



# Poly(*m*-phenylene isophthalamide) separator for improving the heat resistance and power density of lithium-ion batteries



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## HIGHLIGHTS

- PMIA separators with a sponge-like structure are developed.
- Excellent thermal stability and non-flammability contribute to higher safety.
- Separators exhibit superior cell performances than commercial PP-based separators.

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## ABSTRACT

A microporous poly(*m*-phenylene isophthalamide) (PMIA) separator with high safety (high-heat resistance and self extinguishing), high porosity and excellent liquid electrolyte wettability was prepared by the traditional nonsolvent introduced phase separation process. Due to the high-heat resistance of PMIA material, the as-prepared separator exhibited a negligible thermal shrink ratio at 160 °C for 1 h. Meanwhile, benefiting from its high porosity and excellent wettability in liquid electrolyte, the liquid electrolyte uptake and the ionic conductivity of the separator were higher than that of the commercial PP-based separators. Furthermore, the cell assembled with this separator showed better cycling performance and superior rate capacity compared to those with PP-based separators. These results suggested that the PMIA separator is very attractive for high-heat resistance and high-power density lithium-ion batteries.

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## 1. Introduction

Lithium-ion batteries have gained an unprecedented importance as the energy storage of portable devices such as laptop computers, cell phones and so on. To expand their applications in electric vehicles and energy storage systems, lithium-ion batteries with increased energy and power densities, as well as improved safety are required [1–3]. As one of critical components in lithium-ion batteries, the separator not only plays an important role in preventing physical contact between the electrodes, but also in retaining liquid electrolyte and conducting lithium ions. Its structure and properties considerably make a difference on the power density and safety of lithium-ion batteries.

Currently, the materials for conventional separators used in lithium-ion batteries are polyolefins, predominantly polyethylene or polypropylene. These polyolefin separators have many advantages, however, their inferior thermal stability, poor wettability and low porosity restrict their application in high performance lithium-ion batteries. To circumvent these problems of the polyolefin separators, extensive studies have been carried out, such as surface coating [4–6], surface grafting [7–9] and blending [10]. On account of the more facile operating process, surface coating is widely adopted, focusing on ceramic particle [6,11–16] coating and polymer coating [17–20]. Jung et al. [21] have coated a thin ceramic layer onto the surface of polyolefin separator by atomic layer deposition technology. It demonstrated that the thin ceramic coating layer could significantly suppress the thermal shrinkage and increase the liquid electrolyte wettability of the modified separator. Fang [5] have coated a polyvinylidene fluoride layer on

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the polyolefin separator by a dip-coating method followed by a dry-cast process. Benefiting from the enhanced affinity between coating layer and liquid electrolyte, the wettability of the modified separator was obviously improved. Meanwhile, owing to the higher melting point of polyvinylidene fluoride (172 °C), the dimensional stability of the modified separator was substantially enhanced. Even when exposed at 150 °C for 1 h, the shrinkage ratio of the modified separator was below 60.0%, while that of the bare polyolefin separator was nearly 100%. Although such coating layers have been effective in improving the thermal and electrochemical properties of polyolefin separators, potential issues still exist, such as the weak bonding forces between the polyolefin matrix and the coating materials, the serious pore blockage phenomenon and the inherent low melting points of polyolefin matrix. Therefore, it will be ideal to develop a new material with both high-heat resistance and excellent liquid electrolyte wettability to substitute the polyolefin materials.

Recently, the nonwoven separators prepared by the high-heat resistance polymer materials have drawn considerable attentions, including poly(*m*-phenylene isophthalamide) [22,23], polyimide [24–29], polyethylene terephthalate [30,31] and poly(*p*-phthalazinone ether sulfone ketone) [32,33]. These separators could still retain dimensional stability and effectively isolate the electrodes so as to prevent separator-related short circuits and explosion at high temperature [24]. Poly(*m*-phenylene isophthalamide) (PMIA) is an aromatic polyamide with meta-type benzene-amide linkages in its skeletal chain, which exhibits a high-heat resistance up to 400 °C. Together with its perfect flame retarding ability, the corresponding separator is expected to be beneficial to enhance the safety characteristic of lithium-ion batteries. Moreover, the relatively polar nature of carboxy groups may endow this separator with good wettability in liquid electrolyte, and resulting in excellent electrochemical properties. To the best of our knowledge, the PMIA separators for lithium-ion batteries is mainly prepared by electrospinning technique. However, the excessively large pore size of the nonwoven separators usually lead to serious liquid electrolyte leakage and self-discharge, which would further deteriorate the cell safety and electrochemical performances and finally hinder their successful application in lithium-ion batteries. To overcome these shortcomings, several attempts have been made, i.e. the fabrication of the PMIA-based composite nonwoven separators. To date, the reported articles include the Al<sub>2</sub>O<sub>3</sub> coated PMIA nonwoven separator [34], the PVdF/PMIA/PVdF nonwoven separator [35] and the PMIA/PU nonwoven separator [23]. Therein, the PMIA-based nonwoven separators are mainly used as a support layer for lithium-ion battery separators. Notice that these methods are difficult-to-control, time-consuming and energy-intensive. In comparison, due to its versatility and scalability, the phase inversion method is commercially explored and is one of the most popular membrane formation methods [36]. Very few studies have been carried out on preparing the thermal resistance PMIA separators via phase inversion.

In this work, for the first time, a sponge-like microporous PMIA separator for lithium-ion batteries was prepared by nonsolvent introduced phase separation process. By comparing its thermal shrinkage and electrochemical performances to those of the commercial PP-based separators, the possible application of the PMIA separator in high-heat resistance and high-power density lithium-ion batteries was discussed.

## 2. Experimental

### 2.1. Materials

PMIA fibers were purchased from Taihe New Material Company

and used directly as received. *N,N*-dimethyl formamide (purity >99%, Aldrich) and lithium chloride were supplied by Sino-pharm Chemical Reagent Co., Ltd, China. Herein, lithium chloride was dried at 160 °C for 5 h before using. The liquid electrolyte of 1 M LiPF<sub>6</sub> in Ethylene Carbonate/Dimethyl Carbonate/Ethyl Methyl Carbonate (1/1/1 wt/wt/wt) was supplied by Guotai Huarong Company, China. Commercial PP separator, SiO<sub>2</sub> coated PP separator and PVdF coated PP separator were supplied by Zhongxing Xincai Science and Technology Co., Ltd., China. To facilitate the narrative, they were abbreviated as PP separator, ZC separator and ZP separator, respectively. LiCoO<sub>2</sub> cathode (LiCoO<sub>2</sub>/carbon black/PVdF 90/5/5 wt/wt/wt, loading amount: 11.9 mg cm<sup>-2</sup>) and natural graphite anode (natural graphite/carbon black/carboxymethyl cellulose/styrene butadiene rubber 93/2/1.5/3.5 wt/wt/wt/wt) materials were purchased from Biyuan Electronic Co. (Shenzhen), Ltd., China. The electrode disks (1.77 cm<sup>2</sup>) were punched out and dried under vacuum at 120 °C for 5 h before using.

### 2.2. Preparation of PMIA separator

The schematic illustration for the preparation of PMIA separator was shown in Fig. S1. First, desired amount of PMIA fibers (10 wt%) and lithium chloride (1 wt% to PMIA, as cosolvent [37]) were dissolved in *N,N*-dimethyl formamide at 120 °C to yield a homogenous and transparent casting solution. The as-prepared casting solution was spread to liquid film with a thickness of 150 μm. Subsequently, the liquid film was immersed into water coagulation bath at 30 °C. After solidified, the porous separator was peeled off and washed with deionized water for 24 h to remove the residual solvent and lithium chloride.

### 2.3. Physical and electrochemical characterizations

Morphologies of the separators were investigated using a field emission scanning electron microscope (SIRion FESEM) at an acceleration voltage of 5 kV. Porosity and pore size distribution were determined by mercury intrusion porosimetry (Micromeritics AutoPore IV 9510 porosimeter). Liquid electrolyte contact angle was measured with a contact angle goniometer (OCA20, Dataphysics, Germany) equipped with a video capture. Thermal shrinkage was determined by measuring the dimensional change before and after being subjected to heat treatment (100 °C and 160 °C) for 1 h. Thermal stability was further examined by a thermogravimetric analyzer (Perkin Elmer Pyris 1 TGA, USA) over the range of 50–500 °C under N<sub>2</sub> at 10 °C/min.

Liquid electrolyte uptake (*U*) was determined by measuring the weight change between the dry state and the liquid electrolyte-swollen state, and was calculated according to the equation,  $U (\%) = (w_1 - w_0) / w_0 \times 100\%$ . Where,  $w_0$  and  $w_1$  are the weight of the dry separator and the swollen separator, respectively. The weight change of the swollen separator in a dry argon atmosphere was used to monitor the stability of liquid electrolyte entrapped in the separator. The ionic conductivity ( $\sigma$ ) was calculated according to the equation,  $\sigma = L / (R_b \cdot A)$ , where,  $R_b$ ,  $L$  and  $A$  are the bulk resistance (ohm), thickness (cm) and effective area (cm<sup>2</sup>), respectively.  $R_b$  was measured by an electrochemical work station (Princeton Applied Research 2273, PARC, USA) with a frequency range from 1 Hz to 10<sup>5</sup> Hz in an AC mode. Interfacial resistance ( $R_{int}$ ) was measured same as the bulk resistance, with the assembly of lithium/separator-liquid electrolyte/lithium. The electrochemical window was studied by linear sweep voltammetry with a stainless steel working electrode and a lithium counter electrode from 1.0 V to 6.0 V (vs. Li<sup>+</sup>/Li). To investigate the cycling performance, the cells with LiCoO<sub>2</sub>/separator-liquid electrolyte/graphite were assembled and conducted between 2.7 V and 4.0 V at 0.5 C. The rate

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