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Sandwich-structured composite separators with an anisotropic pore architecture for highly safe Li-ion batteries

Yong-Ting Zhou, Jing Yang*, Hong-Qing Liang, Jun-Ke Pi, Chao Zhang, Zhi-Kang Xu*

MOE Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, People's Republic of China

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ABSTRACT

Safety and electrochemical performance are key concerns for porous separators used in Li-ion batteries. We demonstrate the potential application of a sandwich-structured composite separator (SSCS) for highly safe Li-ion batteries, which is comprised of a poly(vinylidene fluoride) (PVDF) porous bulk and a trapped polyethylene terephthalate (PET) nonwoven fabrics layer. The as-prepared SSCS possesses an anisotropic porous structure with large inner pores while small surface ones arising from a nonuniform cooling process along the thickness direction during thermally induced phase separation. The distinctive structure of SSCS gives rise to excellent properties concerning security, such as electrolyte retention, mechanical strength, thermal stability and thermal-shutdown ability. Furthermore, the higher ionic conductivity as well as lower interfacial impedance of SSCS endows the resulting $LiFePO_4$/Li battery with enhanced discharge capacity and cycle stability compared to the cell assembled by the commercialized Celgard 2400 separator. Therefore, the SSCS is expected to be a promising candidate for Li-ion batteries with high cell performances and enhanced safety.

1. Introduction

Li-ion batteries have become the most dominant and promising power source for a wide variety of portable electronic devices and electric vehicles due to their high energy density, no memory effect, and long cycle life [1,2]. Nowadays, there has been a growing awareness that battery safety issues should be paid more attention in addition to persistent endeavors focusing on the enhancement of battery performances such as high power density and energy density [3]. From the viewpoint of safety assurance, a porous separator placed between the cathode and the anode is considered as a key component of preventing internal short circuit failures to maintain normal running of battery [4]. The most commercially available separators at present for Li-ion batteries are microporous polyolefins such as polyethylene, polypropylene or their laminates thanks to the reliable preparation method and quality control, chemical stability and low cost [4–6]. However, their poor thermal shrinkage, low porosity, and inferior electrolyte wettability still remain concerns for further achievements of high performance Li-ion batteries with great security through the material screening and structure control of porous membranes for separators.

A precise tuning of porous morphologies in polymer separator membranes is of great importance to the performance and safety of lithium ion batteries [7]. For instance, relatively large pores at micro-scale are more favorable to increase ionic conductivity, thus enhancing the electrochemical performance of battery (*i.e.*, discharge capacity and rate performance). However, too large pores sometimes easily cause an internal short circuit [5]. Hence, from the standpoint of safety and long-term cycle life, small pores at sub-micro scale are more acceptable due to the depression effect on Li dendritic growth, thereby suppressing the self-discharge and internal short-circuit of batteries [7,8]. To achieve a reasonable trade-off between battery performance and safety, advances have been made to successfully generate the multi-sized porous structure within a single separator. The first morphology displays small pores embedded in large ones by the aid of controlled nonsolvent induced phase separation (NIPS) upon a precise tuning of good solvent/poor solvent mixture [7,9]. The second structure manifests small pores on the membrane surfaces while large ones in the bulk either by breath figure method [10,11] or thermally induced phase separation (TIPS) [8]. Such morphologies can not only guarantee a high ionic conductivity but also suppress short-circuit and ensure a long cycle life.

Concerning the strategy to facilely prepare separator membranes with controllable pore structure, the TIPS technique has recently received increasing attentions due to relatively fewer influence factors compared with NIPS [12] or breath figure [13] methods. The formation of anisotropic pore structure across the membrane thickness was accomplished by using solvent evaporation to induce a concentration

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* Corresponding authors.
E-mail addresses: jing_yang@zju.edu.cn (J. Yang), xuzk@zju.edu.cn (Z.-K. Xu).

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gradient prior to phase separation [14–16]. However, the resulting pore sizes are usually several microns or even larger, which seems unsuitable for battery separators. Currently, an alternative temperature gradient induced by a nonuniform cooling upon the polymer solution precursor is promising to construct well controlled pore architectures. For example, an oriented pore structure vertically distributed through the membrane can be constructed by a temperature gradient upon the precursor solution from one surface to the other [17,18]. Moreover, our group recently report a well-controlled dual-asymmetric porous morphology produced by a nonuniform cooling process *via* TIPS approach in which a temperature gradient was achieved from the middle of polymer solution to the surfaces [8]. It is interesting to obtain multi-sized pores within membranes, *i.e.*, large interconnected ones in bulk (~1.0 μm) and small ones on both surfaces (~0.03 μm). The bulk large pores provide a high electrolyte uptake and fast permeation, while the surface small ones prevent the leakage of electrolyte. Such a design of multi-sized pores within an anisotropic separator membrane seems to be an ideal solution to balance the performance/safety issue of batteries, because small pores on the surface can efficiently inhibit the electrolyte outflow and thus avoid accidents. However, with regard to practical applications for Li-ion batteries, there are still some deficiencies to overcome: (1) mechanical properties should be further strengthened because the multi-scale porous structure could to some extent reduce the tensile strength; (2) the thermal stability is required to be enhanced because the restricted melting temperature of PVDF could cause structural instability under unexpected overheating accidents.

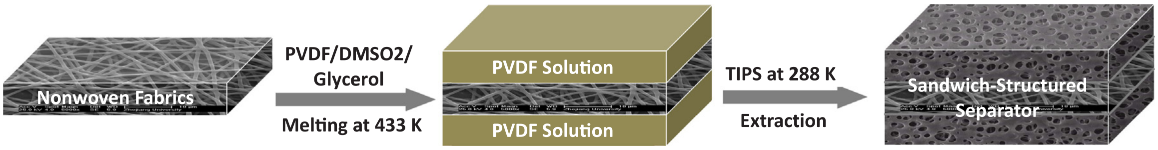
In this communication, we report a novel type of sandwich-structured composite separators (SSCSs) with an anisotropic pore structure *via* a nonuniform cooling process by TIPS using dimethyl sulfone (DMSO2) and glycerol as a mixed diluent (see Scheme 1). On the one hand, poly(ethylene terephthalate) (PET) nonwoven fabrics sandwiched in the middle were chosen as the mechanical support for separators due to their superior thermal and dimensional stabilities at high temperature, which can maintain batteries in safety under abnormal heating or stretching deformation [19]. On the other hand, poly (vinylidene fluoride) (PVDF) have great advantages such as strong polarity, suitable mechanical properties, chemical inert, good wettability by electrolyte and contact with electrodes. Thus, it served as a pore size controller for PET nonwoven fabrics, where the pore morphology is tuned by the nonuniform cooling in TIPS. Moreover, a detailed mathematical description of the nonuniform cooling process during TIPS upon polymer solution was highlighted to well understand the formation mechanism of anisotropic pore structure. The obtained SSCSs exhibit high tensile strength and thermal stability thanks to the PET nonwoven fabrics as well as unique multi-sized pores within the separator. These particular features of SSCSs endow $LiFePO_4$/Li batteries with improved cycle stability and rate performance compared to commercialized Celgard 2400 separators. Such SSCSs are promising to alternate current commercialized separators for lithium ion batteries with high safety.

2. Results and discussion

Experimental section can be found in Supporting Information (SI). SEM images in Fig. 1(a) visualize both the membrane structure and pore morphology. First, the middle layer of PET nonwoven fabrics is sandwiched between two PVDF layers, resulting in a so-called "sandwich-like" structure. An interpenetration structure is also visible among the PVDF matrices and the PET nonwoven fabrics. This behavior can be ascribed to the pressing effect applied to the membrane in which the PVDF/dimethyl sulfone/glycerol solution is penetrated through the nonwoven fabrics. Second, the pore size distribution is characterized in Fig. 1(b). On the one hand, there are highly interconnected bulk pores with a size distribution from 1.4 to 1.9 μm which corresponds to the cross-sectional SEM image in Fig. 1(a). On the other hand, the membrane also displays small pores with a distribution around 0.2 μm, which is in accordance with the SEM images of both the top surface and the bottom surface. Therefore, the as-prepared SSCS possesses an anisotropic pore structure along the thickness direction from the bulk to the surfaces. This morphology is similar to the previously reported dual-asymmetric structure in our group in which the multi-sized pores are well constructed by the nonuniform cooling-controlled TIPS. These results also indicate that the interpenetration of PVDF layer can serve as a pore size controller to effectively narrow the pore size and distribution of the PET layer in which the pristine nonwoven fabrics hold much larger size and wider distribution of pores in the range from several micrometers to hundreds of micrometers (see Fig. S1 in SI).

To deeply understand the formation of such anisotropic pore structure, a mathematical model is used to describe the cooling kinetics of the polymer solution precursor at different positions, *i.e.*, from the central region to borders (The model is listed in SI in detail). Fig. 1(c) shows the temperature (t) evolution as a function of time (τ) and position (x). Note that the temperature for whole polymer solution can achieve an equilibrium value as same as the cooling bath within 0.5 s, indicating a very rapid cooling process which is comparative to other similar modeling researches [20,21]. Generally, the heat transfer of the inner solution undergoes a sequential process, *i.e.*, first through the neighboring part and then *via* the surface. So we can predict that there is a gradient of cooling rate along the thickness direction. As a matter of convenience, Fig. 1(d) displays two typical kinetic curves of temperature variation (t-τ curves) within 0.1 s occurring in two extreme cases, *i.e.*, the surface ($x = \sigma/2$) and the middle ($x = 0$) of the analytical solution. The difference in cooling rate mentioned above can be well reflected by the existences of temperature disparity (Δt) and coarsening time gap ($\Delta\tau$). For example, the temperature on the surface is around 5 °C lower than that in the middle after 0.04 s. Similarly, the coarsening time for surface diluent-rich droplets is about 0.01 s shorter than that for middle ones when the temperature decreases down to 135 °C. Therefore, there is enough time for diluent-rich droplets in the middle of polymer solution to grow before the solidification *via* liquid-solid phase separation, leading to relatively large pores. On the contrary, the shorter coarsening time gives rise to small pores on the surface. A well-defined anisotropic pore structure along the thickness direction of the membrane is thus constructed conveniently. Through the detailed mathematical analyses above, the formation of the multi-sized pore morphology is due to the coarsening time gradient within the polymer solution caused by the difference in cooling rate. This distinctive and facilely achieved anisotropic pore morphology undoubtedly opens a novel door to fabricate membrane separators with satisfactory properties for Li-ion batteries, subsequently advancing the security and performance thereof.

As we know, separators should be able to absorb a significant amount of liquid electrolyte and then to hold them in pores for ion transport under cell operation. Wettability of the separators is evaluated by measuring the contact angles of the liquid electrolyte droplet



Scheme 1. Schematic representation of the preparation process of SSCS.