

Poly(vinylidene fluoride) Separators with Dual-asymmetric Structure for High-performance Lithium Ion Batteries*

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Abstract Dual-asymmetric poly(vinylidene fluoride) (PVDF) separators have been fabricated by thermally induced phase separation with dimethyl sulfone (DMSO2) and glycerol as mixed diluents. The separators have a porous bulk with large interconnected pores (~1.0 μm) and two surfaces with small pores (~30 nm). This dual-asymmetric porous structure endows the separators with higher electrolyte uptake amount and rapider uptake rate, as well as better electrolyte retention ability than the commercialized Celgard 2400. The separators even maintain their dimensional stability up to 160 °C, at which temperature the surface pores close up, leading to a dramatic decrease of air permeability. The electrolyte filled separators also show high ion conductivity (1.72 mS·cm⁻¹) at room temperature. Lithium iron phosphate (LiFePO₄)/lithium (Li) cells using these separators display superior discharge capacity and better rate performance as compared with those from the commercialized ones. The results provide new insight into the design and development of separators for high-performance lithium ion batteries with enhanced safety.

Keywords: Polymer separator; Lithium ion battery; Dual-asymmetric structure; Porous membrane; Thermally induced phase separation.

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INTRODUCTION

Lithium ion batteries have gained unprecedented attention in the fields of large-scale power sources and energy storage devices owing to their high energy density and long cycle life^[1–6]. Despite the endeavors to further improve the performances of lithium ion batteries, the safety issues are also of great concern. The separator, as one of the critical components, is considered to play a vital role in the safety characteristics of lithium ion batteries. It acts as a spacer between anode and cathode while permitting free flow of lithium ions^[7–11]. Currently, polyethylene (PE), polypropylene (PP), and PE/PP composite membranes are the most widely used separators for lithium ion batteries. Although these separators possess good electrochemical stability, relatively high mechanical strength and thermal shutdown ability, it is still challenging that PE and PP often suffer from severe dimensional instability and poor electrolyte affinity^[12, 13]. Severe dimensional instability may cause internal short-circuit or thermal runaway especially for use in batteries at high charge/discharge current. Poor

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electrolyte affinity will result in serious electrolyte leakage, volatility, and spontaneous combustion of electrolyte. These safety issues have become a major obstacle for the further advancement of lithium ion batteries. Therefore, it is mandatory to develop highly safe separators with good electrolyte wettability, low electrolyte leakage, and superior thermal properties for advanced lithium ion batteries.

It is well recognized that the porous structure of separators is of great importance for the performance and safety of lithium ion batteries^[14–16]. Separators with large pores are beneficial for increasing ionic conductivity that is related to the initial capacity and high-rate performance of lithium ion batteries. On the other hand, small pores are much better than large ones when considering safety and long-term cycle life of the batteries, as they can efficiently prevent the growth of lithium dendritic and the leakage of electrolyte. Consequently, the battery performance and safety are affected by the pore size inversely. It forms a tradeoff that must be overcome for the development of lithium ion batteries. Recently, membranes with multi-scale pore structures were proposed to be used as separators^[17–19]. Kim and Park prepared a poly(vinylidene fluoride-co-hexafluoro-propylene) (PVDF-HFP) based separators with small pores embedded in large pores^[17]. The unique multi-scale pore structures endow the separators with high ionic conductivity and excellent cycle performance, but without positive effect on the retention of electrolyte. On the other hand, Zhang *et al.* simply assembled two honeycomb-like porous membranes together to fabricate a battery separator with multiple pores^[18]. The separator has smaller pores on the outside surfaces than those in the bulk, and such structures are suggested to be beneficial for both battery performance and safety. Remained challenges include to scale-up these honeycomb-like porous membranes by the breath and to improve their mechanical strength for practical application. Therefore, facile method is still needed for the fabrication of polymer separators with multi-scale pore structures to develop high performance lithium ion batteries with enhanced safety.

In the present work, a novel kind of poly(vinylidene fluoride) (PVDF) separators with dual-asymmetric pore structure were fabricated for the first time *via* thermally induced phase separation (TIPS) by using dimethyl sulfone (DMSO2) and glycerol as mixed diluent. PVDF and its copolymer membranes show great advantages as separators in comparison to polyolefins and other materials due to their strong polarity and high dielectric constant, which can assist ionization of lithium salts^[9, 20–22]. Our PVDF separators combine one porous bulk with large interconnected pores ($\sim 1.0\ \mu\text{m}$) and two porous surfaces with much small pores ($\sim 30\ \text{nm}$). This special multi-scale pore structure endows the separators with high electrolyte uptake and retention ability, as well as excellent thermal properties. The $\text{LiFePO}_4/\text{Li}$ batteries using the separators also exhibit outstanding cycle stability and rate performance. Such unique structured separators show tremendous potentials for practical application in lithium ion batteries with high performance and safety.

EXPERIMENTAL

Materials

PVDF ($M_n = 1.1 \times 10^5\ \text{g}\cdot\text{mol}^{-1}$, Solef 6010) was a commercial product of Solvay Solexis, Belgium. It was dried to constant weight before use. DMSO2 (99%) was purchased from Dakang Chemicals Co., China. Glycerol, ethanol and hexane were supplied by Sinopharm Chemical Reagent Co. Ltd, and used without further purification. Deionized water was used as the extractant. The electrolyte solution of LiPF_6 in solvent mixture of ethylene carbonate (EC), dimethyl carbonate (DMC) and diethyl carbonate (DEC) (LiPF_6 concentration = $1\ \text{mol}\cdot\text{L}^{-1}$, EC/DMC/DEC = 1/1/1, *V/V/V*) was supplied by Zhuhai Smooth way Electronic Materials Co., Ltd, China. Commercialized separator (Celgard 2400) was purchased from Celgard Company (USA).

Preparation of Dual-asymmetric Separators

A PVDF/DMSO2/Glycerol mixture was heated at $160\ ^\circ\text{C}$ to form a homogeneous solution. After degassing air bubbles, the solution was quickly poured into a stainless steel plate, and then covered by another one as soon as possible (less than 10 s). Both the stainless steel plates were preheated in an oven at $160\ ^\circ\text{C}$. A Teflon module ($200\ \mu\text{m}$) with a circular opening (diameter = 10 cm) was inserted between the plates to adjust membrane thickness and size. The self-made mold was then quenched in a $30\ ^\circ\text{C}$ water bath to induce phase separation of the solution. Afterwards, the nascent membrane was taken out of the mould and immersed in deionized water. A

wet membrane was formed as soon as the diluent was completely extracted. To gain a dry membrane, the wet one was washed with an ethanol-hexane sequence, and then dried in vacuum for 24 h at 60 °C.

Characterization

Morphologies of the separators were examined by field emission scanning electron microscopy (FESEM, Hitachi S4800, Japan) with an accelerating voltage of 10 kV. The porosity and pore size were evaluated using a mercury injection apparatus (Auto Pore IV9500, Micromeritic, USA). Attenuated total reflectance FTIR spectroscopy (FTIR/ATR, Nicolet 6700, Nicolet. Co., USA) was performed on the separators to analyze the crystal phases of PVDF. Differential scanning calorimetry (DSC, Q20, TA instruments, USA) was used to determine the melting and crystallization temperatures of the polymer/diluent mixture and the prepared separators. Wide-angle X-ray diffraction was carried out on a Rigaku D/Max-2550PC X-ray diffractometer (Panalytical, Netherlands) to investigate the crystal phases of the separators. The phase separation process was visualized by an optical microscope (Nikon Eclipse E600POL, Japan). The temperature is denoted as cloud point when the polymer solution becomes turbid. Light scattering measurements were carried out to determine the droplet growth behavior with a self-made detector. The hot stage was located between a He-Ne laser (3 mW) and a detector. Air permeability was examined by an airmeter (YG461H, Ningbo Textile Instrument Factory, China) which determined the time needed for a pre-determined amount of air to pass through a membrane under a given pressure. To evaluate its thermal shrinkage behavior, the separator was placed in an oven and heated at 160 °C for 1 h. Thermal shrinkage ratio (TSR) was calculated according to Eq. (1):

$$\text{TSR}(\%) = (S_0 - S/S_0) \times 100\% \quad (1)$$

Here, S_0 and S represent the area of the separator before and after thermal treatment, respectively. Electrolyte uptake and retention were measured as description in reference^[23]:

$$\text{Uptake} = \frac{W_1 - W_0}{W_1} \times 100\% \quad (2)$$

$$\text{Retention} = \frac{W_x - W_0}{W_1 - W_0} \times 100\% \quad (3)$$

where W_0 is the weight of separator, W_1 is the initial weight of the separator after absorbing the electrolyte for 1 h, W_x is the equilibrium weight of the wet separator placed between two filter papers with 100 g glass plate on the top of the filter paper.

Electrochemical Characterization of the Dual-asymmetric Separators

Ionic conductivity was evaluated by sandwiching the separator samples between two stainless steel electrodes *via* AC impedance technique. The measurement was performed using an electrochemical workstation (CHI604E, China) over a frequency range from 0.01 Hz to 1 MHz at room temperature. The ionic conductivity was then calculated by using formula: $\sigma = L/R_b A$, where L is the thickness of the separator and A is the contact area between the separator and the stainless steel electrode, R_b is the bulk resistance. Tortuosity of the membranes was calculated by using the following relationship:

$$\tau = \left(\frac{\sigma_0}{\sigma} \times P \right)^{1/2} \quad (4)$$

where σ_0 and σ are the conductivity of the neat liquid electrolyte and electrolyte-soaked membrane, respectively, and P is the porosity of the membrane^[24]. The interfacial resistances between the liquid electrolyte-soaked membranes and lithium metal were investigated by measuring the impedances of symmetrical lithium cells. The frequency range used was varied from 1 MHz to 0.01 Hz. The charge-discharge tests of LiFePO₄/Li cells containing liquid electrolyte-soaked membranes were conducted using CR2025 coin-type cells. The LiFePO₄ cathode was prepared by blending LiFePO₄ powder (80 wt%), carbon black conductor (10 wt%) and PVDF binder (10 wt%). Land tester (CT2001A) battery cycler was used in a potential range of 4.2–2.5 V at a current

density of 0.2 C to evaluate the cycling performance. In order to evaluate C-rate performance, different C-rates (0.2 C, 0.5 C, 1 C, 2 C, and 5 C) were applied to cells.

RESULTS AND DISCUSSION

Preparation and Structures of the Dual-asymmetric Separators

Figure 1 shows SEM images and pore size distribution of the prepared PVDF membranes. The membranes have multi-scale porous structures with three different pore sizes. An interconnected porous structure can be seen inside the membrane with the largest pore size of (957.0 ± 7.8) nm. These large pores will facilitate a fast lithium ion transportation across the separator. On the other hand, the pore sizes are smaller by one order of magnitude for the two membrane surfaces. The small surface pore size is beneficial for the enhanced safety of the battery. Moreover, the two surfaces exhibit different pore sizes. For convenience, the surface in direct contact with the bottom plate is denoted as the bottom surface, and the other surface in direct contact with the cover plate is called the top surface. It demonstrates that pores on the bottom surface ((33.2 ± 0.4) nm) are slightly larger than those on the top surface ((13.7 ± 0.2) nm). This is resulted from the evaporation of diluent from the top surface under high temperature before covering the top stainless steel plate onto the polymer solution. The evaporation of diluent leads to an increased polymer concentration on the top surface, resulting in an increased viscosity and relatively small pores^[25–27]. Thus, the as-prepared membranes possess a unique structure with a porous bulk with large pores and two porous surfaces with small pores. This special structure is denoted as dual-asymmetric structure in this work.

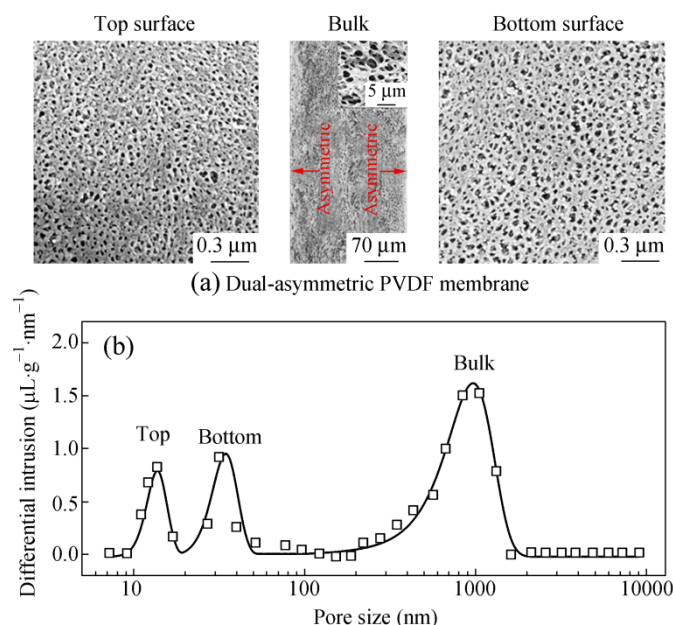


Fig. 1 (a) SEM images for the surface and cross-section of PVDF-8 separator which has a dual-asymmetric structure (The inset is the enlarged cross-sectional SEM image.); (b) Pore size distribution of the prepared PVDF-8 separator

The dual-asymmetric structured PVDF separators are formed from the TIPS process. It is achieved by controlling the different phase separation behaviors between polymer solution surface and bulk which is seldom mentioned in literatures about TIPS^[28–30]. The preparation procedure is illustrated in Fig. 2(a). PVDF/DMSO2/glycerol mixtures were first heated at 160 °C to form homogeneous solution, and then sealed between two stainless steel plates. Then the mold was quickly cooled in a water bath at 30 °C. Thermodynamically, the system undergoes liquid-liquid (L-L) phase separation when it was cooled to its cloud point. The homogeneous solution separated into a polymer-rich matrix phase and a diluent-rich phase before

polymer solidification (Fig. 2b), which was recorded by a real-time optical microscope (Fig. S1 in supporting information, SI). Moreover, the system underwent a spinodal decomposition mechanism during the L-L phase separation process, which was the origin of the interconnected porous structure in the membrane bulk. This was verified by a series of spectra from small-angle light scattering (Fig. S2 in SI), in which the scattered light intensity versus angle went through the maximum value^[31, 32].

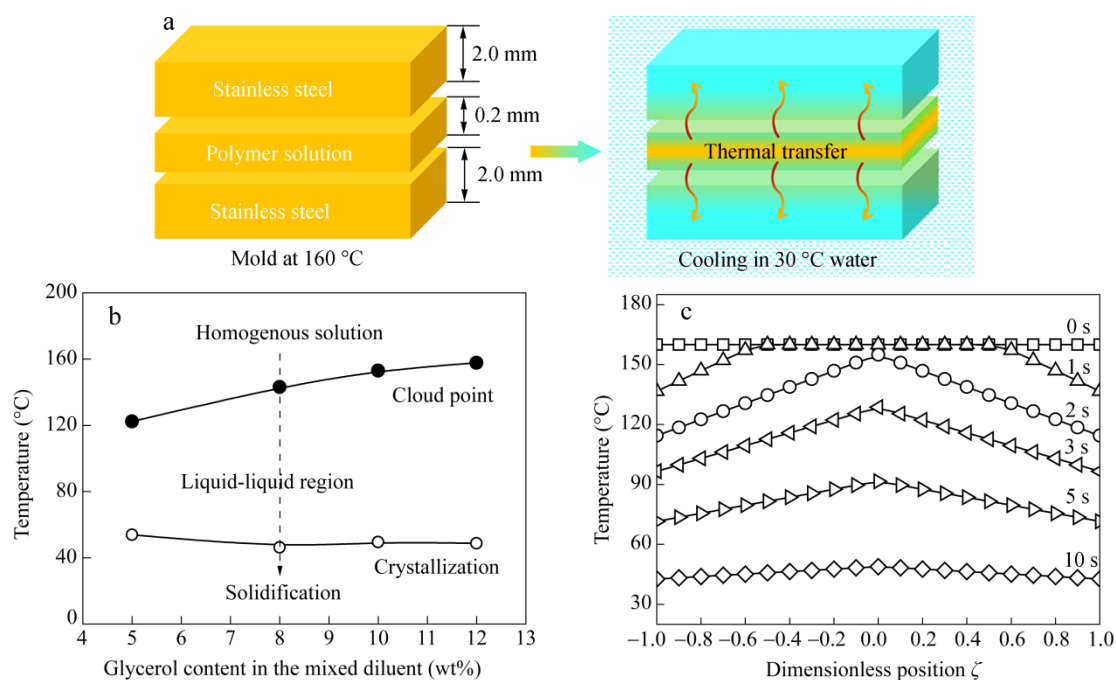


Fig. 2 (a) Schematic illustration of the fabrication process for the dual-asymmetric PVDF separators, (Polymer solution was first heated at 160 °C, and then sealed between the two stainless steel plates. The mold was then quenched in a 30 °C water bath to induce the solution to phase separate.) (b) dynamic phase diagram of the PVDF/DMSO2/glycerol ternary system, (The content of glycerol in the mixed diluent (DMSO2 and glycerol) is from 5 wt% to 12 wt%. PVDF concentration is fixed at 20 wt%.) (c) dimensionless temperature profiles of the polymer solution in variation of time between two stainless steel plates (Dimensionless position $\zeta = 0$ denotes the middle position of the polymer solution, while $\zeta = 1$ or -1 means the surface of the polymer solution which directly contact the stainless steel plate.)

Although the route is the same for the polymer solution to undergo phase separation, the dynamics is quite different between those on the surfaces and that in the inner section, because TIPS is a dynamic process of thermal conduction^[33–35]. It always takes time for heat transferring from one side to another side through a specific media. In the present cases, the two stainless steel plates have a very high thermal conductivity (Table S1 in SI), indicating that their thermal energy can be quickly transferred into the cooling bath. As a consequence, the cooling rate is very fast for those polymer solutions which are in contact with the two stainless steel plates directly. Therefore, the diluent-rich droplets near the two plate surfaces do not have enough time to grow before being frozen by the solidification of polymer and diluent. It leads to small droplet sizes as well as small membrane pores on the separator surfaces^[36–39]. On the other hand, the thermal conductivity is much lower for the polymer solution than the stainless steel plates. It should be noted that the thermal conductivity further reduces after the solidification of polymer and diluent. Consequently, the heat exchange rate gradually decreases from the two surfaces to the inner section of the polymer solution. Figure 2(c) shows that the cooling rate is much slower in the central region than those on the surface. Thus the droplets inside the polymer solution have more time to grow up, leading to a porous morphology with large pores in the separator bulk. It should be noted that the thickness also play an essential role in obtaining the dual-asymmetric membrane. The larger thickness of

our membranes results in larger heat resistance and lower cooling rate for the inner section of the polymer solution. Consequently, more obvious dual-asymmetric structure can be obtained.

It is much appealing that the multi-scale pores can be easily manipulated by adding different glycerol content to prepare the dual-asymmetric separators. The as-prepared separators are denoted as PVDF-5, PVDF-8, PVDF-10, and PVDF-12 respectively, depending on the glycerol content in the mixture diluent. Figure 3 shows that all the separators possess the dual-asymmetric structure with a bicontinuous porous bulk and two dense surfaces. Polymer solution with high glycerol content produces separator with large pores under the same cooling condition. It is due to that the L-L phase separation region enlarges when increasing the glycerol content in the mixture diluent. As shown in Table 1, both the bulk pores and the surface pores increase with the glycerol content for the separators. It should be mentioned that the fabricated separators are much thicker (around 178 μm) than the commercial Celgard 2400, which is unfavourable for the volumetric energy density of cells. Nevertheless, thinner dual-asymmetric separators can be easily prepared with smaller bulk pore size and stronger mechanical strength by adopting a thinner Teflon module, which will be investigated in our future work.

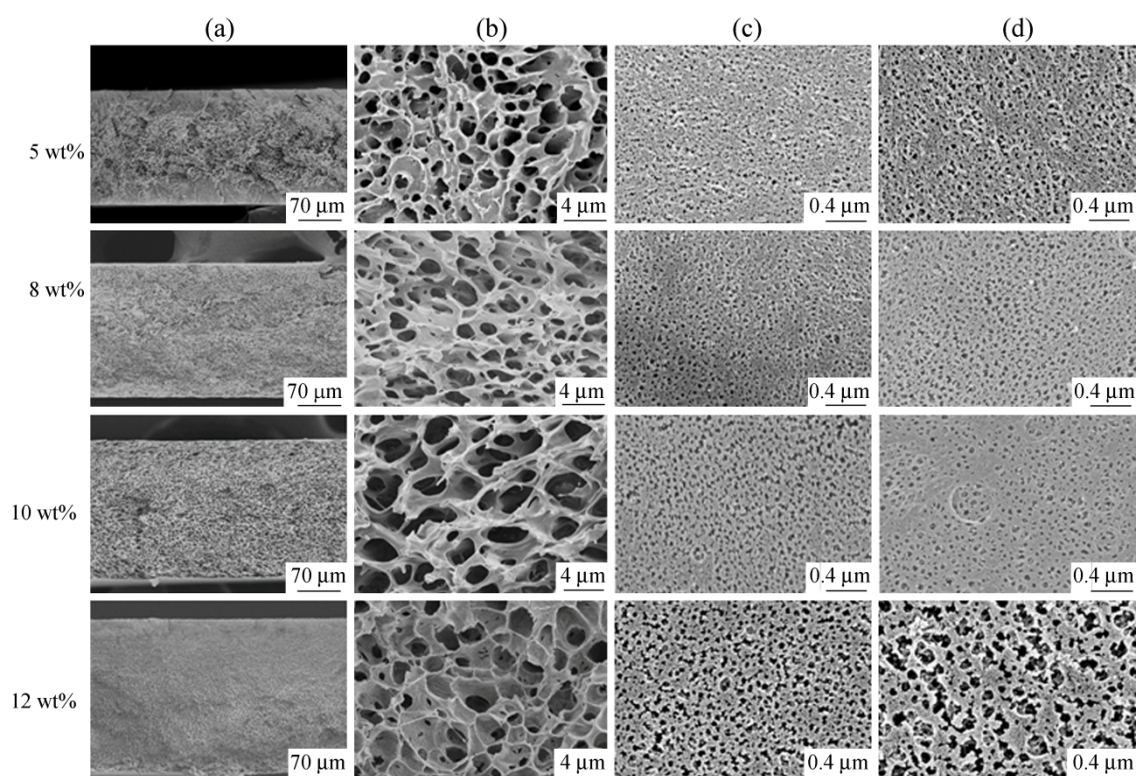


Fig. 3 SEM images of PVDF membranes prepared from 20 wt% PVDF: (a) cross-section, (b) cross-section, (c) top surface, (d) bottom surface

Glycerol content in the mixed diluent varies from 5 wt% to 12 wt%. The membranes were prepared in water bath at 30 °C.

Table 1. Physical properties of the studied separators

Sample	Thickness (μm)	Porosity (%)	Pore size (nm)			Uptake (%)	Tortuosity
			Top	Bulk	Bottom		
Celgard 2400	30	41		50×125^a		184.7 ± 12.8	2.5
PVDF-5	175.0 ± 3.9	79.2	14.1 ± 0.4	720.5 ± 37.2	31.4 ± 1.5	410.4 ± 22.4	2.3
PVDF-8	182.7 ± 1.8	78.9	13.7 ± 0.2	957.0 ± 7.8	33.2 ± 0.4	427.9 ± 28.5	2.1
PVDF-10	178.0 ± 1.9	77.8	28.9 ± 2.1	1120.6 ± 14.6	39.8 ± 2.9	427.0 ± 34.9	2.0
PVDF-12	178.8 ± 1.9	76.6	34.6 ± 3.9	1053.8 ± 40.2	46.3 ± 6.4	446.6 ± 23.2	1.8

^a The data is provided by the Celgard Company.

Properties of the Dual-asymmetric Separators

It has been well accepted that the uptake and leakage behaviors of liquid electrolyte are of great concern for porous polymer separators^[12, 23]. Figure 4(a) compares the uptake behaviors of the dual-asymmetric PVDF-8 separator with that of the commercial Celgard 2400. Both separators exhibit a similar electrolyte uptake behavior: the uptake increases dramatically at first and then slows down to equilibrium. Here, we take the uptake after 1 h as the saturated value. Obviously, the dual-asymmetric PVDF-8 separator has much higher saturated electrolyte uptake than Celgard 2400. The uptake of PVDF-8 reaches as high as $(427.9 \pm 28.5)\%$, while that of Celgard 2400 is only $(184.7 \pm 12.8)\%$. Moreover, the electrolyte uptake rates are also much higher for the dual-asymmetric PVDF separators. The uptake process is almost stabilized within 2 min for our dual-asymmetric separators. However, it takes more than 5 min for Celgard 2400 to reach its uptake equilibrium. These results are further evaluated by contact angle measurements with the liquid electrolyte on the separator surfaces (Fig. 4c). The liquid electrolyte droplets rapidly penetrate into the pores within 1.5 s when they are dropped onto the surfaces of dual-asymmetric PVDF-8 separator. On the other hand, Celgard 2400 shows a much different behavior. The contact angle is as high as 40.6° at first, and gradually declines with time. After 3 min, the liquid electrolyte still remains on the separator surface with a contact angle of 20.1° .

The high uptake amount and the rapid uptake process of the dual-asymmetric PVDF separators can be ascribed to three factors. First, high porosity is beneficial for electrolyte uptake. Table 1 shows that our dual-asymmetric separators have a much higher porosity than Celgard 2400. Porosity is around 78% for the dual-asymmetric separators, while Celgard 2400 only has a porosity of 41%. Secondly, PVDF, as the separator matrix, possesses much better affinity to the liquid electrolyte than polypropylene matrix. When the PVDF separators are immersed in the liquid electrolyte, the liquid can diffuse and occupy all pores. Thirdly, the dual-asymmetric structure plays a very important role in the uptake process.

The dynamic electrolyte uptake process includes two steps, *i.e.* absorption and permeation^[40]. As shown in Fig. 4(d), the uptake process is first driven by the capillary pressure stemmed from the surface pores. Then the absorbed liquid permeates into the separator bulk. The capillary pressure is inversely proportional to the pore size, according to the Laplace-Young equation as follows:

$$p_c = \frac{2\gamma \cos \theta}{a} \quad (5)$$

where p_c represents the capillary pressure, γ is the surface tension of the liquid-gas interface, θ is the contact angle, and a is the pore radius. On the other hand, the permeability of porous materials scales with the square of the pore size based on the Washburn law:

$$l = \sqrt{\frac{\gamma a \cos \theta}{2\mu} t} \quad (6)$$

where l denotes the meniscus depth, μ is the dynamic viscosity of the liquid, and t is the adsorption time^[41]. According to these two equations, the pore size affects the adsorption and permeation process in opposite ways. For Celgard 2400 which has an isotropic structure (Fig. S3 in SI), the liquid absorption dynamics is monotonously dependent upon the pore size based on the balance of the two mechanisms. Nevertheless, the tradeoff between the two mechanisms can be broken by the dual-asymmetric structure in our cases. The small surface pores can produce large driving force to pull the liquid electrolyte into the porous separators. As soon as the electrolyte penetrates into the surface pores, the large bulk pores with high permeability quickly transport the liquid deep into the separators (Fig. 4d). Owing to the synergetic effects of large driving force of small surface pores and fast permeation of large bulk pores, the dual-asymmetric separators exhibit a much faster electrolyte uptake than Celgard 2400.

In addition to fast electrolyte uptake dynamics, the dual-asymmetric structure is also beneficial for excellent electrolyte retention ability. It can be seen from Fig. 4(b), the dual-asymmetric PVDF-8 separator has a high retention ability with a leakage $< 15\%$ after 1 h, while almost 50% electrolyte leaks out from Celgard 2400. The

high retention is also attributed to the combined effects of good affinity of PVDF to the liquid electrolyte and the tailored pore structures of the separators^[42]. The electrolyte leakage can be greatly inhibited by the small surface pores of the dual-asymmetric separators, according to Eq. (5). This excellent electrolyte retention is conducive to enhance the safety of lithium ion battery.

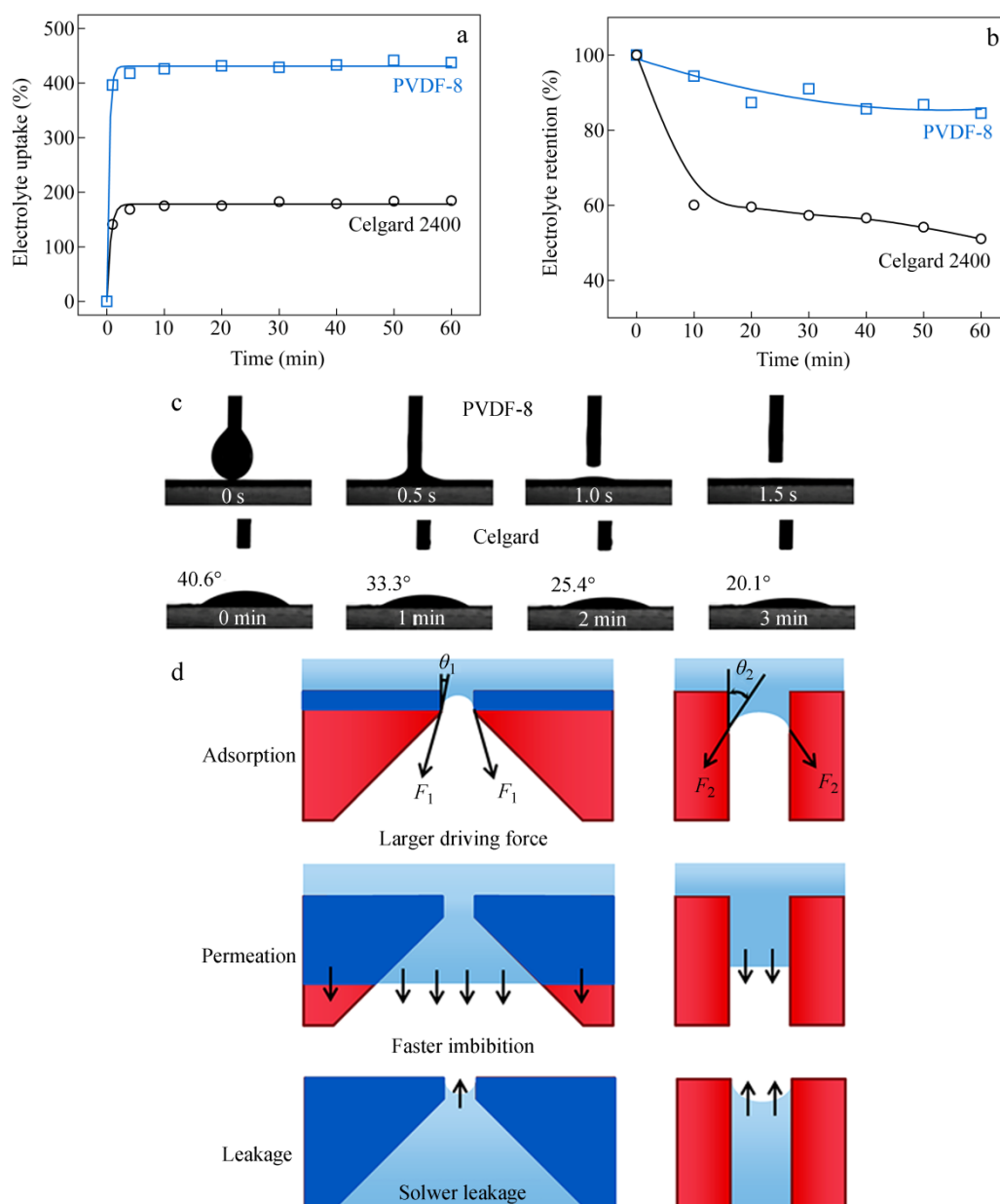


Fig. 4 (a) Electrolyte uptake of PVDF-8 separator and Celgard 2400 as a function of time, (b) time dependence of electrolyte retention of PVDF-8 separator and Celgard 2400, (c) the contact angle photographs of electrolyte solvent droplet on PVDF-8 separator and Celgard 2400, (d) schematic diagram of electrolyte uptake and leakage process for different pore structures (The left represents the dual-asymmetric separator with small surface pores and large bulk pores, while the right denotes Celgard 2400 with isotropic pores.)

Thermal property is another essential factor for the separators to evaluate safety characteristics and battery performance^[24, 43]. Figures 5(a)–5(d) show the photographs of PVDF-8 and Celgard 2400 before and after heat

treatment at 160 °C for 1 h. It can be seen that PVDF-8 has a negligible dimension change, while Celgard 2400 undergoes significant shrinkage. The thermal shrinkage ratios are below 5% (Fig. S4 in SI) for all the dual-asymmetric separators, indicating excellent thermal dimensional stability. In addition, SEM images in Figs. 5(e) and 5(f) reveal that most of the surface pores close up after heat treatment at 160 °C for 1 h. This is in good agreement with the results of air permeability. Figure 5(g) demonstrates that the air permeability of PVDF-8 separator stays stable at about 1.1 mm·s⁻¹ below 120 °C, and dramatically decreases after the separator is exposed to temperature higher than 120 °C. After the separator is heat treated at 160 °C for 1 h, the air permeability declines to 0.55 mm·s⁻¹, which is only half of the initial value. Considering that almost no dimensional change is observed after heat treatment, the decrease of air permeability is mainly ascribed to the close of the surface pores. Combining the results of SEM observation and air permeability, it is suggested that our dual-asymmetric PVDF separators may possess thermal auto-shutdown ability, which is beneficial for improving the safety performance of lithium ion batteries. The closed pores would inhibit the conduction of lithium ions, hence decrease the ionic conductivity, and finally shut the cell down before an explosion occurs^[44].

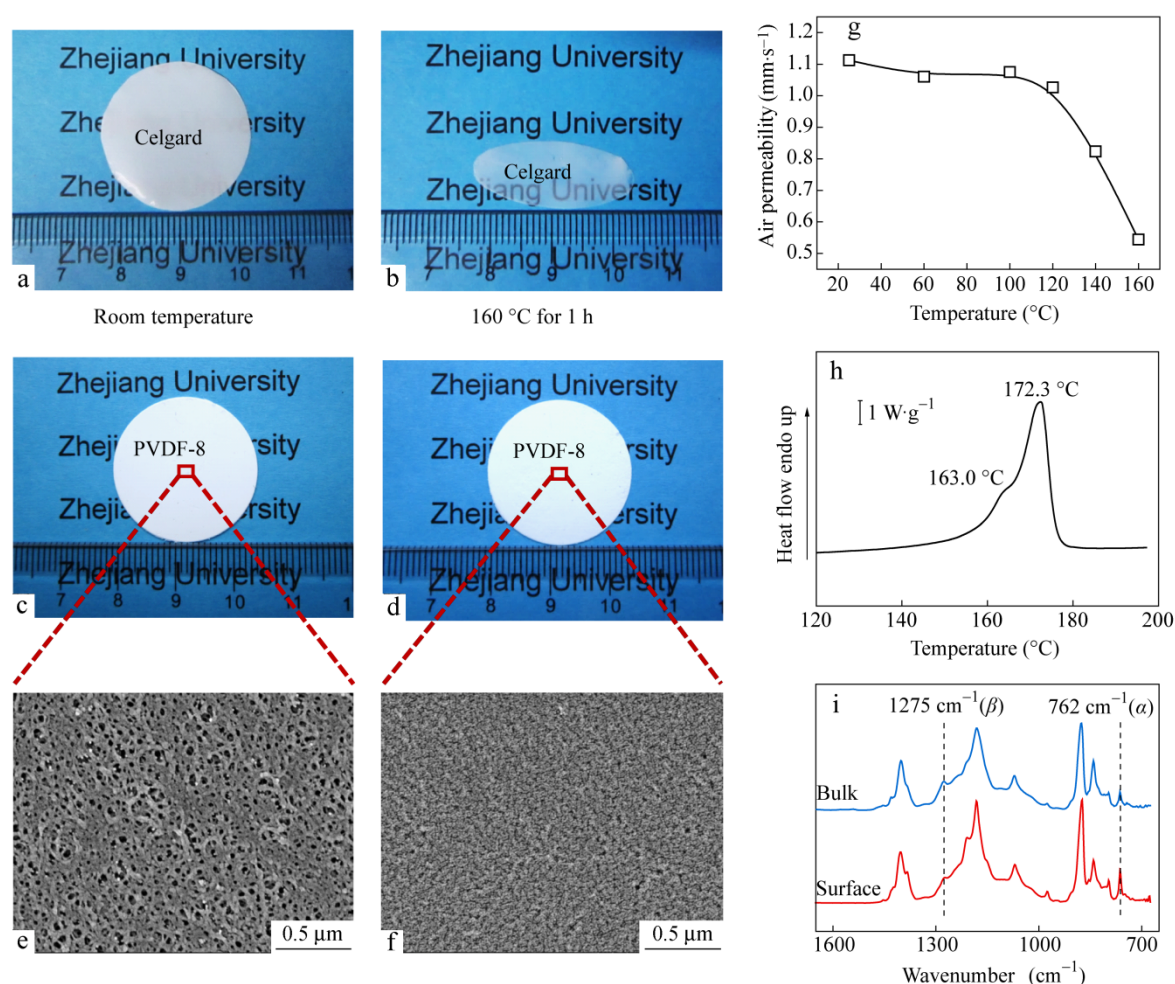


Fig. 5 Photographs of Celgard 2400 (a) before and (b) after heat treatment at 160 °C for 1 h, photographs of PVDF-8 separator (c) before and (d) after heat treatment at 160 °C for 1 h, SEM images of the PVDF-8 separator surface (e) before and (f) after heat treatment at 160 °C for 1 h, (g) temperature dependent of air permeability of PVDF-8 separator, (h) DSC thermogram of PVDF-8 separator, (i) ATR-FTIR spectra of PVDF-8 separator before and after surface removing

The auto-shutdown ability can be mainly ascribed to two factors. Firstly, the surface pores are very small compared to those of the bulk pores in the dual-asymmetric separators. It is very easy for the surface pores to close up. Secondly, it is believed that the thermal property has a great relationship with the crystal phases of PVDF matrix. Figure 5(h) shows DSC thermogram of the dual-asymmetric separators. There are a main endothermic peak at 172.3 °C and a shoulder peak at 163.0 °C. It is well known that the endothermic peak at 172.3 °C is the characteristic peak of β phase PVDF, while 163.0 °C is the melting point of α phase PVDF. Thus the whole separator is composed of two crystal phases of PVDF, in which β phase is the dominant one. ATR-FTIR is further used to analyze the crystal phases of the separators. Adsorption peaks at 762 and 1275 cm^{-1} in Fig. 5(i) are unique peaks of α and β phase PVDF, respectively. Thus the absorbance at 762 and 1275 cm^{-1} can be used to calculate the ratio of crystallinity of α and β phases using the following equation

$$\frac{X_{\beta}}{X_{\alpha}} = \frac{A_{1275}}{A_{762}} \times \frac{K_{\alpha}^{762}}{K_{\beta}^{1275}} \quad (7)$$

where X_{α} and X_{β} are the mole fractions of the α and β phases, respectively. A_{762} and A_{1275} are absorbances at 762 and 1275 cm^{-1} respectively. K_{α}^{762} represents the absorption coefficient at 762 cm^{-1} for the α phase, while K_{β}^{1275} denotes the absorption coefficient at 1275 cm^{-1} for the β phase^[45]. It can be seen that the ratio of β and α phase near the separator surface is 2.0 for PVDF-8, while the separator bulk shows a ratio of 3.9 between β and α phase. It demonstrates that there is more β phase in the separator bulk than on the separator surfaces, while α phase mainly exists on the separator surfaces. The results are in accordance with that of X-ray diffractograms (Fig. S5 in SI), which indicates that β phase mainly appears in the separator bulk. The large amount of β phase in the separator bulk ensures the dimensional stability at high temperature (such as 160 °C) due to the high melting point of β phase. On the other hand, the α phase near the separator surfaces will melt down when heated to 160 °C, resulting in the close of the surface pores. It can be concluded that the unique distribution of different crystal phases is responsible for the outstanding thermal properties. The thermal stability as well as the thermal shut-down performance further enhances the safety performance of lithium ion batteries.

Mechanical strength, especially puncture strength, is also crucial for the safety performance and battery performance of the lithium ion battery. Poor puncture strength causes lithium dendrite growth and internal short circuiting. Although the PVDF and co-polymer membranes *via* TIPS for lithium ion batteries have been reported in literatures, the poor mechanical properties greatly limit the practical application^[46–49]. In our work, the PVDF-8 dual-asymmetric separator has a puncture strength of (1.8 ± 0.3) N, Fig. S6 in SI). Although it is lower than Celgard 2400 $((2.7 \pm 0.1)$ N), it is stronger than isotropic PVDF membrane with a similar bulk pore size $((1.0 \pm 0.1)$ N, Fig. S7 in SI). It indicates that the dual-asymmetric structure with large bulk pore size and the dense surfaces are beneficial for the enhancement of puncture strength of separators. Meanwhile, these separators also possess proper tensile strength for application in lithium ion batteries (Fig. S8 in SI). The PVDF-8 separator possesses a tensile strength of 3.4 ± 0.2 MPa, which is lower than that of Celgard 2400 $((10.5 \pm 0.6)$ MPa), but higher than those reported for PVDF-based separators^[46–49].

Performance of Cells Constructed with the Dual-asymmetric Separators

Ionic conductivity and interfacial resistance of the polymer electrolyte play an essential role in achieving excellent electrochemical performance of lithium ion batteries. As previously shown in the SEM images, the dual-asymmetric separators exhibit a porous bulk with large and interconnected pores. As a consequence, the tortuosity of the dual-asymmetric separators is lower than that of Celgard 2400 as shown in Table 1. This low tortuous structure can greatly enhance the ion transportation inside the dual-asymmetric separators. Figure 6(a) demonstrates the ionic conductivities of all the dual-asymmetric separators are higher than that of Celgard 2400. It can be seen that the ionic conductivity of the dual-asymmetric separators increases with the increase in the glycerol content in the mixed diluent. Taking PVDF-8 separator as an example, its ionic conductivity reaches as high as (1.72 ± 0.08) $\text{mS}\cdot\text{cm}^{-1}$. It is interesting that PVDF-8 separator also exhibits a lower interfacial resistance than Celgard 2400 separator (Fig. 6b). This is closely related to the high electrolyte uptake and good interfacial

compatibility of the dual-asymmetric separators. High ionic conductivity and low interfacial resistance are beneficial to improve the cycling stability and rate performance of lithium ion batteries.

Figure 6(c) compares the cycle performances of cells using PVDF-8 and Celgard 2400 as separator, respectively. It is characterized by the discharge capacity as a function of cycle number. The lithium iron phosphate (LiFePO_4)/lithium (Li) cells are cycled between 2.5 and 4.2 V at constant charge/discharge current density (0.2 C/0.2 C). A large drop of capacity in the first cycle is observed for both PVDF-8 separator and Celgard 2400, which is due to the formation of the SEI layer. For PVDF-8 separator, the specific capacity of cells increases from 159.6 to 164.3 $\text{mAh}\cdot\text{g}^{-1}$ within the first 6 cycles, and then tends to stabilize. Nevertheless, it takes 10 cycles for cell with Celgard 2400 to stabilize its specific capacity. As mentioned above, the PVDF dual-asymmetric separator has a better wettability, which leads to a better contact with electrodes and lower interfacial resistance and thus higher reversibility. With the dual-asymmetric separator, the formation and manufacturing time for lithium ion batteries can be greatly shortened, which can potentially decrease the manufacturing time and lower the battery cost^[50].

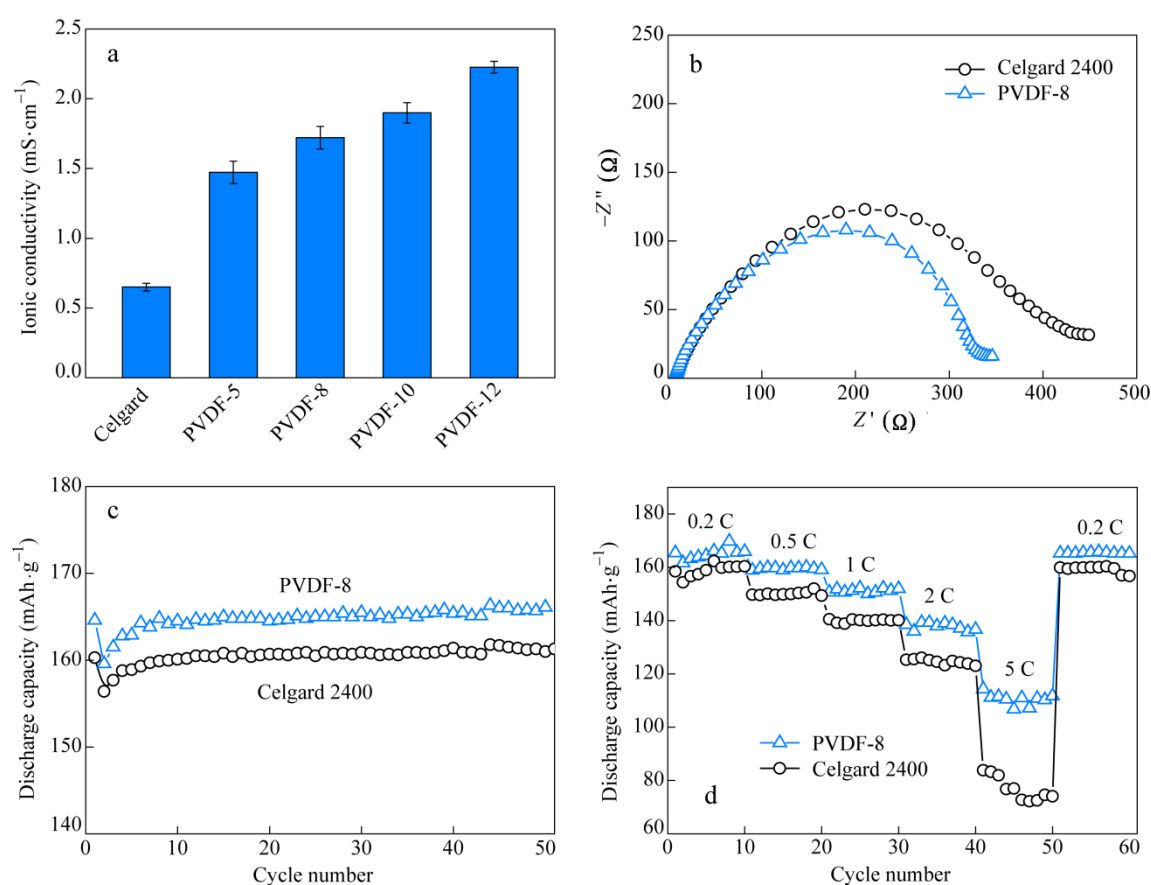


Fig. 6 (a) Ionic conductivities of dual-asymmetric separators and Celgard 2400 separator, (b) electrochemical impedance spectra of Li/polymer electrolyte/Li cells based on dual-asymmetric separators and Celgard 2400 separator, (c) cycling performances of the $\text{LiFePO}_4/\text{Li}$ cells using dual-asymmetric separators and Celgard 2400 separator, (d) rate performances of the $\text{LiFePO}_4/\text{Li}$ cells using dual-asymmetric separators and Celgard 2400 separator

Figure 6(d) compares the cell performances at different discharge rates using PVDF-8 and Celgard 2400 as separator, respectively. The cells are cycled between 0.2 C and 5 C rate for 10 cycles each continuously and then at 0.2 C rate for 10 cycles. A capacity drop is observed with increasing C-rate in both cells. Nevertheless, both the discharge capacity and the capacity retention of the dual-asymmetric separator are higher than those of Celgard 2400 at all the rates. The discharge capacity of PVDF-8 can maintain as high as 110.3 $\text{mAh}\cdot\text{g}^{-1}$ with

capacity retention of 66.7% at a high discharge rate of 5 C. It is much higher than that of Celgard 2400 with discharge capacity of 72.2 mAh·g⁻¹ and capacity retention of 45.6%. Moreover, the capacity can almost recover to the initial capacity at the end of the rate capability test, indicating that less ohmic polarization is produced in the cell using the dual-asymmetric PVDF separator. The battery performances of batteries using dual-asymmetric separators show strong advantages in comparison with those batteries using same electrodes but different separators^[22, 51–54]. It can be reasonably suggested that the facile ionic conduction and low interfacial resistance of the dual-asymmetric separator is beneficial in increasing the rate performance of lithium ion batteries.

CONCLUSIONS

In conclusion, we demonstrate a simple thermally induced phase separation method to prepare PVDF separators with dual-asymmetric structure. The dual-asymmetric PVDF separators have a porous bulk with large and interconnected pores and two dense surfaces with small pores. The large and interconnected pores provide high electrolyte uptake and ionic conductivity, ensuring high discharge capacity and excellent rate performance. The small surface pores prevent the leakage of electrolyte as well as lithium dendrite growth, and provide thermal auto-shutdown ability, which eliminate the safety concerns and ensure a long and sufficient cycle life of lithium ion batteries. All the behaviors reveal that the PVDF separators with dual-asymmetric structure are a promising alternative to commercialized separators.

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