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Closely packed x-poly(ethylene glycol diacrylate) coated polyetherimide/poly(vinylidene fluoride) fiber separators for lithium ion batteries with enhanced thermostability and improved electrolyte wettability

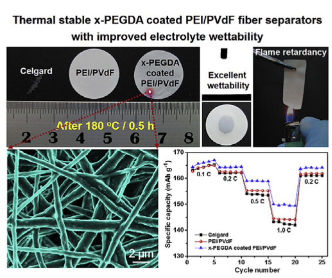
Yunyun Zhai [a, b], Ke Xiao [a], Jianyong Yu [c], Bin Ding [a, c, *]

[a] State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, College of Materials Science and Engineering, Donghua University, Shanghai 201620, China
[b] College of Biological, Chemical Sciences and Engineering, Jiaxing University, Jiaxing 314001, China
[c] Key Laboratory of Textile Science & Technology, Ministry of Education, College of Textiles, Donghua University, Shanghai 201620, China

HIGHLIGHTS

- Successful cross-linking of PEGDA decreases packing density and average pore size.
- Introduction of x-PEGDA improves the affinity, wettability and ionic conductivity.
- x-PEGDA coated PEI/PVdF membranes show superior thermostability and nonflammability.
- x-PEGDA coated PEI/PVdF fibers demonstrate higher rate capability than Celgard.

GRAPHICAL ABSTRACT



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ABSTRACT

The x-polyethylene glycol diacrylate (x-PEGDA) coated polyetherimide/polyvinylidene fluoride (PEI/PVdF) membranes are obtained by the facile combination of dip-coating and free radical polymerization of PEGDA on the electrospun PEI/PVdF fiber membranes. Successful cross-linking of PEGDA increases the average fibers diameter from 553 to 817 nm and reduces the packing density, which not only increases the tensile strength of x-PEGDA coated PEI/PVdF membranes, but also decreases the average pore diameter. Besides, the x-PEGDA coated PEI/PVdF membranes are endowed with good wettability, high electrolyte uptake, high ionic conductivity and improved electrochemical stability window because of the good affinity of PEI and PEGDA with liquid electrolyte. Benefiting from the synergetic effect of PEI and PVdF, the x-PEGDA coated PEI/PVdF membranes exhibit excellent thermal stability and nonflammability, which are beneficial for enhancing the safety of lithium ion batteries. More importantly, the x-PEGDA coated PEI/PVdF membranes based $Li/LiFePO_4$ cell exhibits comparable cycling stability with capacity retention of 95.9% after 70 cycles and better rate capability compared with the Celgard membrane based cell. The results clearly demonstrate that the x-PEGDA coated PEI/PVdF membranes are the promising separator candidate with improved wettability and safety for next-generation lithium ion batteries.

* Corresponding author. College of Materials Science and Engineering, Donghua University, Shanghai 201620, China.
E-mail address: binding@dhu.edu.cn (B. Ding).

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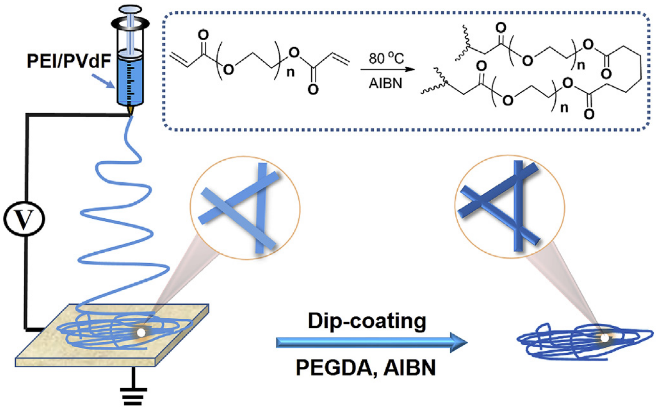
1. Introduction

Lithium ion batteries (LIBs) have attracted significant interest as an appealing power sources for a wide variety of applications, such as portable electronic devices, energy storage system and electric and hybrid electric vehicles, due to their high energy density, high operational voltage and low self-discharge rate [1,2]. But, further applications of LIBs in high power equipment are mostly restricted by safety issues, such as ignition and explosion [3,4]. The separator, an electrically insulating membrane that separates the cathode from the anode and allows rapid transfer of ionic charge carrier, is crucial to the safety and reliability of LIBs [5,6]. Currently, polyolefin membranes have been the most predominant one in commercial LIBs owing to their low cost, high mechanical strength and good electrochemical stability [7]. However, the low thermostability at elevated temperature due to their relatively low melting temperature triggers internal shorting between electrodes and results in the thermal runaway, and thus incurring safety issues [8]. Besides, polyolefin membranes demonstrate poor wettability to polar liquid electrolyte due to their intrinsic hydrophobicity and low porosity, which hinders the improvement of electrochemical property [8]. Therefore, there is a great need for further development of safer and more reliable separators.

Various approaches (i. e. modification of polyolefin membranes [9–12], phase separation [13–15], hard template [16] and electrospinning [17–19]) have been reported to overcome the abovementioned shortcomings of polyolefin membranes. Among them, electrospinning has attracted significant attentions because of its ability to produce nanofibers of a wide variety of polymers [20,21]. The advantageous features of controllable fiber diameter, high porosity and interconnected porous structure endow the electrospun membrane with high ionic conductivity, which is beneficial for enhancing the cyclability and rate capability. Moreover, if necessary, the nanofibers can be further functionalized to better control the property (i.e. pore size and thermal stability), and thus improving the performance of the membrane-based cell. These characteristics make electrospun membranes well-suited as separators for LIBs.

Polyetherimide (PEI) is a soluble amorphous polymer with excellent electrical insulation performances, high chemical stability, good dimensional stability (>200 °C) and inherent flame resistance [8,15,22]. Meanwhile, the carboxyl (C=O) and oxy-ether bonds (–O–) in its molecular structure are expected to strengthen the affinity of PEI based separators with high polar liquid electrolyte. Polyvinylidene fluoride (PVdF) is the host polymer commonly used for preparing separators owing to its high dielectric constant ($\varepsilon = 8.4$), excellent chemical stability, high polarity and excellent compatibility with electrodes [23,24]. However, the poor wettability because of their hydrophobic surface and low surface energy and low heat resistance due to their low melting point severely restrict the improvement of rate capability, cyclability and safety of the PVdF membrane-based cell [19,25]. Therefore, combining PEI with PVdF is a potential strategy to overcome the abovementioned limitations of PVdF membranes.

In the present study, we demonstrate a facile approach to fabricate closely packed x-polyethylene glycol diacrylate (x-PEGDA) coated PEI/PVdF membranes with nonflammability and improved electrolyte wettability. This strategy is based on integration of electrospinning technique and in-situ free radical polymerization reaction (Scheme 1). Advantages of this kind of separator are relatively high tensile strength, good electrolyte wettability and high ionic conductivity due to the introduction of x-PEGDA. Moreover, the x-PEGDA coated PEI/PVdF membranes demonstrate excellent thermal stability and nonflammability, indicating that they are promising separators to enhance the safety issue of LIBs.



Scheme 1. Schematic illustration for the fabrication of x-PEGDA coated PEI/PVdF fiber membranes.

Our findings may lead to robust polymer separator designs that will improve the thermal stability and electrolyte wettability, and thus enhancing the safety and reliability of LIBs.

2. Experimental

2.1. Materials and reagents

Polyetherimide (PEI, Ultem 1000, Saudi Basic Industries Corporation) was supplied from Dongguan Jiangxin Plastic Co., Ltd., China. PVdF (HSV 900, Arkema) was purchased from Cmdic Xiamen Imp. & Exp Co., Ltd., China. Polyethylene glycol diacrylate (PEGDA, Mn = 600), 2,2′-Azobis (2-methylpropionitrile) (AIBN), *N,N*-dimethylacetamide (DMAc) and ethanol were obtained from Aladdin Chemistry Co. Ltd. The Celgard 2320 membrane (Celgard, China) with a thickness of about 20 μm were used as the separator for a comparative study. All chemicals were of analytical grade and used as received without further purification.

2.2. Fabrication of x-PEGDA coated PEI/PVdF fiber membranes

A 18 wt% PEI/PVdF (1/3, w/w) blended solution was prepared by dissolving PEI and PVdF into DMAc at 50 °C with vigorous stirring for 10 h. The PEI/PVdF blended solution was loaded into a syringe and injected through a plastic needle with a flow rate of 1.0 mL h^{-1}. A high voltage of 30 kV was applied to the needle tip and the distance between the spinneret and an aluminum foil-covered grounded rotating collector (rotating rate of 100 rpm) was fixed at 25 cm. The ambient temperature and relative humidity were 23 ± 2 °C and 45 ± 3%, respectively. Then, the free-standing fiber membranes were dried at room temperature on the collector for 6 h to prevent the further shrinking and then removed from the collector. The resulting PEI/PVdF composite membranes were dried in a vacuum oven at 70 °C for 12 h to remove the residual solvent and transferred to a dry box for further use.

To prepare the coating solution, a certain amount of AIBN (10 wt % of PEGDA) was added into ethanol, followed by adding PEGDA under vigorously stirring for 12 h to form a concentration of 15 wt% PEGDA coating solution. The electrospun PEI-PVdF membranes were first mounted on 10 cm × 10 cm plastic frame, followed by soaking in the coating dispersion by a dip-coating process (limiting the amount of PEGDA to 5 wt% amount of PEI/PVdF). Then the coated separators were squeezed at 0.03 MPa and left at room temperature for 1 h to evaporate the solvent, then the obtained separators were heated at 80 °C for 4 h to initiate the free-radical polymerization of PEGDA, and finally they were further vacuum