Da, analytical reagent) and polyethyleneimine (PEI, MW = 600 Da, analytical reagent) were purchased from Aladdin Chemistry Co. Ltd. China and used directly as received. The liquid electrolyte (1 M LiPF$_6$ in the mixture of ethylene carbonate/dimethyl carbonate/ethyl methyl carbonate (1:1:1, mass ratio)), LiCoO$_2$ cathode (Load amount: 11–13 mg cm^{-2}, LiCoO$_2$/carbon black/PVdF (8:1:1, mass ratio)) and natural graphite anode (Load amount: 4–6 mg cm^{-2}, natural graphite/carbon black/carboxymethyl cellulose/styrene butadiene rubber (90:5:1.5:3.5, mass ratio)) were supplied by Kejing Co. Shenzhen, Ltd., China. The commercial PP separator was obtained from Celgard Company (Celgard 2500, USA), used as the polymer substrate and a contrast sample. Ultrapure water was produced by a Millipore water purification system (18.2 MΩ, Millipore, USA). All solutions were freshly prepared for each experiment.

2.2. Preparation of TA/PEI modified PP separators

PP separators were first cleaned with alcohol in an ultrasonic bath for 30 min before use and rinsed with alcohol subsequently. The cleaned and alcohol-wetted separator was immersed into an alkalescent Tris-HCl buffer solution (pH 8.5) of TA (2.0 mg mL^{-1}) for 10 min, then taken out, rinsed by ultrapure water to remove the unstable adsorption residues, subsequently immersed into PEI aqueous solution (0.5 mg mL^{-1}) for another 10min and rinsed with ultrapure water again. The resulted separator was named as PP-1. The steps above were repeated one and two more times to gain the PP-2 and PP-3 separators. Finally, the modified separator were thoroughly washed with ultrapure water and dried in a vacuum oven at 60 °C for 24 h.

2.3. Characterization

The surface chemical composition of the separators was characterized by X-ray photoelectron spectroscopy (XPS) and attenuated total reflectance fourier transform infrared spectroscopy (ATR-FTIR). The surface morphologies of the separators were observed by field emission scanning electron microscope (FE-SEM, Hitachi S4800, Japan). In addition, the element mappings were also obtained by energy dispersive spectroscopy (EDS) using the FE-SEM. Electrolyte contact angles measurement via a contact angle goniometer (OCA20, Dataphysics, Germany) were utilized to characterize the affinity of the separators to the electrolyte (the drop volume was 3 μL). The porosities of the separators are determined by mercury intrusion porosimeter (Micromeritics AutoPore IV 9510 porosimeter). The electrolyte uptake (U) was measured as follow: put the dry membrane (w_d) into 1 mol/L LiPF6 solution for 1 h, then taken it out and wiped the excess electrolyte absorbed on the surfaces, weighed the swollen separator and recorded as w_w. The electrolyte uptake (U) was calculated from the following Equation: $U(\%)=(w_w-w_d)/w_d \times 100\%$.

2.4. Electrochemical characterization

The ion conductivity (σ) was determined from the AC impedance by using a CHI 660C (CH Instruments Inc., China) and calculated according to the equation, $\sigma = L/(R_b \cdot A)$, where L, R_b and A are the thickness (25 μm), effective area (1.96 cm^2) and bulk resistance (ohm) of the cell assembled of stainless steel (SS)/separator-liquid electrolyte/SS, respectively. Interfacial resistance (R_{int}) was also measured by AC impedance using cells made up of Li/separator-liquid electrolyte/Li. The R_{int} was tested again after stored for 7 days to detect the interfacial stability. Lithium ion transference number (t_+) was investigated by the combination of EIS and steady-state current technique [26]. A small polarization potential (10 mV) was given to the cell assembled by Li/separator-liquid electrolyte/Li and the R_{int} of the cell was measured before and after the polarization. The t_+ is defined by the equation [27]: $t_+ = I_{ss}(\Delta V-I_0R_0)/I_0(\Delta V-I_{ss}R_{ss})$, where I_0 and I_{ss} represent the initial current and steady-state current, respectively. ΔV is the polarization potential. R_0 and R_{ss} are the interfacial resistances before and after polarization, respectively. The electrochemical stability of the separators was examined via linear sweep voltammetry (LSV) using a SS/separator-liquid electrolyte/Li cell with the potential ranging from 1.0 to 7.0 V (vs. Li$^+$/Li) at the sweep rate of 10 mV s^{-1}.

A coin-type full-cell consisted of LiCoO$_2$/separator-liquid electrolyte/graphite was used to investigating the battery performance. The cycle stability measurement was carried out at room temperature with the voltage range from 2.7 V to 4.2 V at a current density of 1C (100 mA g^{-1}) by using a testing system (Neware, CT-3008, China). To further investigate the rate capability of the full cell, the charge/discharge current varying from 0.2C/0.2C (20 mA g^{-1}) to 7C/7C (700 mA g^{-1}) was applied. All the cells used for test were assembled in an argon-filled glove box.

3. Results and discussion

3.1. Surface coating of TA/PEI on the PP separator

The coating process is demonstrated in Fig. 1. The self-assembly behavior of the TA/PEI occur not only because of the hydrogen bonding interaction between TA and PEI, but also the oxidation polymerization of the two coating precursors [28,29]. The structural formulas and possible mechanism of the oxidation