



Zeolitic imidazolate framework-67 based separator for enhanced high thermal stability of lithium ion battery

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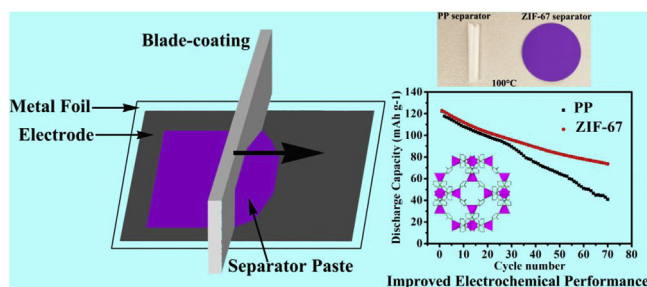
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HIGHLIGHTS

- ZIF-67 is demonstrated to use as the separator.
- ZIF-67 based separator is directly coated on the $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ electrode.
- ZIF-67 based separator has higher thermal stability than polypropylene separator.

GRAPHICAL ABSTRACT



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ABSTRACT

The separator is a crucial part of lithium ion battery, such as preventing internal short-circuit and offering ion-conducting routes. However, conventional separators are usually based on polymer materials, which show the low thermal stability and poor electrolyte wettability, thus greatly restricting the electrochemical performance of lithium ion battery, especially for high-temperature safety. In this study, zeolitic imidazolate framework-67 (ZIF-67) was employed as separator via direct coating onto the surface of $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ electrode through a facile blade-coating technique. Comparing with the conventionally used polypropylene (PP) separator, the new ZIF-67 based separator features superior electrolyte uptake (154%), higher ionic conductivity ($0.00164 \text{ S cm}^{-1}$) and thermal stability. Notably, at a high temperature of 55°C , the cell with ZIF-67 based separator exhibits nearly 2 times higher capacity retention than the PP separator (ZIF-67: 61.20% vs PP: 35.09%). In view of its advantages, the ZIF-67 based separator shows significant potential in the design of safe lithium ion batteries.

1. Introduction

With the advantages of high energy and power density, no memory effect, as well as environmentally friendliness, lithium ion batteries have been widely used in hybrids, electric vehicles, and grid storages [1–3]. The separator is a crucial component in lithium ion batteries; it is electronically insulated and placed between the positive and negative

electrodes, preventing their physical contact while enabling lithium ion transport. It plays a key role in the safety performance of lithium ion batteries, strongly influencing battery charge/discharge, cycle life, rate, and other properties [4,5]. To date, microporous polyolefins including polypropylene (PP), polyethylene (PE), and their blends, have been mostly used as separator materials in lithium ion batteries owing to their good performance and low cost. However, polymer separators

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have some disadvantages which limit the practical application of lithium ion batteries. For example, polymer separators have the poor wettability due to their nonpolar properties. Besides, it could be easily punctured by lithium dendrites that may grow at high charge-discharge rates or long-term cycles [6]. Generally, lithium ion battery based on polymer separator has the poor performance in high-rate discharge, heat resistance, dimensional stability, the capability to adsorb and maintain electrolytes for long-term energy storage devices in high-end markets. In particular, there will be a fire and explosion hazard in electric vehicle applications. Therefore, developing separators with high thermal resistance and good wettability has become an urgent need for lithium ion battery industry.

The shrinkage and melting of polymer separators are mainly responsible for their low thermal stability. Therefore, a separator with high thermal stability can prevent short circuit at high temperature and thermal runaway [5]. One possible solution is to use pure inorganic separators which exhibit good wettability and excellent high temperature performance, such as Al_2O_3 , SiO_2 , and MgO , etc [7,8]. Despite their good thermal stability, pure inorganic separators are inherently weak and fragile. So they are not mechanically enough to withstand handling in battery winding and assembly [9–11]. To improve the stability of separator, coating a commercial polyolefin separator with inorganic particles is one of the most economical and effective way [12,13]. Inorganic composite separators, with their high hydrophilicity and absorbability of inorganic particles and the flexibility of the polymer separator, exhibit superior performance. For instance, Lee et al. [14] coated the Al_2O_3 particles on polyimide (PI) nanofiber separators, showing higher capacity and better cycle and rate performance of the coated PI separators, which can be comparable with those of pure organic PI membranes. Wang et al. [15] synthesized porous Al_2O_3 particle-polyvinylidene fluoride (PVDF) composite separators to address the problem of brittleness. Yang et al. [6] coated the porous PE with poly (methyl methacrylate) modified SiO_2 sub-microspheres, which significantly improved the thermal stability and wettability of the PE separator. Zeolitic imidazolate frameworks (ZIFs), a new class of metal organic frameworks formed by the assembly of metal ions (or metal clusters) and electron-donating organic ligands, have drawn more attention in recent years. They have large surface areas, tunable porosities, excellent thermal and chemical stabilities [16–19], which are mostly applied in many fields, such as gas adsorption [20–22], molecular separation [23,24], catalysis [25] and so on [26,27]. ZIFs were first reported by Shao et al., who applied them for the improvement of lithium ion battery electrodes [28]. Bai et al. [29,30] used zeolitic imidazolate skeleton as a lithium-sulfur battery separator, and the battery showed excellent charge-discharge performance.

Herein, we directly coated ZIF-67 on the cathode material through the blade-coating technique to replace the conventional PP separator. ZIF-67 micro-particles possess a highly porous structure, which potentially facilitate lithium ion diffusion. Therefore, ZIF-67 based separator (abbreviated as ZIF-67 separator) shows higher porosity, ion conductivity and better thermal stability than the PP separator. More importantly, this new separator improves the cycling performance and safety performance of lithium ion batteries.

2. Experimental

2.1. Material synthesis

All chemicals were used directly after purchase and without further treatment. In a typical synthesis of ZIF-67 particles, 1.455 g of cobalt nitrate hexahydrate and 1.642 g of 2-methylimidazole were dissolved in 40 ml of methanol solution, respectively. Then, 2-methylimidazole solution was added to the cobalt nitrate hexahydrate solution under vigorously stirring for 1 min, and the mixture was aged at room temperature for 24 h. The resulting purple precipitates were collected by centrifugation, rinsed repeatedly with dehydrated alcohol for three

times and then dried in vacuum at 80 °C for 24 h [31].

The positive electrode of the cell was made of $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ (NCM), acetylene black and PVDF, which were dispersed and stirred into slurry in *N*-methyl-2-pyrrolidone (NMP) at a mass ratio of 8:1:1. The slurry was then uniformly coated on aluminum foil and dried at 120 °C in vacuum for 12 h to be used as the positive electrode. The as-prepared ZIF-67 was grounded into powder in an agate mortar and then was added into a mixed solution of PVDF and NMP, in which the PVDF and ZIF-67 were mixed at a mass ratio of 6:100. Afterward, the samples were stirred for 24 h at room temperature to form uniform slurry. The as-prepared NCM positive electrode was coated with the uniform slurry by blade-coating method and then vacuum dried at 100 °C for 12 h to evaporate the solvent. The separator with a thickness of 66 μm was obtained by controlling the amount of ZIF-67. The dry ZIF-67 separator was cut into a circle with diameter of 16 mm to assemble the cell. The experiments were tested with a half-cell system using CR2032 coin cells in an argon-filled glove box. The cells including the electrode-supported separator and lithium negative electrode were infiltrated with 1 M LiPF_6 electrolyte solution, which consisted of ethylene carbonate/diethyl carbonate/diethyl carbonate (1:1:1, volume ratio). For comparison, the PP separator was used in a contrast experiment. The gasket and shrapnel were placed in the cells and sealed to avoid loosening.

2.2. Sample characterization and electrochemical measurements

The microstructure and morphology of the separators were examined by scanning electron microscopy (SEM, Hitachi, Japan). Energy dispersive X-ray (EDX) spectra were used to determine the elemental distribution of the cross-sectional ZIF-67 separator. The crystal phase composition of ZIF-67 was characterized by X-ray diffraction (XRD, PANalytical X'Pert PRO) with $\text{Cu K}\alpha$ ($\lambda = 1.5406 \text{ \AA}$) radiation. Thermal shrinkage was observed by heat treatment in a vacuum oven at 100 °C for 1 h. The thermal stability of the separators was measured with differential scanning calorimetry (DSC, Q2000) and thermogravimetry analysis (TGA) at a heating rate of 10 °C min^{-1} under N_2 flow. Cyclic voltammetry (CV) measurement was carried out at a rate of 0.1 mV s^{-1} between 3.0 and 4.2 V. The charge-discharge test of the cells was performed between 3.0 and 4.2 V at different rates (0.2 C, 0.5 C, 1.0 C, 2.0 C, 5.0 C).

The electrolyte uptake and retention of the separator were determined by the followed equations [32]:

$$\text{Electrolyte uptake} = (W_1 - W_0) / W_0 \times 100\% \quad (1)$$

$$\text{Electrolyte retention} = (W_x - W_0) / (W_1 - W_0) \times 100\% \quad (2)$$

where W_0 is the initial weight of the separator, W_1 is the weight of the separator after soaking the separator in the electrolyte for 1 h, the separator was taken out and the excess electrolyte was wiped off with filter paper [33], W_x is the weight of the separator at intervals in an oven at 50 °C.

As previously reported [34,35], the ionic conductivity of the separator was calculated by electrochemical impedance spectroscopy. The electrolyte-soaked PP separator and ZIF-67 separator were sandwiched between two stainless steel plates. Impedance was then measured by an electrochemical workstation (CHI660E, Chenhua, Shanghai) in a frequency range of 1 Hz–100 kHz with an amplitude of 5 mV between 3.0 V and 4.2 V.

The ionic conductivity could be calculated according to the following equation:

$$\sigma = L / AR \quad (3)$$

Where L , A , R and σ are the thickness, the area, the total resistance and the ionic conductivity of the separator, respectively.

The following expression was used to calculate the porosity:

$$\text{Porosity (\%)} = (W_0 - W_2) / (\rho \times V) \times 100\% \quad (4)$$

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