

Fibrous Separator with Surface Modification and Micro-Nano Fibers Lamination Enabling Fast Ion Transport for Lithium-Ion Batteries

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Electronic Supplementary Information

Abstract Appropriate materials collaborated with reasonable structure can significantly increase the separator performance for lithium-ion batteries. In this work, taking the advantages of microfibrillar and nanofibrillar membranes and compensating for their defects, we developed a composited separator (GOPPH) with excellent overall performance by first wetting-modifying the polyethylene terephthalate microfibrils and then laminating a polyvinylidene fluoride-hexafluoropropylene nanofiber layer. Such a combination not only offers the GOPPH separator, from the perspective of structure, with high porosity and hierarchical structure in terms of fiber diameter and pore size, but also provides satisfactory features including wettability, mechanical strength and thermal shutdown function that benefit from the selected materials. Meanwhile, as determined by experimental and theoretical approaches, the obtained GOPPH separator exhibits considerably enhanced lithium ion transport ability with a high lithium ion transference number and transport rate, which thereby endowing the cell with superior cycling stability with a capacity retention of 93% after 200 cycles at 1 C. Therefore, considering battery safety and performance, the GOPPH fibrous membrane could be a promising separator candidate for lithium-ion batteries.

Keywords Fibrous separator; Surface modification; Micro-nano fiber lamination; Ion transport; Lithium-ion batteries

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INTRODUCTION

Nowadays, lithium-ion batteries (LIBs) have become the most dominant and promising power source for various portable electronic devices and electric vehicles, because of their high energy density, long cycle life, low cost and environmental friendliness.^[1] LIBs generally consist of four indispensable components: cathode, anode, electrolyte and microporous separator. The separator, which is placed between anode and cathode electrodes, serves not only to isolate the electrodes contacts but also to take charge of the ion transport, significantly affecting the operation safety and performances of LIBs.^[2] Therefore, an ideal separator can simultaneously meet the requirements of porous structure, electrolyte wettability, mechanical, thermal and electrochemical stability.

As an electrolyte reservoir, the separator has a considerable impact on ion transport, depending on the following two factors. The first is separator morphology,^[3] which includes porosity, pore size distribution and tortuosity, and the second is separator surface chemistry,^[4] which primarily af-

fects the affinity to electrolyte. Currently, microporous polyolefin separators, such as polyethylene (PE) and polypropylene (PP), are the most extensively employed for LIBs, and they have numerous strengths like easy fabrication, robust mechanical properties, and excellent electrochemical stability.^[5] However, their inherent limitations, specifically, the low porosity (30%–50%) caused by the wet/dry process, and the poor wettability to electrolyte stemmed from the chemical composition of polyolefin, often raise concerns in terms of the ion transport, due to the resultant low ionic conductivity and low lithium ion transference number.^[6,7] Indeed, a large number of approaches have been undertaken to overcome the electrolyte wettability issue, which contains coating inorganic particles^[8–10] or grafting polar molecules or polymers^[11,12] on the surface of polyolefin separators. Unfortunately, these polyolefin-based modifications are usually ineffective, if not harmful, in increasing porosity. In comparison to wettability, high porosity of the separator with appropriate pore size should be the more fundamental requirement, ensuring that there is enough space for electrolyte to be retained in the separator and, as a result, more lithium and counter ions can pass through the separator.

Fibrous separators have sparked a lot of attention in recent years, with the goal of increasing the porosity of the separator. Typically, nanofibrillar membrane fabricated, for example,

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by electrospinning technique has a porosity of 70%–90%, mainly owing to the randomly aligned fibers with hundreds of nanometers in diameter.^[13] Nevertheless, poor mechanical properties are unavoidable as a consequence of such fineness,^[14] hindering the advances and applications of nanofibrous separator in LIBs. Another representative is the polyethylene terephthalate (PET) nonwoven fabric made with microfibers that are mostly manufactured using the melt-blown method, which appears to be an ideal substrate for battery separator. Reasons for being the separator candidate are attributed to its good thermal stability and mechanical strength, as well as the three-dimensional pore structure with high porosity.^[15] Whereas the reasons for it just being a base material are primarily because of its excessively large pore size (*i.e.*, a few to tens of microns), and the insufficient electrolyte wettability, consequently leading to poor liquid retention capacity and, on rare occasions, electrodes contact resulting in battery failure.^[16]

Ceramic-coating is the most commonly utilized approach to address the flaws mentioned above.^[17] For instance, Li *et al.*^[18] fabricated a PET/Al₂O₃ composite separator *via* simply depositing Al₂O₃ nanoparticles on two sides of PET nonwoven fabric. Because of the nanoparticle filling, the pore size was reduced significantly, and the electrolyte wettability was increased as well thanks to the polar groups of nanoparticles, giving the composite separator acceptable electrochemical performance. Nonetheless, these advancements come at the cost of losing its advantage of high porosity. Combining the nanofibrous and microfibrous membranes can retain the merits of both, preserving the acceptable porous structure of nanofiber layer while maintaining the desirable mechanical strength of microfiber layer. It has been reported by Zhu *et al.*^[19] that they prepared a PET reinforced poly(vinylidene fluoride) (PVDF) nanofiber hybrid separator with a uniform pore size (0.28 μm) and high porosity (80%). However, how the micro-nano fiber lamination affects ion transport was not addressed, and the poor wettability of PET has yet to be resolved. Hence, it is highly desirable to develop a fibrous separator with reasonable structure design and effective surface modification, maximizing the separator's involvement in ion transport.

In this contribution, a fibrous and composite separator for LIBs was developed by the combination of surface modification and micro-nano fibers lamination, and the effects of such combination on the porous structure, mechanical and thermal properties, wettability, ion transport and battery performance are explored. The as-obtained separator was capable of (i) being facilely fabricated *via* modifying the PET microfibrous membrane followed by electrospinning the polyvinylidene fluoride-hexafluoropropylene (PVDF-HFP) on the top of PET, (ii) retaining the robust mechanical strength and being endowed with shutdown function, (iii) possessing hierarchical pores in a range from 464 nm to 24.7 μm , high porosity of 88%, and high electrolyte affinity, (iv) presenting high ionic conductivity (5.4 mS/cm) and lithium ion transference number (0.56), which accelerates the ion transport and greatly favors the battery cycle performance. The striking features of the fibrous separator make it a promising candidate for LIBs with high safety and performance.

EXPERIMENTAL

Materials

PET nonwoven fabric (30 g·m⁻²) was provided by Jiangsu Yingyang Nonwoven Machinery, Ltd., China. Glycerol propoxylate triglycidyl ether (GPTE, molecular weight 434, epoxy value 0.16) was supplied by Hubei Yunmagnesium Technology Co., Ltd., China. Octadecylamine (ODA), 1-methylimidazole, *N,N*-dimethylformamide (DMF) and polyvinylidene fluoride-hexafluoropropylene (PVDF-HFP, $M_w=45500$) were supplied by Sigma-Aldrich (Shanghai, China). Liquid electrolyte, 1 mol/L lithium hexafluorophosphate (LiPF₆) in ethylene carbonate, ethyl methyl carbonate, and dimethyl carbonate (EC/EMC/DMC, 1/1/1, V/V/V), poly(vinylidene fluoride) (PVDF), carbon black (Super P-C45), LiFePO₄, and *N*-methyl-2-pyrrolidone (NMP) were supplied by Ferro Corp. A Celgard 2400 PP membrane was used for comparison. All chemicals were used as received without further purification.

Preparation of the Fibrous and Composite Separator (GOPPH)

Firstly, the PET nonwoven fabric was impregnated in a mixed solution for 1 h followed by curing at 150 °C for 1 h. The mixed solution was prepared by adding GPTE, ODA, and one drop of 1-methylimidazole into 100 mL of ethanol and stirred overnight. The ratios of GPTE to ODA were set as 15:1 (W/W). After curing, the modified PET nonwoven fabric was rinsed with anhydrous ethanol and then dried at 100 °C for 15 min. The modified PET nonwoven fabric was named GOP. Secondly, PVDF-HFP nanofibrous membrane was electrospun onto the GOP, forming a micro-nano fibers laminated membrane denoted as GOPPH. The PVDF-HFP electrospinning solution with a concentration of 20 wt% was prepared by dissolving PDVF-HFP in DMF and kept at 60 °C for 12 h with vigorous stirring. The obtained solution was electrostatically spun at a voltage of 13.5 kV with a distance of 15 cm, and a flow rate of 1 mL·h⁻¹. Finally, the GOPPH separators with a final thickness of ~200 μm were obtained by rolling press for thickness control and electrostatic elimination. Also, the composite separator without surface modification was prepared for comparison and denoted as PPH.

Characterizations

The morphologies of the microfibrous/nanofibrous membranes and GOPPH composite separators were observed with a field-emission scanning electron microscope (FE-SEM, Hitachi S4800). The surface chemical compositions of GOP samples were verified by Fourier transform infrared (FTIR) spectra recorded on a Nicolet 5700 instrument with attenuated total reflectance (ATR) mode. The pore size of the microfibrous and nanofibrous membranes was measured using a Porometer 3G through-pore size analyzer. The porosity of the separator was determined using the *n*-butanol uptake method based on the equation $\text{porosity (\%)} = (m_w/\rho_w)/(m_w/\rho_w + m_d/\rho_d) \times 100\%$, where m_w is the mass before absorbing *n*-butanol and m_d is the mass after absorbing *n*-butanol for 2 h; ρ_w and ρ_d represent the densities of *n*-butanol and polymer, respectively.

The electrolyte contact angle of the separator were measured using a DSA100 apparatus (Krüss Company, Germany). The weight change of the separator before and after immersion in electrolyte for 2 h was used to determine the electrolyte uptake. Separator thermal shrinkage was determined by

measuring the dimensional change before and after heat treatment at 150 and 200 °C for 1 h. The shutdown temperature of the separator was examined by using a differential scanning calorimeter (DSC, TA Instruments), and the sample was scanned from 30 °C to 300 °C at a heating rate of 10 °C·min⁻¹ under a nitrogen atmosphere. The tensile strength of the separator was tested by an Instron Universal testing machine (Instron, 5967) at a rate of 20 mm/min with a gauge length of 50 mm, and five specimens for each sample were used for average.

The electrochemical performances of all separators were measured using an electrochemical workstation (BioLogic SP-300). Linear sweep voltammetry (LSV) was used to measure the electrochemical stability of separators by assembling the SS/ liquid-electrolyte-soaked separator/Li cell. LSV measurements were carried out from 3.0 V to 6.0 V versus Li/Li⁺ at a scan rate of 1 mV·s⁻¹. The interfacial resistance of the separator was tested for interfacial compatibility analysis by electrochemical impedance spectroscopy (EIS) over the frequency range from 0.1 Hz to 0.1 MHz with an amplitude of 10 mV. Separators for measurement were sandwiched in the Li/liquid-electrolyte-soaked separator/Li cell.

The ionic conductivity of the separator was determined using EIS. The separator is placed between two stainless steel electrodes and the coin-type test cell is immersed with the electrolyte solution (1 mol/L LiPF₆, EC/DEC/DMC, 1/1/1, V/V/V) to measure the AC impedance. The impedance data were obtained in the frequency range of 10 Hz–100 kHz with an amplitude of 10 mV at room temperature. The ionic conductivity (σ) was obtained from equation $\sigma = d/(R \times A)$, where d is the thickness of the separator, A is the area of the separator, and R is the bulk resistance obtained at the high-frequency intercept of the Nyquist plot on the real axis. The lithium ion transference number (t_{Li^+}) was determined by AC impedance and DC polarization techniques with a symmetric Li/liquid-electrolyte-soaked separator/Li cell following the formula $t_{\text{Li}^+} = (I_s - (V - I_0 R_0))/(I_0 - (V - I_s R_s))$, where I_0 and I_s are the initial and steady-state current values, respectively, R_0 and R_s correspond to the resistance of cell before and after polarization, V refers to the potential applied for the cell.

The electrochemical performance of the separator was investigated by using 2025 coin-type half-cells. The separator was placed between the lithium metal anode and cathode of LiFePO₄ (LiFePO₄/acetylene black/PVDF=80/10/10) and soaked with the liquid electrolyte (1 mol/L LiPF₆ in EC/DEC/DMC, 1/1/1, V/V/V). The cycle performance and rate discharge tests were carried out using a battery cycle tester (BTS 5 V 10 mA, Neware Company, China) over a voltage range of 2.5–4.2 V. A charge/discharge cycling test was performed for 200 cycles at a current density of 1 C. Rate capability measurements were performed at a current density of 0.1, 0.2, 0.5, 1, 2 and 5 C.

RESULTS AND DISCUSSION

Morphologies Analysis

Fig. 1(a) illustrates the fabrication process of the GOPPH composite separator via a surface modification to enable PET more affinity with electrolyte, followed by the electrospinning of PVDF-HFP on top of the treated PET (GOP). The surface

morphologies of PET and GOP are shown in Figs. 1(b) and 1(c), respectively. The PET membrane is interwoven with numerous randomly orientated microfibers with an average diameter of 13 μm . The bonding between the fibers of the PET membrane can be seen in the inset of Fig. 1(b). This is because the PET nonwovens are usually reinforced by hot pressing. After being immersed into the GPTE-ODA mixed solution and then cured, the fibers in the GOP became rougher compared with those in the untreated PET. This was because an epoxy-amino coupling reaction and etherification reaction between GPTE and ODA had sequentially happened in the mixing and curing processes, respectively, and the final reaction product as a coating layer was formed on the fiber.^[20] As verified by FTIR in Fig. 1(d), after the coating treatment, the spectra present new bands at 2927 and 2863 cm⁻¹, which are attributed to the C—H stretching vibrations of methylene in the alkyl group. The new band at 1371 cm⁻¹ is assigned as a CH₃ symmetric deformation. The band at 1096 cm⁻¹ is strengthened, corresponding to the C—O—C stretching vibration. The new band at 931 cm⁻¹ occurs, which was assigned to the asymmetric vibration of the epoxy group. These results indicated the presence of GPTE-ODA on the fiber surface, and also suggested the existence of polar groups like C—O, C—OH, epoxy, etc., on fiber surface after the reactions between GPTE and ODA.^[20] Actually, the effect of the ratio of GPTE to ODA on the structure of PET was explored (Fig. S1 in the electronic supplementary information, ESI). It can be found that with the increasing ratio from 10:1 to 20:1, the reaction products agglomerated on fibers became increasingly evident (Figs. S1a and S1b in ESI) whereas the typical bands in FTIR spectra were not significantly intensified (Fig. S1c in ESI), which should be because that the reaction between GPTE and ODA could be saturated, especially as the ratio reaches 20:1, and excessive GPTE would be solidified after cured. Meanwhile, the coating treatment is designed to improve the wetting property of PET and whether the ratio affects the wettability is also studied. As shown in Fig. S1(c) (in ESI), the GOP with a ratio of 15:1 demonstrated superhydrophilicity with a water spreading time less than 0.1 s, and wettability to water changes not too much with increasing ratio. Hence, the GPTE to ODA ratio of 15:1 was selected for the following process. Meanwhile, the PET microfibrillar layer was laminated with a layer of PVDF-HFP nanofibers after surface modification (Fig. 1e), resulting in a composite micro-nano fibers separator with a thickness of 200 μm . (Figs. 1f and 1g). The GOPPH separator used in this study has a thickness of ~200 μm , which is significantly thicker than the average commercial separator's thickness of ~25 μm . This is because that the PET substrate with an areal density of 30 g/m² has large thickness (~110 μm). On one hand, the thickness can be reduced by selecting a PET nonwoven fabric with low density, which has been customized and is still under our investigation on the effect of PET thickness on the properties of GOPPH. On the other hand, it is possible by pressing the PET or GOPPH membrane through a press roller to a thickness that is similar to the commercial separator's 25 μm , but doing so would go against the purpose of using fibrous separator because the fibers would be completely flattened, pores would disappear and porosity would be significantly reduced.

As a separator applied for LIBs, the porous structure of the separator is vital to the safety and performance of batteries.

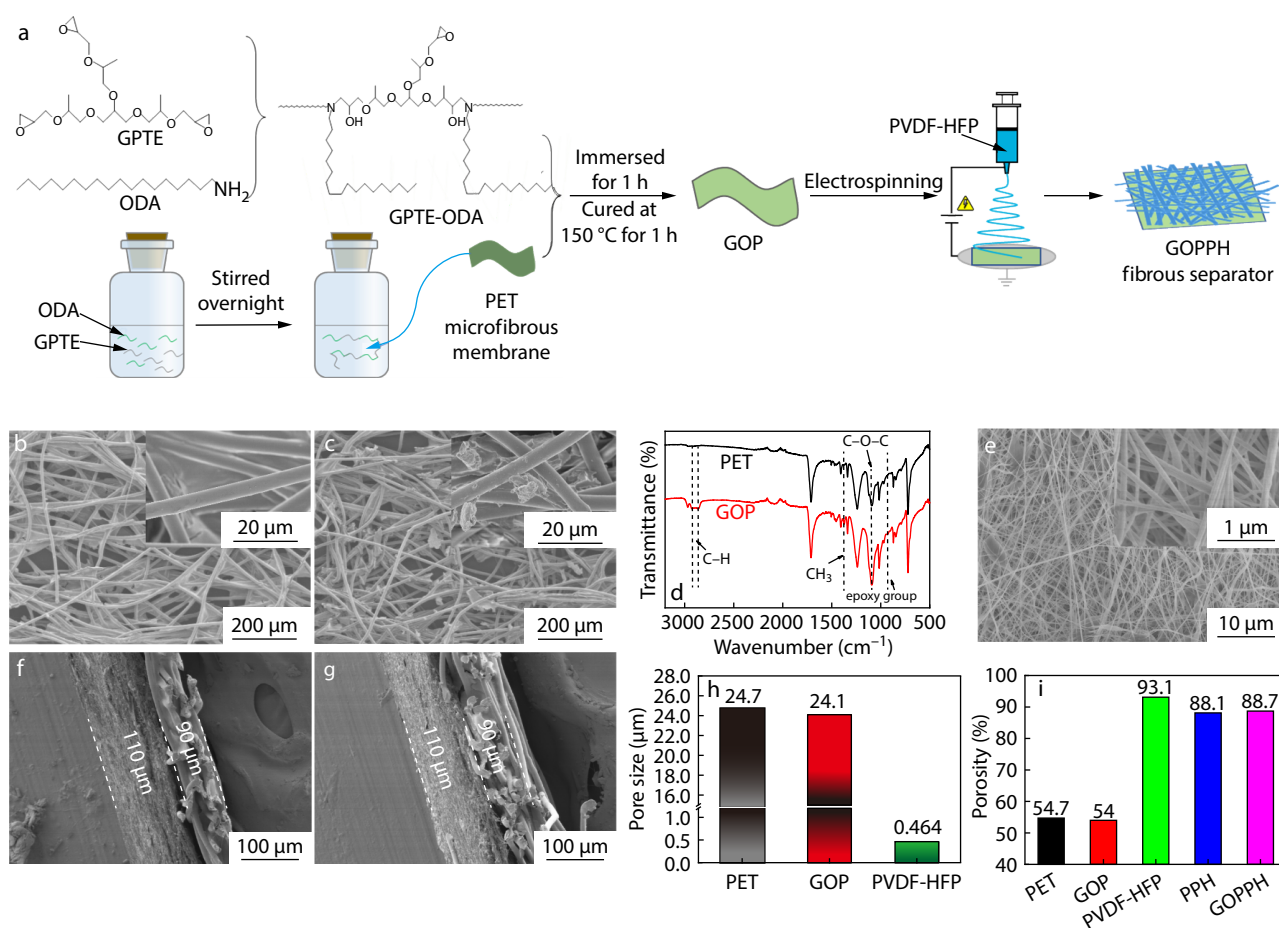


Fig. 1 (a) Schematic representation of the preparation of GOPPH composite separator. SEM images of surface morphologies for (b) PET and (c) GOP; (d) FTIR spectra of PET and GOP; SEM images of (e) surface morphology for PVDF-HFP, the cross-section for (f) PPH, and (g) GOPPH; (h) Pore size of PET, GOP, and PVDF-HFP; (i) Porosities of all separators.

Fig. 1(h) displays the average pore sizes of these fibrous membranes. As shown, the PET membrane has large pores, with an average pore size of 24.7 μm, and the pore size does not change considerably after the coating treatment. The pore size value is too large to match the separator requirement, as a result, the PET before and after surface modification cannot be used individually as a battery separator. As expected, the PVDF-HFP nanofibrous membrane has an average pore size lower than 1 μm, and the coverage of the nanofiber layer on the PET or GOP makes the composite appropriate for use as a separator. It should be noted that the pore size of these fibrous separator is much larger than that of commercial PP separator (a few tens of nanometers), which is mainly ascribed to the difference in separator fabrication method. Pores of PP are produced by mechanical stretching during wet or dry process, while pores of PET or PVDF-HFP are created by the interwoven fibers fabricated by melt-blowing or electrospinning techniques. As for the porosity (**Fig. 1i**), the PET or GOP and PVDF-HFP layers have higher porosities than the commercial PP separator, and the lamination of the two layers also can maintain the advantage of high porosity. According to the morphologies and porous structure analysis, it can get that the composite GOPPH separator, on the premise of holding high porosity, exhibits the hierarchical feature not

only in the fiber diameter but also in the pore size, which is supposed to have a great influence on the separator performance.

Electrolyte Wettability and Stability

The excellent electrolyte wettability of separator can facilitate electrolyte absorption and promote ion transport, thus improving the electrochemical performance of the separator.^[21] **Fig. 2(a)** gives the electrolyte contact angle evolution with the time of different separators. Let's first focus on single-layer separators and their wettability. The contact angle of PET to electrolyte was 27.5°, whereas electrolyte dropped on GOP separators spread out completely within 0.1 s, owing to the lyophilic property derived from the endowed polar groups on the fiber surface and the interconnected porous structure of fibrous separator. The PVDF-HFP separator also can be wetted completely, though it takes a bit longer time (>10 s) for electrolyte spreading. Move on to the laminated separators and the wettability of both sides was explored. It can be seen from **Fig. 2(a)** that as the PVDF-HFP was laminated with PET, the electrolyte on the PET side is thoroughly wetted in less than 0.5 s, but the electrolyte on the PVDF-HFP side requires 2.16 s. This indicates that PPH has better wettability than single-layer PET or PVDF-HFP membranes due to the structure provided by the

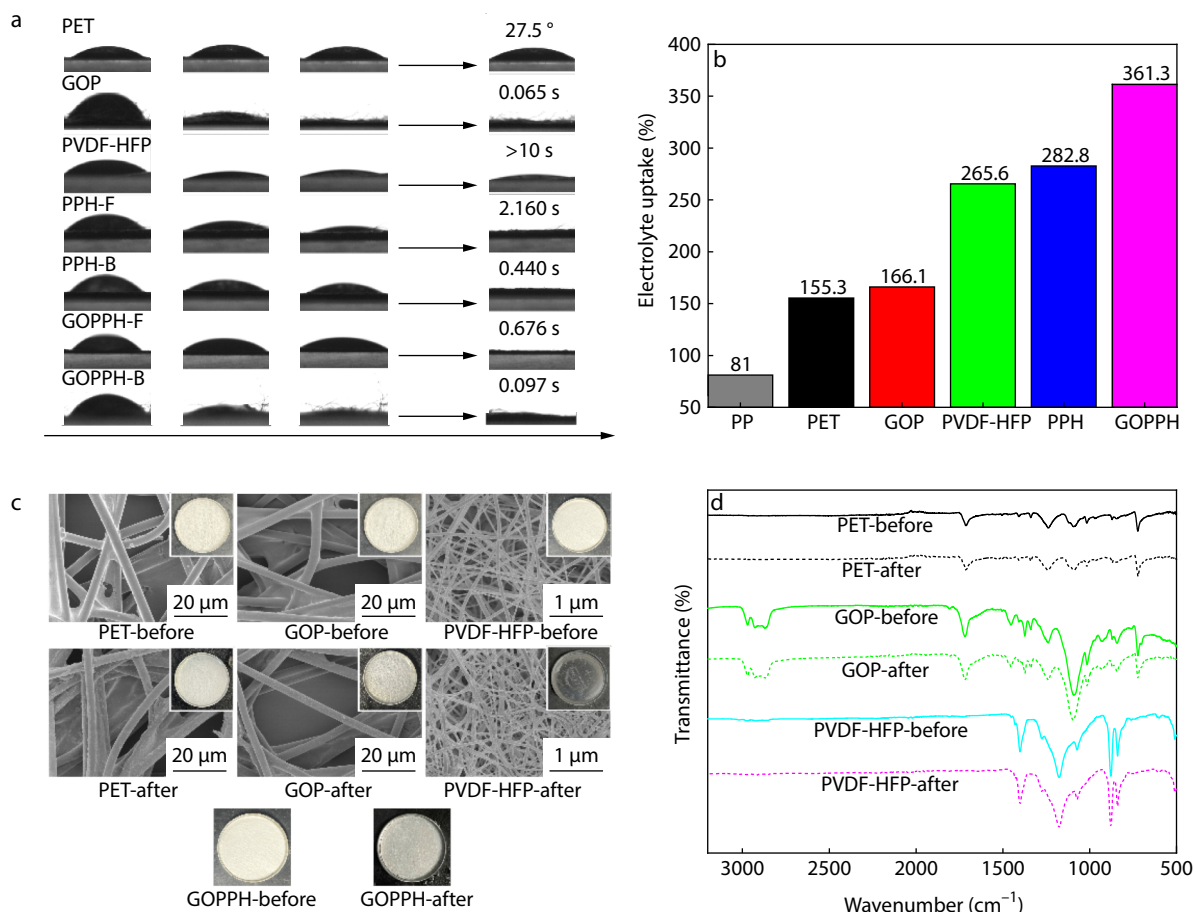


Fig. 2 (a) Electrolyte contact angle changes with spreading time (F: the PVDF-HFP side and B: the PET or GOP side); (b) Electrolyte uptake for different separators; (c) SEM images and photographs and (d) FTIR spectra of separators before and after immersing electrolyte for 2 days.

lamination of two composite membranes with large and small pore sizes. In the GOPPH composite separator, the complete wetting time of the GOP layer was less than 0.1 s, while the complete wetting time of the PVDF-HFP layer was less than 0.7 s. Meanwhile, compared with the PVDF-HFP and PPH nanofibrous separators, the electrolyte wetting property of the composite separator is greatly enhanced, also because of the hydrophilic nature of the GOP layer which acts as a moisture conductor in the PVDF-HFP layer.

Fig. 2(b) describes the separator electrolyte uptake that is greatly dependent on the porosity and wettability of the separator. The uptake values of PET and GOP separators are 155.3% and 166.1%, respectively. Although they are higher than the PP separator, it is much lower than the nanofibrous separator (PVDF-HFP, 265.6%) primarily owing to the large pore size of PET/GOP. When the PET was composited with PVDF-HFP, the electrolyte uptake value was almost the same as that of the nanofibrous separator, whereas the value for the GOPPH separator reached 359.4%, which could be attributed to the high porosity in the 3D fibrous structure, providing more space to save the electrolyte,^[22] and to the improved wettability, being beneficial to absorb more electrolytes by fixing electrolyte molecules with polar groups.^[23] Meanwhile, the dimensional and chemical stability of PET and

its composite separators in electrolyte were examined. As Fig. 2(c) shows, these fibrous separators keep its original dimension after immersing in electrolyte for two days. Similarly, the FTIR spectra (Fig. 2d) of all separators did not exhibit distinct changes after soaking electrolyte. The results indicate that the as-prepared composite separators possessed desirable dimensional and chemical stability in electrolyte, actually satisfying the basic requirement of LIBs for separators. The desirable electrolyte wettability and stability of GOPPH is supposed to have a great influence on ion transport and electrochemical performance, which will be discussed in the following section.

Mechanical and Thermal Properties

One of the goals of this research is to compensate for the nanofibrous membrane by utilizing the mechanical and thermal properties of the microfibrous membrane. As expected, the flexible PET microfibrous membrane with high modulus possesses largely higher tensile strength than the soft PVDF-HFP nanofibrous membrane (Fig. 3a). Meanwhile, the stress-strain curve of GOP is nearly identical to that of PET, implying that the coating treatment had no discernible effect on PET's mechanical capabilities. Furthermore, the modulus and tensile strength of the PPH and GOPPH composite membranes are comparable to that of PET and PVDF-HFP, respectively, which could be ascribed

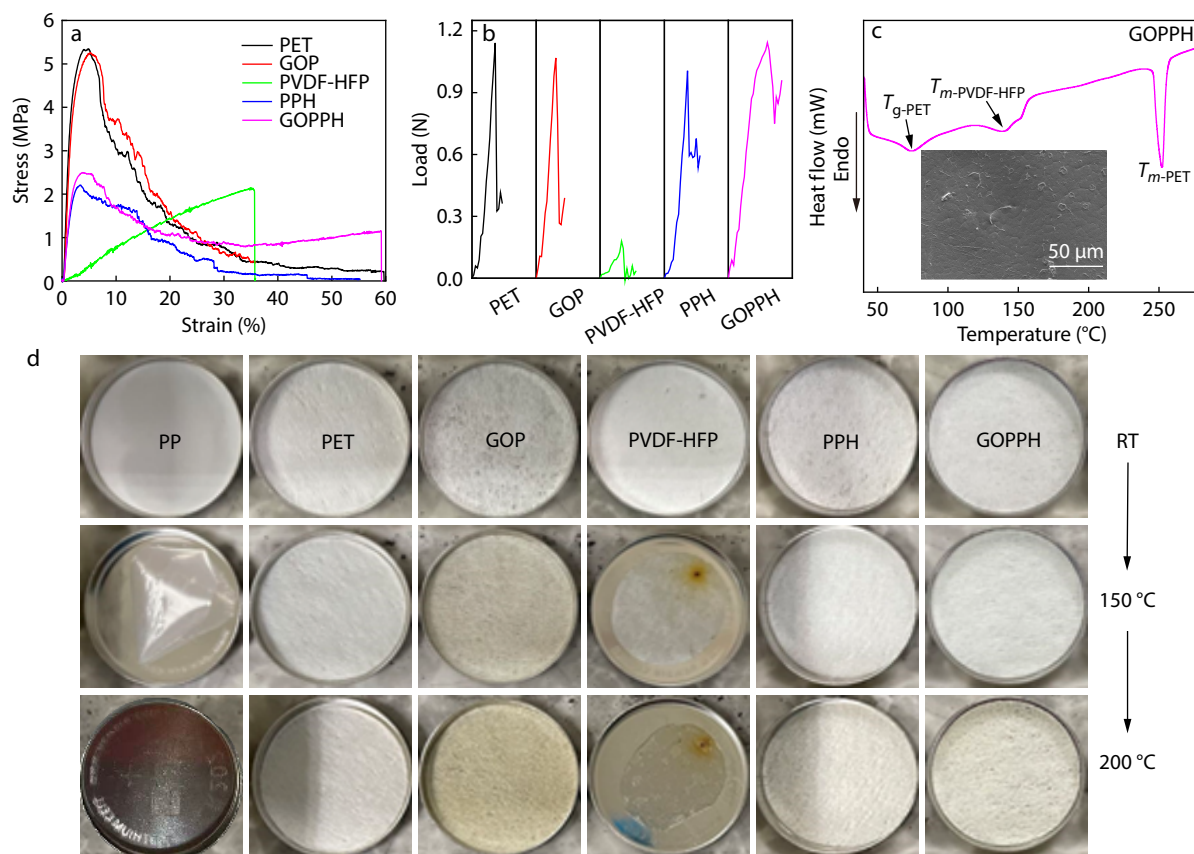


Fig. 3 (a) Stress-strain curves and (b) puncture resistance of separators; (c) DSC curve of GOPPH separator in the heating scan (inset is the SEM image of GOPPH after heating at 150 °C); (d) Optical photographs of the separators treated at different temperatures for 1 h.

to the fracture heterogeneity of the microfibrillar and nanofibrillar layers.^[24] The puncture load curves of separators that change with deformation are shown in Fig. 3(b). Since all separators have same thickness, the puncture load is used to indicate the puncture resistance property. As can be observed, the PVDF-HFP nanofibrillar membrane exhibits the lowest puncture load due to its nanoscaled nanofibers and weak tensile strength. Meanwhile, PET and GOP had nearly identical puncture loads, both greater than 1 N, suggests that the wetting modification applied to PET had no impact on the material's puncture resistance. Moreover, the laminated PPH and GOPPH separators also presented comparable puncture loads with PET and GOP, indicating that the lamination might make up for the puncture property of the nanofibrillar separator.

The thermal properties of separators were examined by DSC and thermal shrinkage tests. Endothermic peaks at 150 and 250 °C can be observed in the DSC curve of GOPPH (Fig. 3c), which should be assigned to the melting of PVDF and PET components, respectively. As a result, the GOPPH separator can be endowed with a function of thermal shutdown, which means that as the temperature goes up, the separator has the ability to block the pores by the melting PVDF-HFP and timely cut down ion transport while maintaining its dimensional integrity until the temperature rises enough to melt the PET. The shutdown ability was verified by an SEM image (the inset in Fig. 3b) of the GOPPH separator after 1 h of treatment at 150 °C, where the pore occlusion can be clearly viewed. The

shape variations of different separators following thermal treatment at various temperatures are shown in Fig. 3(d). When exposed to 150 °C for 1 h, the PP separator distorted and curled, and when exposed to 200 °C, it totally melted, losing its shape and function as a separator. PVDF-HFP also shrunk significantly after being continuously heated at 150 °C, easily leading to the electrode contact and resulting in an internal circuit short. Separators made of PET or GOP, on the other hand, were able to maintain their dimensions even after being heated to 200 °C. The above results indicate that, in comparison to a single-layer or single-component separator, the GOPPH separator exhibits a shutdown function and high thermal stability, enabling it to stop the electrochemical reaction timely and also reduce the probability of thermal runaway.

Ion Transport Ability

Here, it should be pointed out that the PET and GOP samples are not appropriate for the LIBs separators owing to the quite large pore size and the cell with the two membranes cannot be charged well in our work, as a result, the following discussion on electrochemical performance is based on the PP, PVDF-HFP, PPH and GOPPH separators.

One of the most significant roles of the separator is to act as porous channels for ion transport, therefore, the ion transport ability of the as-designed GOPPH separator is thoroughly investigated. The Nyquist plots of cells with different separators sandwiched between two stainless steel elec-

trodes are presented in Fig. 4(a), from which the bulk resistance and the ionic conductivity values can be calculated. The ionic conductivity values for the fibrous separator are higher than that of 0.51 mS/cm for PP, which can be attributed to the three-dimensional network structure of fibrous membrane with high porosity, which could provide more channels for ion transport.^[25] Meanwhile, the GOPPH separator has the highest ionic conductivity (5.40 mS/cm) than the PVDF-HFP (3.60 mS/cm) and PPH (3.74 mS/cm), mainly due to the combined effect of high porosity, high electrolyte uptake and improved electrolyte wettability, and allowing more ions to travel across the separator.^[15]

Another important indicator of electrochemical performance is the lithium ion transference number (t_{Li^+}), which is the ratio of the number of lithium ions to the sum of anions and cations passing through one cross-section per unit of time. The higher the t_{Li^+} value is, the higher the percentage of Li^+ transfer, indicating that the electrolyte is more efficient in transferring charge between the cathode and anode.^[26] Fig. 4(b) depicts the DC polarization diagrams and AC impedance spectra of Li/Li symmetric cells with different separators, and the t_{Li^+} values can be calculated for these separators. The t_{Li^+} of the PP separator is 0.31, lower than those of fibrous separator (0.32 and 0.36 for PVDF-HFP and PPH, respectively). As the microfibrillar and nanofibrillar layers were laminated,

there were large increases in the value of t_{Li^+} . Evidently, the t_{Li^+} value of the GOPPH separator can reach up to 0.56. Such a noteworthy increase in t_{Li^+} is closely related to the high porosity and improved wettability of the GOPPH separator, which could promote the transport of ions more efficiently and is beneficial to polarization reduction and battery cycle and rate performances.^[27–29] Based on the above ion conductivity and lithium ion transference number values, it can be concluded that the GOPPH separators performed better in terms of lithium ion transport quantity.

In order to further illustrate the collaboration of surface modification with lamination in ion transport, the lithium ion transport rate in the porous channel is calculated by using Newman's mode,^[30] and the detailed calculation process is described in ESI. As shown in Fig. 4(c), the transport rate of lithium ions via the GOPPH separator is higher than those through PVDF or PPH separator, suggesting the joint acceleration effects of pore size and surface modification. What's more, the acceleration of the GOPPH separator on ion transport can be explained using an ideal physics acceleration mode, which can be utilized to calculate the time required for lithium ions to travel through the separator. A full explanation of the calculation process is also presented in ESI. The time that lithium ions took to pass through the separator is presented in Fig. 4(d). When the microfibrillar separator was

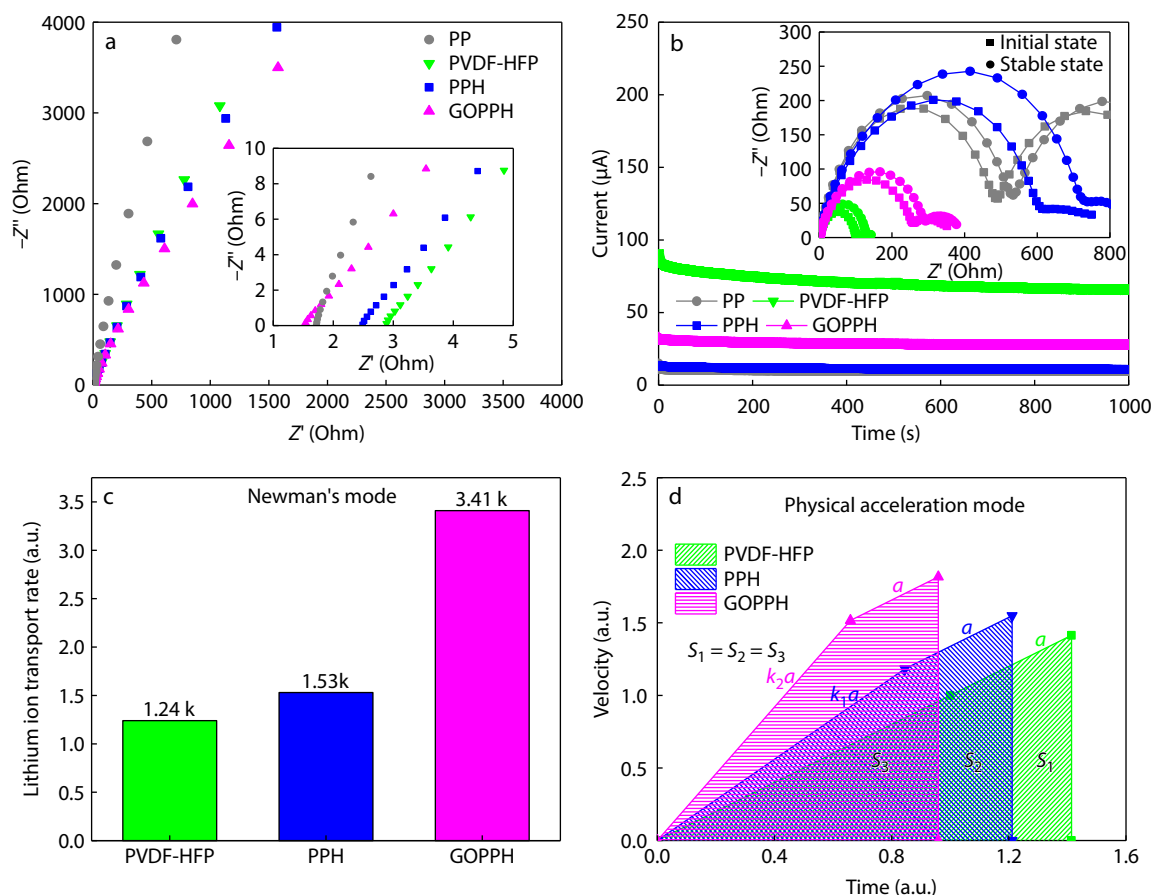


Fig. 4 (a) Nyquist plots of SS/separator/SS cells using PP, PVDF, PPH, and GOPPH separators; (b) The potential polarization curves of all separators (the insets are Nyquist plots of separators before and after polarization); (c) Lithium ion transport rate and (d) lithium ion transport time is used for passing through the separator.

surface modified and laminated with a nanofibrous membrane, the time for GOPPH was shorter than that for PPH or PVDF-HFP, respectively. The result was well consistent with the lithium ion transport rate in Newman's mode. Therefore, the theoretical calculation above both confirmed that the surface modification and micro-nano fiber lamination can speed up lithium ions transport within the separator, which was highly helpful in achieving high power density in LIBs.^[31]

The reasons for such a large improvement in ion transport of the GOPPH separator can be attributed to the following aspects, and a schematic representation of ion transport through the separator is shown in Fig. 5. Assuming that all separators are of the same thickness and firstly compared with the PVDF-HFP nanofibrous membrane, the GOPPH composite separator reveals higher porosity and electrolyte uptake that benefits from the lamination with a microfibers layer with a larger pore size, resulting in a higher total number of ions transported through the separator. Meanwhile, ions moving through a layer with a bigger pore size and greater porosity have a lower resistance, allowing them to move more quickly. Secondly, in comparison with the PPH separator, the PET layer in the GOPPH were surface-modified with coating polymers containing lots of polar functional groups (e.g., hydroxyl and epoxy group). On one hand, these groups could promote the separator to absorb more electrolytes by fixing them with interactions including electrostatic, van der Waals, and hydrogen, resulting in an increase in the total amount of ions transported by the separator. On the other hand, it has been reported that the hydrogen atom in the hydroxyl group presents a positive charge due to the strong electronegativity of the oxygen atom.^[32] As a result, the anions (PF_6^-) in the electrolyte, which exhibit electronegativity, have a strong electrostatic attraction to these hydrogen atoms, and are bonded or fixed by the electrostatic force on the GOP surface, in turn promoting the migration of lithium ions.^[27] Therefore, it is the synergistic consequence of micro-nano fiber lamination and surface modification that makes the GOPPH separator superior in lithium ion transport.

Electrochemical and Battery Performance

The reliability of separators should be ensured by their electrochemical stability immersed in the electrolyte. Thus, the electrochemical stability of the GOPPH separator is evaluated by the LSV experiment and compared to the PP, PVDF-HFP nanofibrous separator and PPH composite separator. As can be seen from Fig. 6(a), the PP exhibits anodic stability up to 3.9 V versus Li^+/Li , while the values of the PVDF-HFP, PPH, and GOPPH

are greater than 4.5 V. Such a wide electrochemical stability window demonstrates that the introduction of the 3D fibrous and porous network increases the interfacial affinity of the separator in the liquid electrolyte,^[33] which is conducive to improving the interfacial stability, and thus the GOPPH could be a promising separator applied for high-voltage LIBs. Another important parameter that determines the battery property is the interfacial compatibility between separators and the Li electrode. The interfacial compatibility of cells with various separators is evaluated by the EIS and the corresponding Nyquist plots are displayed in Fig. 6(b). The radius of the semicircle in the impedance spectrum represents the electrode-electrolyte interfacial resistance (R_{in}). The PP, PVDF-HFP, PPH and GOPPH separators have R_{in} values of 332.5, 256.4, 337.5 and 172.3 Ω , respectively. It is generally known that the interfacial resistance of separator is greatly dependent on the thickness of separator; therefore, when a separator merely varies in thickness, the larger the thickness, the higher the interfacial resistance. But when two separators differ in material, thickness, porosity, pore size, etc., the interfacial resistance of separator would not be decided by the thickness.^[34] In our case, the GOPPH is a type of fibrous separator that, despite its heavier thickness, has higher porosity (Fig. 1i), larger pore size (Fig. 1h), superior electrolyte wettability (Fig. 3a), and higher electrolyte uptake (Fig. 3b) than the commercial PP separator, thus resulting in a decreased interfacial resistance. This also implies that using a GOPPH separator improved the interfacial compatibility between the composite separator and the Li electrode, which is beneficial for ions transport at the electrode-electrolyte interface, which could lead to lower cell resistance and improved battery performance.

The battery cycling and C-rate performance with the GOPPH separator were examined with the control groups of PVDF-HFP, PPH and commercial PP. As shown in Fig. 6(c), the $\text{LiFePO}_4/\text{Li}$ cell with GOPPH separator has a higher initial discharge capacity (146.2 $\text{mAh}\cdot\text{g}^{-1}$) than the cells other separators (109.6, 123.5 and 130.5 $\text{mAh}\cdot\text{g}^{-1}$ for PP, PVDF-HFP, and PPH, respectively). The discharge capacity of cells with PP separators decreases more quickly during cycling than cells with fibrous separators. After 200 cycles at 1 C, the cell assembled with the composite GOPPH separator has a stable specific capacity with a capacity retention of 93%, and the coulombic efficiency is kept at 98.0%. Moreover, the morphologies of PP and GOPPH separator after 200 cycles are presented in Fig. S3 (in ESI). As shown, some of pores on the surface of PP separator became blocked possibly because of the lithium dendrites growth and nonuniform distribution, seriously impairing

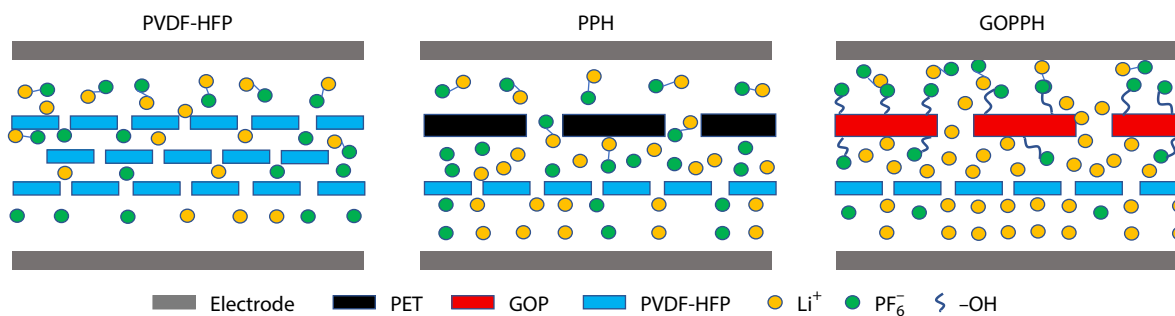


Fig. 5 Schematic representation of ion transport passing through the separator.

battery performance. However, GOPPH separator's circle-shape and size, as well as PET microfibers and PVDF nanofibers' shape and diameter, all stayed unchanged after the charge-discharge cycles, confirming its excellent stabilization for use in practical batteries. These results demonstrate that the utilization of GOPPH membrane as LIBs separator is feasible in terms of achieving high battery performance owing to the strong affinity for electrolyte and the micro-nano fibers lamination with hierarchical porous structure. Fig. 6(d) describes the C-rate capacities of cells for 5 cycles at different rates. The cells containing the PP, PVDF-HFP, and PPH separators deliver discharge specific capacity of about 135.1, 145.2 and 154 mAh·g⁻¹ at 0.1 C, respectively, which decrease to

28.4, 24.7 and 23.2 mAh·g⁻¹ at 5 C. By comparison, the battery using the GOPPH separator exhibits an initial capacity of about 155.4 mAh·g⁻¹ at 0.1 C, and drops to 78.8 mAh·g⁻¹ at 5 C. The discharge specific capacity is restored as the rate goes back to 0.1 C, indicating the excellent reversibility of the batteries. The improvement in the rate performance of the GOPPH separator could be explained by the strengths of surface modification collaborative with pore design in terms of excellent wettability and fast and efficient ion conductivity.

Table 1 provides comparisons with other reported fiber separators that use PET or other microfibers as substrate. When compared to previous studies using PET nonwoven as a substrate,^[17,18,35–38] our pre-wetting treatment of PET resul-

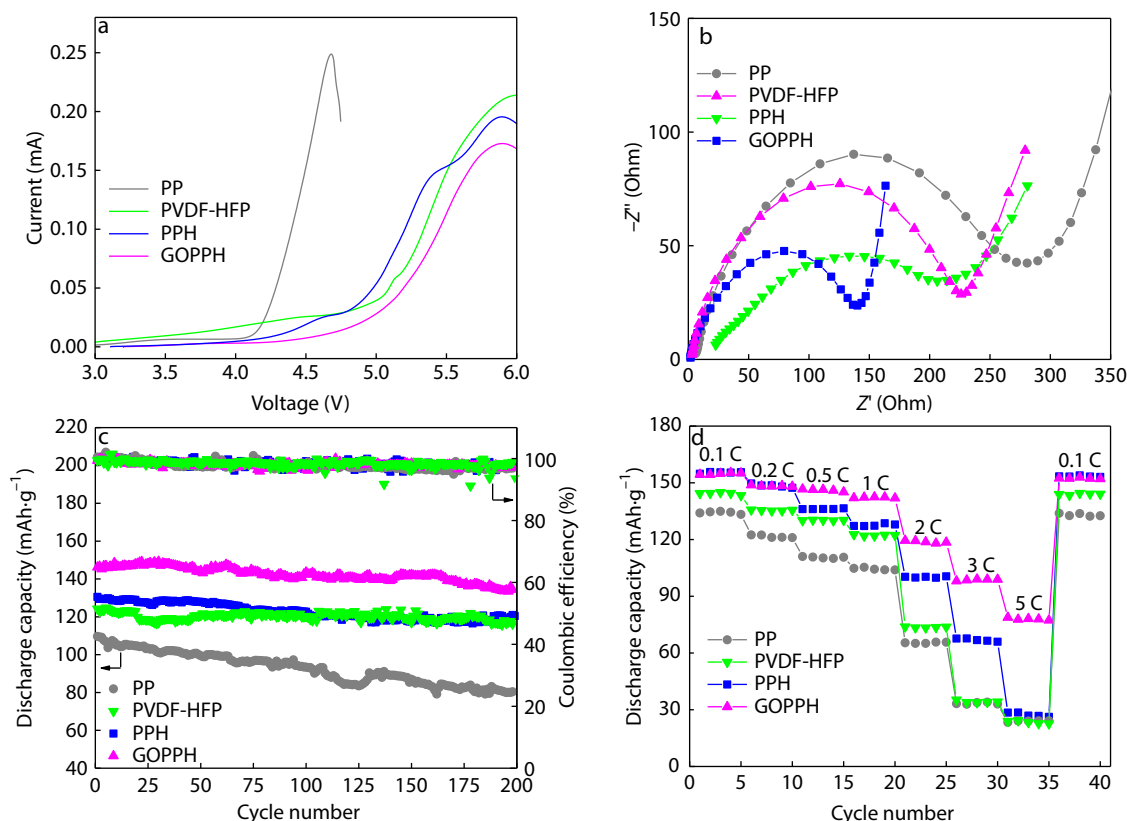


Fig. 6 (a) LSV curves of Li/separator/SS cells from 3 V to 6 V; (b) Nyquist plots of Li/separator/Li cells; (c) Cycling performance and (d) rate capabilities of LiFePO₄/separator/Li cells with PP, PVDF-HFP, PPH and GOPPH separators.

Table 1 Performance comparisons of separators with PET or other microfibers for lithium ion batteries.

Separator	Preparation method	Electrolyte uptake (%)	Ionic conductivity (mS/cm)	Cyclability	Ref.
PET	Electrospinning	500	2.27	95% after 50 cycle at 0.1C	[35]
Al ₂ O ₃ /PET	Dip-coating	121.5	1.13	92% after 100 cycle at 1C	[18]
PET-SiO ₂ /Al ₂ O ₃	Dip-coating	146	1.22	94% after 100 cycle at 1C	[36]
SSCS	Thermal induced phase separation	259.7	0.98	95% after 100 cycle at 0.2C	[37]
PVDF-HFP/PET	Coating	95	0.83	87% after 100 cycle at 1C	[17]
Al ₂ O ₃ @PVA-co-PE/PET/PVA-co-PE	Coating	—	0.92	99% after 100 cycle at 0.5C	[38]
PVDF-HFP/colloidal Al ₂ O ₃	Phase inverse	371	0.7	95% after 100 cycle at 0.5C	[39]
PMIA@PVDF-HFP	Electrospinning	460	0.68	87% after 100 cycle at 1C	[14]
PVDF-HFP/PET/PVDF-HFP	Electrospinning/Phase separation	282	6.39	86% after 100 cycle at 1C	[40]
GOPPH	Electrospinning	361.3	5.4	93% after 200 cycle at 1C	This work

ted in a GOPPH composite separator with a higher electrolyte uptake, which in turn led to a higher ionic conductivity. While PVDF-HFP has been used in other studies as one of the separator substrates,^[39–41] our preparation method of electrospinning can directly supply the composite separator with good ion channels during the cycling process. Therefore, the GOPPH separator in this work demonstrated a comparable wetting property and stable electrochemical performance, making it a promising candidate as the separator for lithium ion batteries.

CONCLUSIONS

In summary, using sequential processes of surface modification of PET microfibrinous layer and lamination of a PVDF-HFP nanofibrinous layer, we successfully manufactured a composited separator that could largely combine the merits of materials with micro-/nano-fibrous structure. This combination endowed the as-resulted GOPPH separator with high porosity of ~90% and hierarchical pore size in a range of 0.464–24.1 μm , and also with satisfactory wettability, mechanical strength and thermal shutdown function. Moreover, the GOPPH separator exhibited excellent ion transport ability, reflected in the number of ions transported as well as the ion transport rate. Consequently, the cell with the GOPPH separator was offered superior cycling and rate performance with a capacity retention of 93% after 200 cycles at 1 C. Therefore, the features of composite separator would be conducive to the development of high-safety and high-performance lithium-ion batteries.

NOTES

The authors declare no competing financial interest.

Electronic Supplementary Information

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