



Zeolite coated polypropylene separators with tunable surface properties for lithium-ion batteries



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ARTICLE INFO

Article history:

Received 10 October 2015

Received in revised form

2 January 2016

Accepted 1 February 2016

Available online 6 February 2016

Keywords:

Lithium ion battery

Separator

MFI zeolite

Dip-coating

Wettability

ABSTRACT

The separator is a critical component in liquid electrolyte batteries, and closely related to the battery performance such as cycle number and safety. In this work, thin (~2 μm) films of MFI zeolite with different Si/Al ratios are coated on both sides of the commercial polypropylene separator for lithium ion batteries. The electrolyte solvent wettability of the MFI zeolite coated separators decreases with increasing Si/Al ratio of the zeolite films. Polypropylene separator coated with MFI zeolite (Si/Al = 25) film (ZCPP25) shows very high wettability for electrolyte. The Li₄Ti₅O₁₂/Li cell with ZCPP25 separator exhibits best charge and discharge performance among the cells with pure or coated polypropylene separators. Under relatively high current rate, the cell with MFI zeolite coated separator shows better charge and discharge capacities and cycling stability than that of uncoated polypropylene separator. The cell with MFI zeolite coated separator also performs better than the cell with uncoated polypropylene separator in a wider temperature range. The enhanced performance for cells with MFI zeolite coated separator is caused by the better filling of the electrolyte at the separator/electrode interface due to the improved electrolyte solvent wettability.

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1. Introduction

Lithium-ion batteries (LIBs) are now widely used in portable electronic devices [1,2]. They are also gaining popularity in the emerging electric vehicles [1,3] and regarded as a promising means for storage of new sustainable energy in a smart grid [4]. Safety, cost effectiveness and long life are key requirements for these large scale applications of LIBs [5,6]. In a LIB, a separator, which physically hosts lithium ion conducting liquid electrolyte and separates anode and cathode, plays an important role in achieving high performance, reliability, and safety of the device [8]. Ideal separator must be chemically and thermally stable, highly wettable by electrolyte and mechanically robust [7,8]. Commercially available separators for LIBs are made of polyolefin, predominantly polyethylene (PE) and polypropylene (PP), because of their desired electrochemical and mechanical properties and low cost [7,9]. However, due to their low surface energy and generally non-polar properties, the polyolefin separators suffer from poor wettability towards some of the commonly used electrolytes such as ethylene carbonate (EC),

propylene carbonate (PC), diethyl carbonate (DEC), and dimethyl carbonate (DMC) [7,9]. This may result in a relatively high internal resistance and low electrochemical performance [10,11]. Furthermore, polyolefin separators usually show high tensile strength but relatively low anti-puncture strength [8,9]. During the high current rate charging or after long cycling applications, the lithium dendrites may form on the anode and penetrate through the microporous polyolefin separator, causing short-circuit of the LIB [12,13]. This will convert essentially all the chemical energy stored in the LIB to heat, resulting in smoke evolution, fire, and even explosion [14].

To overcome these weaknesses of the commercial separators, various approaches have been reported in recent years. Most of the efforts focus on the optimization of polymer based separators, such as the development of composite polymer (with inorganic fillers) separators [15–17] and polymer blend (copolymer) separators [18–20]. These studies are well reviewed by Lancers-Méndez and co-workers [21,22]. The main characteristics of the modified polymer separators, e.g., ionic conductivities and related properties are listed and compared well with each other in these review papers. It has been confirmed that the introduction of inorganic particles into the bulk polymer is one of the most promising strategies.

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Additionally, Wang and coworkers [23–25] reported a series of self-supported Al_2O_3 , SiO_2 , and anodic aluminum separators with excellent electrolyte wettability, high rate capability and good low-temperature performance. To further improve the brittle characteristic of the thin self-supported ceramic separators, flexible pure alumina nanowire based separator was developed and shows higher rate capacity and much better cycle performance at 120 °C than the commercialized polypropylene (PP) separator [26]. However, the main challenge with these self-supported inorganic separators is the difficulty for scale-up in both separator fabrication and battery assembly.

Another approach to prepare improved separator is to coat the surface of polyolefin based separators with inorganic particles, such as Al_2O_3 , SiO_2 or TiO_2 powders [27–31]. This approach has attracted increasing attention because of its effectiveness in improving the wettability and preventing the thermal shrinkage and mechanical breakdown of polyolefin based separators while keeping their intrinsic advantages. PP separators coated with uniform SiO_2 nanoparticles show significant improvement in tensile strength, contact angles, electrolyte uptake and battery performance as compared to the uncoated PP separator [28]. LIBs with polyimide nanofiber mat coated with a thin Al_2O_3 layer exhibit enhanced capacity, cycling ability, and rate capability as compared the LIBs with the uncoated separator [29]. In general, these studies show improved thermal stability, considerable electrolyte wettability and outstanding electrolyte retention for the polymer separator coated with these dense metal oxide particles. However, the surface properties of these inorganic particles can not be readily tailored except by additional surface modifications [30].

Microporous zeolite molecular sieves have been widely used in separation and catalysis owing to their well-ordered microstructure and unique framework chemical properties. Recently, zeolites (such as NaA, NaY and MCM-41) embedded (filled) polymer separators have been reported for lithium ion batteries with improved performance [32–34]. Such approach is very similar to zeolite filled polymer membranes for gas separation. However, to our best knowledge, no one reported LIBs with a polymer separator coated with a pure zeolite layer.

Compared with traditional inert ceramic particles that have been used to coat the surface of polymer separators, microporous zeolites have several advantages including high surface area, tunable surface property (such as hydrophobicity/hydrophilicity or basicity/acidity), and high mechanical strength. The tunable surface properties of zeolites potentially allow tailoring the separator to host different electrolyte required for LIBs for different application environment (as defined by the temperature range and dis/charge voltage characteristics) [35,36]. Compared with the composite polymer separators with zeolite fillers, the zeolite coated polymer separators can keep the intrinsic advantages of polymer separators, such as suitable pore size and porosity, and low preparation cost.

This paper reports the first effort to coat MFI type zeolite film on the surface of polyolefin separator for LIBs. A series of MFI zeolites with the Si/Al ratio of 25, 50, 100, 200 and ∞ (surface property changes from hydrophilic to hydrophobic) were synthesized and coated on commercial (PP) separators to demonstrate the effectiveness of zeolite coating with tunable surface property on the performance of LIBs.

2. Experimental

2.1. Synthesis of MFI zeolite crystals

MFI zeolite crystals were synthesized via a hydrothermal process using a precursor with a composition of 6.2 g tetraethyl orthosilicate (TEOS, Aldrich), 60 g H_2O , 0.27 g NaOH, 1.77 g

Tetrabutylammonium bromide (TPABr, Aldrich), and 0.4 g, 0.2 g, 0.1 g and 0.05 g $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ for the Si/Al ratio of 25, 50, 100 and 200, respectively. Hydrothermal synthesis was conducted at 175 °C for 12 h. Silicalite crystals were prepared by a hydrothermal process at 120 °C for 12 h using a synthesis solution with a composition of 5.0 g SiO_2 (fumed silica, Aldrich), 25 mL Tetrapropylammonium hydroxide solution (TPAOH, 1M, Aldrich) and 0.35 g NaOH [37]. The as-prepared zeolite crystals were purified by repeated centrifugation washes with deionized water. After drying, the crystals were calcined at 550 °C for 8 h to remove the template.

2.2. Preparation of MFI zeolite coated PP separators

For the synthesis of MFI zeolite coated PP separators, polyvinylidene fluoride (PVDF, Alfa Aesar) was used as the binder of zeolite crystals. Typically, 1.5 g PVDF powder was dissolved into a mixed solvent of 24.5 g dimethylformamide (DMF, Alfa Aesar) and 24.5 g 2-butanone (or methyl ethyl ketone, MEK, Alfa Aesar) to prepare 3 wt% PVDF. 0.675 g zeolite powder was then dispersed into a mixed solution of 2.5 g 3 wt% PVDF and 20 g MEK to prepare a homogeneous suspension with ultrasonic treatment for 30 min and continues stirring for 5 h. The weight ratio of zeolite to PVDF is 9:1 in the suspension.

Commercialized PP separator (Celgard 2500, USA) was dipped into the MFI zeolite suspension for 5 s and then dried in the hood at room temperature for 3 h. To prepare a continuous zeolite coating layer, the dip-coating process was repeated. The MFI zeolite coated PP separator was dried at 60 °C under vacuum for overnight. Two clips were used to stretch the coated PP separators to avoid mechanical deformation due to the stress induced in the drying process (Fig. S1). Subsequently, the separator was cut into 19 mm diameter for assembling the cell. In order to simplify the narration, the symbols ZCPP25, ZCPP50, ZCPP100, ZCPP200 and SCPP are used to denote the zeolite coated PP separators with MFI zeolite having Si/Al ratio of 25, 50, 100, 200 and ∞ , respectively.

2.3. Characterization

The crystal structure of the membranes was characterized by X-ray diffraction (XRD, Bruker AXS-D8, Cu K α radiation). Diffraction patterns were collected at room temperature in the range of $5^\circ < 2\theta < 50^\circ$, with a step width of 0.05° and a scan rate of 0.2 s per step. The morphology of the MFI zeolite coated PP separators was characterized using a scanning electron microscopy (SEM, Philips, XL 30) after gold deposition.

Wetting behaviors of PP and MFI zeolite coated PP separators were recorded by a digital camera. For each sample, 16 μL liquid electrolyte (EC, DEC and DMC with the volume ratio of 1:1:1) dropped onto the surface of separators. Considering the toxicity of LiPF_6 , it has not been added in wettability analysis. The contact angles of liquid electrolyte on PP and MFI zeolite coated PP separators were analyzed by the Kruss EasyDrop Contact Angle. The liquid drop was 4 μL . The dynamic contact angles were recorded by a high speed camera (30 pictures per second).

Electrolyte infiltration and retention of the separators were evaluated using the commonly used method [24–26]:

$$\text{Electrolyte uptake} = \frac{w_1 - w_0}{w_0} \times 100\% \quad (1)$$

$$\text{Electrolyte retention} = \frac{w_x - w_0}{w_1 - w_0} \times 100\% \quad (2)$$

where W_0 is the weight of dry separator, W_1 is the weight of the separator after absorbing the electrolyte for 1 h, extra electrolyte

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