A SuperLEphilic/Superhydrophobic and Thermostable Separator Based on Silicone Nanofilaments for Li Metal Batteries

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HIGHLIGHTS
A superLEphilic/superhydrophobic separator is first reported for Li metal batteries

The separator has low moisture uptake and could improve performance of Li/Li cells

The separator features fast LE diffusion, high LE uptake, and Li⁺ conductivity

The separator could enhance performance of high-voltage Li metal batteries

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A SuperLEphilic/Superhydrophobic and Thermostable Separator Based on Silicone Nanofilaments for Li Metal Batteries

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SUMMARY
Conventional polyolefin separators suffer from poor wettability to liquid electrolytes (LEs). Although some modified separators exhibit improved wettability, they are hydrophilic, causing inevitable moisture uptake. Trace water could result in poor performance and safety hazard of Li metal batteries. Here, we report a design idea of superLEphilic/superhydrophobic and thermostable separators by modifying the Celgard separator using silicone nanofilaments. The separator features low moisture uptake (~0%), fast LE diffusion (454 ms), and high LE uptake (287.8%), LE retention rate, and Li+ conductivity. Consequently, the Li/LiFePO4 cells show high cycling stability (96.05% after 350 cycles), good rate performance (125 mA h g⁻¹ at 5.0 C), low resistance, and stable open circuit voltage at 160 °C. Moreover, the separator could improve performance of the other Li metal batteries with high-voltage cathodes and the LiFePO4/graphite pouch cells. This work provides an avenue for designing advanced separators by using bioinspired superwetting surfaces.

INTRODUCTION
Li batteries are widely used, for example, in mobile communications, portable electronic devices, and automotive technology (Seh et al., 2016; Zhang et al., 2017). However, ignition and explosion accidents of Li batteries have become more frequent recently, such as the well-known Samsung Note 7 and iPhone issues, which have caused serious safety concerns (Liu et al., 2018a). Some studies suggest that these accidents are closely related to the separator (Li et al., 2017d; Liu et al., 2018a; Palacin and de Guibert, 2016). The separator plays a key role in the capacity, cycling stability, and safety of Li batteries (Liu et al., 2018b; Lu et al., 2017). Currently, microporous polyolefin membranes are widely used as separators in commercial Li batteries because of their fascinating properties (Lu et al., 2017). However, polyolefin separators show poor wettability toward liquid electrolytes (LEs) and low LE uptake (Ryou et al., 2011), which lead to low Li⁺ conductivity and high internal resistance (Lee et al., 2014). Moreover, polyolefin separators exhibit inferior thermostability (Arora and Zhang, 2004; Lee et al., 2014), which may cause internal short-circuiting, ignition, and even explosion of Li batteries. These intrinsic drawbacks limit the development of advanced Li batteries (Lee et al., 2014).

To overcome these drawbacks, some efforts have been made to construct separators using materials other than polyolefins (Kim et al., 2017; Lin et al., 2016). However, these separators cannot efficiently balance all the requirements and may introduce new drawbacks, such as inferior mechanical properties (Dai et al., 2016). Considering that polyolefin separators possess many excellent properties, surface modification via coating (Dai et al., 2016; Hu et al., 2016; Ryou et al., 2011) and grafting (Abbas et al., 2017; Li et al., 2017b) is an effective approach to overcome the drawbacks. Ceramic and/or polymer coatings have been used to modify polyolefin separators (Cho et al., 2017; Jeon et al., 2016). Despite improvements in wettability and thermostability, the coatings show defects, including blocked pores, increased thickness, and reduced Li⁺ conductivity, which cause serious performance degradation of Li batteries. In contrast, surface grafting of functional groups and/or polymers could minimize the thickness increase and maintain the microporous structure (Yu et al., 2016). Although the modified polyolefin separators show improved wettability and thermostability, they are also hydrophilic (Chen et al., 2016; Dai et al., 2016; Ryou et al., 2011). Thus, moisture uptake is inevitable during the use and storage periods, which is unfavorable for the assembly and performance of Li batteries, especially for Li metal batteries. At present, Li metal anode is receiving great attention owing to its highest theoretical specific capacity (3,860 mA h g⁻¹) and lowest redox potential (~3.04 V versus standard hydrogen electrode) (Cha et al., 2018; Fan et al., 2018; Liu et al., 2017). However, the uncontrollable dendrite Li growth in Li metal batteries caused many issues, such as low Coulombic...
efficiency, poor cycling stability, and safety hazard, which are the huge barriers to their real-world applications (Li et al., 2017a, 2018c; Xu et al., 2018). In fact, trace water could be involved in side reactions at the interface of electrodes (Li et al., 2018c). For example, even if there is trace water in Li metal batteries, the exothermal reactions between Li metal and water will not only induce consumption of Li anode and LEs but also accelerate dendrite Li growth, resulting in poor performance and serious safety hazard of Li metal batteries. Furthermore, the exothermal reactions may trigger diverse safety issues of Li metal batteries, such as shrinkage of the separator, ignition of the flammable separator and LE, and even explosion of batteries.

Bioinspired superhydrophobic surfaces, characterized by extremely high water repellancy, have many applications, including waterproof coatings (Erib et al., 2003), self-cleaning surfaces (Zhang et al., 2014), and oil/water separation (Li et al., 2017c). A nonfluorinated superhydrophobic surface is commonly oleophilic or superoleophilic, owing to the big difference in surface tension between water (72.8 mN m⁻¹) and most of organic liquids (<30 mN m⁻¹) (Cheng and Rodak, 2005). The surface tension of common LEs is 26.56–31.35 mN m⁻¹ (Table S1). Thus, there is a great chance to prepare superLEphilic/superhydrophobic polyolefin separators for high-performance Li metal batteries. SuperLEphilic separators are defined as the separators with contact angles (CAs) of LEs close to 0°. The superLEphilicity may enhance LE uptake and retention and Li⁺ conductivity owing to fast and complete wetting of the separator by LEs and thus may improve the battery performance (Lee et al., 2014). Although some LEphilic separators have been reported, superLEphilic separators are rare (Li et al., 2017a; Shi et al., 2016). The superhydrophobicity may eliminate side reactions and safety issues of Li metal batteries by reducing moisture uptake and also avoid additional trouble in battery assembly, as the drying process of separators before battery assembly is energy- and time-consuming. To the best of our knowledge, there has been no report about superLEphilic/superhydrophobic separators to date in rechargeable batteries. It is challenging to rationally design and fabricate superLEphilic/superhydrophobic separators without sacrificing other properties of polyolefin separators.

Here, we report for the first time a design idea of superLEphilic/superhydrophobic separators for Li metal batteries. The separator is prepared by growth of silicone nanofilaments (SNFs) on the surface of a polypropylene separator (Celgard 2400) by hydrolytic condensation of trichloromethylsilane (TCMS) in toluene. The microstructure of the SNFs determines wettability, LE uptake and retention, Li⁺ conductivity, and thermostability of the SNFs-Celgard separator and can be tuned by the water concentration in toluene. The separator can be easily wetted by diverse LEs, and thus the LE uptake and retention and Li⁺ conductivity are substantially enhanced. The separator cannot be wetted by water, and the moisture uptake is extremely low. Consequently, the performance of various Li metal batteries and the LiFePO₄/graphite pouch cells is evidently improved by the SNFs-Celgard separator.

RESULTS
Preparation of SNFs-Celgard Separators
Figure 1A shows the preparation of the SNFs-Celgard separator by O₂-plasma activation and subsequent SNFs growth. O₂-plasma was used to activate the chemically inert Celgard separator by forming reactive hydroxyl groups without evidently changing its microporous structure (Figure S1). Once immersed in the fresh TCMS/toluene solution containing a small amount of water, TCMS will hydrolyze and self-assemble into a highly porous polymeric network that is composed of a large amount of randomly deposited SNFs on the Celgard separator (Figures 1B and S2). The SNFs are 40–60 nm in diameter and several micrometers in length. The SNFs layer is 5.5 μm thick on each side (Figures 1C and S3), which seems to be thick. However, our previous studies have shown that the SNFs layer is soft and highly porous (Chu and Seeger, 2015; Meseck et al., 2014). The volume fraction of the SNFs layer is very low, 2.82% along the y axis (Meseck et al., 2014). Thus, the SNFs layer is compressible during battery assembly and the thickness of the SNFs layer in the coin cells should be ~0.155 μm on each side, assuming 100% strain of the space in the SNFs layer. The SNFs have no influence on the appearance of the Celgard separator (Figure S4). Moreover, the microstructure of the SNFs is tunable simply by the water concentration in toluene. The separators were termed as SNFs-Celgard₀ ppm, SNFs-Celgard₁₀₀ ppm, and SNFs-Celgard₂₀₀ ppm according to the water concentration in toluene.

In the Fourier transform infrared (FTIR) spectrum of the SNFs-Celgard separator (Figure 1D), the new absorption bands ascribed to Si-O-Si and Si-O-C stretching (1,020–1,140 cm⁻¹) and Si-CH₃ bending (1,269 and 782.9 cm⁻¹) were observed (Ward et al., 2003). In the X-ray photoelectron spectra (XPS) of the SNFs-Celgard separator (Figure 1E), the Si 2s, Si 2p, C 1s, and O 1s peaks appeared. This is in agreement
with the elemental maps of the separator (Figure S3B). The O/C/Si atomic ratio is 1/1.48/0.69 on the surface of the SNFs-Celgard separator (Table S2), which is consistent with the theoretical ratio of 1/0.66/0.66 for polymethylsilsesquioxane (Zimmermann et al., 2008). The higher C content is due to organic contamination during storage of the sample at ambient conditions in the interval between preparation and XPS analysis (Zimmermann et al., 2008). The absence of Cl 1s peak indicates complete hydrolysis of TCMS on the surface of the separator. The SNFs are mainly composed of Si-O-Si and Si-C bonds as demonstrated by the Si 2p spectrum of the SNFs-Celgard separator (Figure 1F) (Nozawa and Aramaki, 1999). According to the FTIR and XPS analyses, and the hydrolytic condensation of TCMS in toluene (Figure S5) (Gao and McCarthy, 2006; Zhang and Seeger, 2011b), the chemical structure of the SNFs is shown in Figure 1A.

SuperLEphilicity of SNFs-Celgard Separators

The Celgard separator is microporous with a pore diameter of several hundreds of nanometers (Figure 2A). The Celgard separator shows poor wettability toward the LE ($\text{CA}_\text{LE} = 43.0^\circ$), which not only reduces the power density and cycle life of Li batteries but also makes the Li battery assembly time-consuming, as the LE filling is the slowest step in Li battery assembly (Arora and Zhang, 2004; Dai et al., 2016). O$_2$-plasma activation could make the Celgard separator LEphilic and hydrophilic. However, the CA$_\text{water}$ gradually increased with storage time (Figure S6), owing to spontaneous thermal motion of the polyolefin molecular
Figure 2. SuperLEphlicity of SNFs-Celgard Separators

(A–H) SEM images and CA$_{LE}$ images of the (A and E) Celgard, (B and F) SNFs-Celgard$_{50ppm}$, (C and G) SNFs-Celgard$_{120ppm}$, and (D and H) SNFs-Celgard$_{200ppm}$ separators.

(I and J) Dynamic wetting process of the (I) Celgard and (J) SNFs-Celgard$_{120ppm}$ separators by the LE droplets (6 µL) released from a height of 5 mm. See also Videos S1 and S2.

(K–N) Photographs of the LE droplets (10 µL) after they were dropped onto the (K) Celgard, (L) SNFs-Celgard$_{50ppm}$, (M) SNFs-Celgard$_{120ppm}$, and (N) SNFs-Celgard$_{200ppm}$ separators for 10 s. See also Figures S7 and S8.
chains to minimize the surface energy (Li and Zhang, 2016). After modification with TCMS at a low water concentration of 50 ppm, only sparse and short SNFs were grown on the Celgard separator (Figure 2B), because the hydrolytic condensation of TCMS could not proceed sufficiently. According to the Cassie-Baxter and the Wenzel models (Cassie and Baxter, 1944; Wenzel, 1936), introduction of a proper microstructure could make an LEphilic surface more LEphilic or even superLEphilic owing to the capillary effect (Zhang and Seeger, 2011a). Thus, the SNFs-Celgard50ppm separator has a smaller CALE of 12° compared with the Celgard separator (Figures 2E and 2F). Thick and long SNFs were formed upon increasing the water concentration to 120 ppm (Figure 2C), because the “vertical polymerization” of TCMS was promoted (Fadeev and McCarthy, 2000). Meanwhile, the CALE decreased to ~0° (Figure 2G), indicating formation of the superLEphilic separator. This is because the SNFs loosely stacked together and formed a 3D cross-linked polymeric network with high surface area (Meseck et al., 2014). This is further confirmed by the higher porosity of the SNFs-Celgard120ppm separator (51.9%) than the others (Table S3). With further increasing the water concentration to 200 ppm, a dense layer of short and worm-like SNFs was formed (Figure 2D), because the reaction was too violent. This is consistent with previous studies (Gao and McCarthy, 2006; Zhang and Seeger, 2011b). The SNFs formed at a water concentration of 200 ppm are still sufficient to make the separator superLEphilic (Figure 2H).

The dynamic wetting process of the SNFs-Celgard separators by the LE was observed using a high-speed digital camera with the Celgard separator for comparison. When dropped from a height of 5 mm onto the Celgard separator for 108.2 ms, the LE droplet reached its equilibrium state (Figure 2I and Video S1). No shape change and diffusion of the LE droplet were observed with further increasing the contact time to 1 s. In contrast, the LE droplet wetted and completely diffused into the entire SNFs-Celgard120ppm separator in ~454.2 ms (Figure 2J and Videos S1 and S2), owing to its superLEphilicity. This is faster than all the reported separators, including the recently reported HAP/CF separator, into which the LE droplet penetrated in 5 s (Li et al., 2017a). For the SNFs-Celgard50ppm and SNFs-Celgard200ppm separators, the LE droplets have slower diffusion speed and smaller wetting areas compared with the SNFs-Celgard120ppm separator (Video S1). This is because the SNFs are sparse and short. After 10 s, the LE wetting areas for the SNFs-Celgard120ppm and SNFs-Celgard200ppm separators are 1.75 and 1.61 cm², respectively, which are much larger than that of the SNFs-Celgard50ppm separator (0.51 cm²) and Celgard separator (0.12 cm²) (Figures 2K-2N). The LE filling is the slowest step in the assembly of Li batteries with the Celgard separator. Thanks to the superLEphilicity, the cell with the SNFs-Celgard120ppm separator can be assembled very quickly. During cell assembly, 50 μL of the LE was dripped on the surface of the separator, and the time when the separator was completely wetted was recorded. The Celgard separator was completely wetted in ~39 min, which is about 62 times more than that of the SNFs-Celgard120ppm separator (~37 s).

The SNFs are beneficial to enhance the LE uptake (Table S3). The LE uptake of the SNFs-Celgard120ppm separator is 287.8%, which is much higher than that of the SNFs-Celgard200ppm separator (196.9%), SNFs-Celgard50ppm (165.5%), and Celgard (91.3%) separators and the previously reported separators (80%–253%) (Dai et al., 2016; Li et al., 2017a, 2017b; Ryu et al., 2011). This is because the 3D cross-linked polymeric network of the SNFs provides a large space to accommodate the LE (Figures 2O and S3). Besides high LE uptake, the SNFs-Celgard120ppm separator shows high LE retention rate owing to the high affinity between the LE and the separator. After storage in room conditions for 30 min, the LE retention rate of the SNFs-Celgard120ppm separator is 85.6%, which is higher than that of the SNFs-Celgard200ppm separator (76.2%), SNFs-Celgard50ppm (67.0%), and Celgard (44.2%) separators (Figure S7). After 1 h, the Celgard separator became half dry, whereas the SNFs-Celgard120ppm separator was still completely wetted by the LE, demonstrating a high LE retention rate (Figure S8). It is well known that the Li⁺ conductivity of a separator is closely related to the LE uptake and retention rate (Dai et al., 2016). The Li⁺ conductivity of the SNFs-Celgard120ppm separator is 1.02 mS cm⁻¹, which is higher than that of the SNFs-Celgard200ppm separator (0.832 mS cm⁻¹), SNFs-Celgard50ppm separator (0.740 mS cm⁻¹), and Celgard (0.727 mS cm⁻¹) separators (Figure S9 and Table S3). The Li⁺ conductivity was increased by 40% by introducing SNFs onto the Celgard separator. Moreover, The Si-O groups of SNFs can act as Lewis acid to trap a sufficient amount of Li salt anions (Lee et al., 2007; Wang et al., 2015), thus increasing the dissociation degree of Li salt. Consequently, the SNFs-Celgard120ppm separator showed...
higher Li⁺ diffusion than the Celgard separator. To support this view, the \( t_{Li} \) was measured (Figure S10). The \( t_{Li} \) is 0.43 for the Celgard separator, which is similar to the reported data (He et al., 2018). However, the \( t_{Li} \) was significantly enhanced to 0.59 for the SNFs-Celgard120ppm separator.

To further demonstrate superLEphilicity of the SNFs-Celgard120ppm separator, three commonly used LEs with different surface tensions were studied, e.g., carbonates (27.79 mN m⁻¹), ethers (26.56 mN m⁻¹), and PC (31.35 mN m⁻¹) (Table S1). The Celgard separator showed CALE of 43.0° (carbonates), 47.5° (ethers), and 63.4° (PC), which are similar to the reported data (Hao et al., 2016; Lee et al., 2015). The SNFs-Celgard120ppm separator showed significantly different wettability towards these LEs (Figure 2P). The SNFs-Celgard120ppm separator showed CALE of 0° for both carbonates- and ethers-based LEs, and CAE of 5.2° for the strong polar PC-based LE. After 10 s, the wetting areas of the carbonates-, ethers-, and PC-based LEs on the SNFs-Celgard120ppm separator are 1.75, 1.43, and 1.13 cm², respectively, which are much higher than those of the Celgard separator (Figure S11).

**Superhydrophobicity of SNFs-Celgard Separators**

Wettability of the separators towards water is shown in Figures 3A and 3B. The CA_water is 120.4° for the Celgard separator. The CA_water is 23.2° for the O₂-plasma activated Celgard, as hydroxyl groups were generated on the surface of the separator. The SNFs-Celgard120ppm separator is close to superhydrophobic with a CA_water of 149.5° and a water sliding angle of 42.3°. With increasing the water concentration, the SNFs-Celgard separators became superhydrophobic. The SNFs-Celgard120ppm has a CA_water of 167.4°, and the water droplets could easily roll off the 1° tilted separator. The SNFs-Celgard200ppm separator...
has slightly lower superhydrophobicity, as the SNFs are shorter. According to the Cassie-Baxter and the Wenzel models (Cassie and Baxter, 1944; Wenzel, 1936), introduction of a proper microstructure could make a hydrophobic surface more hydrophobic or even superhydrophobic. In addition, the methyl groups on the surface of the SNFs could decrease the surface energy of the separator, which also contributes to superhydrophobicity of the SNFs-Celgard separators. The dynamic wetting process of the SNFs-Celgard120ppm separator by water is shown in Figure 3B and Video S3. The 6-μL water droplet released from a height of 5 mm bounced ~14 times before settling down on the separator. The water droplet exhibited complete rebounds with a liquid-solid contact time of ~11.5 ms. These results demonstrate high superhydrophobicity of the SNFs-Celgard120ppm separator.

The superhydrophobicity could avoid wetting of the separator by water and may also reduce moisture uptake during the use and storage periods. This is helpful to reduce the side effects of trace water in conventional Celgard separators on the performance of Li metal batteries and additional troubles in Li metal battery assembly. To verify our hypothesis, the moisture uptake of the separators was measured by keeping the separators in a high-humidity environment (relative humidity = 92.6%, 25°C) for 7 days (Figure S13). The moisture uptake of the SNFs-Celgard120ppm separator is ~0% (Figure 3C). In contrast, the moisture uptake is 0.29% for the Celgard separator and is 1.75% for the O2-plasma activated Celgard separator.

To gain more insight into the effects of the superhydrophobicity and the trace water in separators on performance of Li metal batteries, the separators after moisture uptake test (termed as wet separators) were immediately used for assembly of Li symmetric cells. In Li symmetric cells, trace water could be involved in reactions at the interface of the Li anode (Li et al., 2018c), leading to fluctuations of the voltage-time curves. For the hydrophobic Celgard separator, the polarization voltage of the cell started to increase after 135 h (Figure 3D) because of fast dendrite Li growth (Liu et al., 2017). Subsequently, a sudden drop in the polarization voltage was observed after 190 h, suggesting short-circuiting in the cell due to serious dendrite Li growth (Figure S14A). The voltage-time curve of the cell with the wet Celgard separator is stable at the beginning, but the sudden drop in the polarization voltage happened earlier (after 164 h, Figure 3D). This is because the trace water in the wet separator involved in exothermal side reactions at the interface of Li anode. These side reactions not only caused inhomogeneous solid electrolyte interphase (SEI)-formation but also accelerated dendrite Li growth and Li anode pulverization (Figure S14) and ultimately resulted in earlier failure of the cell. For the hydrophilic O2-plasma activated separator, the voltage-time curve of the cell with the wet separator is very unstable compared with that with the normal one (Figure 3E). Also, a sudden drop in the polarization voltage, i.e., short-circuiting, happened after only 76 h. These phenomena are due to the high moisture uptake of the separator. In contrast, the cell with the SNFs-Celgard120ppm separator exhibits a very stable voltage-time curve in 208 h and slow increase in the voltage in subsequent cycles (Figure 3F). No short-circuiting was observed in 250 h, indicating higher stability and safety compared with the cell with the Celgard separator. Also, different from the wet Celgard and O2-plasma-activated Celgard separators, the voltage-time curve of the cell with the wet SNFs-Celgard120ppm separator is very stable and is similar to that with the SNFs-Celgard120ppm separator (Figures 3D–3F). No dendrite Li and Li anode pulverization were observed on the surface of the cycled Li anode in the cells with the SNFs-Celgard120ppm separator or the wet one (Figure S15) owing to its superhydrophobicity. Thus, there is no need to dry the SNFs-Celgard120ppm separator before Li metal battery assembly, which is necessary for conventional separators. This is because the superhydrophobicity of the SNFs-Celgard120ppm separator can efficiently reduce moisture uptake and then avoid the side reactions at the interface of Li anode. The above-mentioned results indicate that the superhydrophobic SNFs-Celgard120ppm separator can improve performance of the Li metal battery and make battery assembly simpler.

Notably, the wettability of the SNFs-Celgard120ppm separator is significantly different from all the previously reported separators (Table S4). These separators are LEphilic, and only a few of them are superLEphilic, e.g., Al2O3/PI-coated PE separator (Shi et al., 2016), HAP/CF separator (Li et al., 2017a), and commercial ceramic-coated separators (Table S4). Meanwhile, all the separators can be easily wetted by water, which means high moisture uptake. However, the SNFs-Celgard120ppm separator is superLEphilic and superhydrophobic simultaneously.

It also can be concluded that the superLEphilicity, LE uptake and retention rate, Li+ conductivity, and superhydrophobicity of the separators are closely related to the microstructure of the SNFs, which can be controlled simply by the water concentration in toluene during hydrolysis of TCMS.
The influence of the SNFs-Celgard separators on electrochemical performance of Li metal batteries was investigated using the Li/LiFePO4 cells (Figure 4). The cycling stability of the cells with different separators at 1.0 C is shown in Figures 4A–4C and S16. After 350 cycles, the cells with the Celgard, SNF-Celgard50ppm, SNFs-Celgard120ppm, and SNFs-Celgard200ppm separators maintained 65.32%, 81.46%, 96.05%, and 89.77% of their initial capacity, respectively. The sharp capacity drop of the cell with the Celgard separator from the 220th cycle is ascribed to the dendrite Li growth, Li anode pulverization, and LE consumption (He et al., 2013; Liu et al., 2017). The voltage hysteresis of the cell with the Celgard separator showed an obvious increase from the 220th cycle (Figure S17), which verified LE consumption (Liu et al., 2017). Obviously, the cell with the SNFs-Celgard120ppm separator has the highest cycling stability, indicating that the separator could effectively alleviate the dendrite Li growth, Li anode pulverization, and LE consumption (He et al., 2013; Liu et al., 2017). The SNFs-Celgard120ppm separator is superLEphilic and has a high LE uptake and retention rate. This means the SNFs have a strong affinity to Li+, which decreased the Li+ concentration gradient before Li+ reaching the Li anode surface (Cheng et al., 2016; Zhao et al., 2018). Consequently, the Li+ distributed homogeneously over the entire Li anode surface during cycling, and the interfacial interaction between Li+ and the Li anode was improved. It is well known that the homogeneous distribution of Li+ is crucial to the dendrite-free Li depositing (Cheng et al., 2017). Figure S19A shows the scanning electron microscopy (SEM) image of the SNFs-Celgard120ppm separator after 350 cycles. The SNFs on the cycled separator is similar to those on the new one. Also, the cycled separator is still superhydrophobic (CAwater = 154.3°, Figure S19B). These results indicate that the SNFs-Celgard120ppm separator has high stability in the cyclic discharge/charge process. This is further supported by the good electrochemical stability of the SNFs-Celgard120ppm separator (Figure S20). This is because the Si-O groups of SNFs can act as Lewis acid to trap a sufficient amount of Li salt anions, thus delaying the irreversible oxidative decomposition of Li salt anions (Lee et al., 2007; Qiu et al., 2004; Wang et al., 2015). The gradual capacity decay of the cells with the SNFs-Celgard120ppm and SNFs-Celgard200ppm separators is because the spare or short SNFs cannot efficiently alleviate the dendrite Li growth and Li anode pulverization.

Figure 4D shows the rate performance of the Li/LiFePO4 cells with different separators. At low discharge rates, e.g., 0.1 C and 0.2 C, the Li+ conductivities of all the separators are enough to support the discharge rates and the cells displayed very similar rate performance (Dai et al., 2016). However, the...
rate performance of the cells at high discharge rates is different from each other. The cell with the SNFs-Celgard120ppm separator has the lowest capacity loss upon cycling. At 5.0 C, the capacity is 125 mA h g$^{-1}$, which is 76.25% of the capacity at 0.1 C. Instead, the capacity retentions of the cells with the Celgard, SNFs-Celgard50ppm, and SNFs-Celgard200ppm separators are 59.28%, 61.03%, and 68.21%, respectively. At high rates, the Li$^+$ conductivity and resistance act as the key factors determining the rate performance (Arora and Zhang, 2004; Dai et al., 2016). Thus, the better rate performance of the cell with the SNFs-Celgard120ppm separator is attributed to the higher Li$^+$ conductivity (Figures S10 and S11) and lower resistance (Figure S21).

The SNFs-Celgard120ppm separator can also be applied in the Li metal batteries with high-voltage cathode materials, such as 4.9 V LiNi$_{0.5}$Mn$_{1.5}$O$_4$ and 4.8 V Li$_{1.3}$Mn$_{0.5}$Ni$_{0.5}$O$_2$. Compared with the Celgard separator, the Li/LiNi$_{0.5}$Mn$_{1.5}$O$_4$ and Li/Li$_{1.3}$Mn$_{0.5}$Ni$_{0.5}$O$_2$ cells with the SNFs-Celgard120ppm separator showed higher stability in the discharge/charge process (Figures S22A and S23A), which is due to good electrochemical stability and unique wettability of the separator. Moreover, owing to higher Li$^+$ conductivity of the SNFs-Celgard120ppm separator and lower resistance of the corresponding cells (Figures S22B, S22C, S23B, and S23C), the cells showed better rate performance (Figures S22D and S23D). For the Li/LiNi$_{0.5}$Mn$_{1.5}$O$_4$ cell, the capacity decay is only 30.4% with increasing the rate from 0.1 to 1.0 C, whereas that of the cell with the Celgard separator is 37.2%. For the Li/Li$_{1.3}$Mn$_{0.5}$Ni$_{0.5}$O$_2$ cell, the value is 34.4% for the SNFs-Celgard120ppm separator and 46.3% for the Celgard separator.

To further demonstrate advantages of the SNFs-Celgard120ppm separator, the electrochemical performance of the Li/LiFePO$_4$ cells with the SNFs-Celgard120ppm separator or commercial ceramic-coated separators was compared (Figure S24). All of the separators were directly used for cell assembly. Obviously, the cycling stability and Coulombic efficiency of the cell with the SNFs-Celgard120ppm separator are higher and more stable than those of the cells with the ceramic-coated separators (Figure S24A). This is because the ceramic-coated separators are hydrophilic or even superhydrophilic (Figure S24B) and the water in the separator was involved in side reactions at the interface of Li anode. All of the cells showed similar interfacial resistance before cycling (Figure S24C); however, the interfacial resistance of the cells with the ceramic-coated separators increased significantly after 100 cycles (Figure S24D). This is because of exfoliation of the ceramic layer from the polyolefin membranes during cell assembly and discharge/charge, as there is no interaction between them (Lee et al., 2014).

**Thermostability of SNFs-Celgard Separators**

The Celgard separator has poor thermostability owing to the low melting point (Figures 5A and S25) (Arora and Zhang, 2004; Lee et al., 2014), which may cause safety issues of Li batteries (Liu et al., 2018a). Therefore, we studied the influence of the SNFs on thermostability of the separator. At temperatures above 120°C, the thermal shrinkage of the Celgard separator is evident. The sparse and short SNFs on the surface of the SNFs-Celgard50ppm separator did not improve the thermostability. The shrinkage of the SNFs-Celgard50ppm separator is similar to that of the Celgard separator at the same temperature (Figure 5B). The very thick and long SNFs on the SNFs-Celgard120ppm separator substantially enhanced the thermostability. The SNFs-Celgard120ppm separator has no visible shrinkage at temperature up to 180°C (Figures 5B and S25). However, the SNFs-Celgard200ppm separator starts to shrink at 170°C and has a shrinkage of 6% at 180°C, as the SNFs are very short. The high thermostability of the SNFs-Celgard120ppm separator was further confirmed by differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA). The endothermic peak of the SNFs-Celgard120ppm separator appeared at 234°C–297°C, much higher than that of the Celgard separator (160°C–220°C, Figure 5C). The evident weight loss of the Celgard separator started at 178°C, whereas that of the SNFs-Celgard120ppm separator started at 215°C (Figure S26). This is because the thermostable SNFs layer functioned as the thermal resistant layer to protect the Celgard separator from shrinking, like the previously reported inorganic or polymer coatings (Dai et al., 2016; Ryou et al., 2012; Yang and Zhang, 2018). Moreover, a part of TCMS molecules diffused into micropores of the Celgard separator and deposited on the wall of the micropores in the hydrolytic condensation process, forming a composite separator, which was confirmed by the cross-section elemental maps of the SNFs-Celgard120ppm separator (Figure S3B). This also contributes to the enhanced thermostability. It is worth noting that the Celgard separator was completely decomposed at 500°C in O$_2$ atmosphere, but there was $\sim$2.40% residual SiO$_2$ for the SNFs-Celgard120ppm separator. This means the weight of the SNFs on the SNFs-Celgard120ppm separator is 2.68%, i.e., 0.04 mg cm$^{-2}$. Thus, the SNFs have negligible influence on the energy density of Li batteries.
To study the effect of the SNFs-Celgard120ppm separator on the safety of Li metal batteries, the open circuit voltage (OCV) curves of the Li/LiFePO$_4$ cells were recorded at 160°C (Figure 5D). If there is serious thermal shrinkage of the separator, battery internal short-circuiting will result in a sudden OCV drop. For the cell with the Celgard separator, the OCV dropped sharply to 0 V after 31.5 min. However, for the cell with the SNFs-Celgard120ppm separator, the OCV is stable throughout the test (300 min). After the OCV test, the Celgard separator almost completely melted (Figure 5E). In contrast, the SNFs-Celgard 120ppm separator remained intact and could still be curved without any fracture (Figure 5F). The results demonstrate that the SNFs-Celgard120ppm separator could evidently enhance safety of Li metal batteries.

General Applicability of SNFs-Celgard Separators

To verify applicability of the SNFs-Celgard separator in Li ion batteries, the LiFePO$_4$/graphite cells were tested. The cycling stability of the cells with different separators at 1.0 C (1.0 C = 133 mA h g$^{-1}$) is shown in Figure S27A. The initial discharge capacity of the cell with the SNFs-Celgard120ppm separator is 106 mA h g$^{-1}$, which is higher than those with the Celgard (94 mA h g$^{-1}$), SNFs-Celgard50ppm (98 mA h g$^{-1}$), and SNFs-Celgard200ppm (102 mA h g$^{-1}$) separators. After 350 cycles, the cells with the Celgard, SNF-Celgard50ppm, SNFs-Celgard120ppm, and SNFs-Celgard200ppm separators maintained 62.55%, 71.53%, 84.9%, and 79.26% of their initial capacity, respectively. The cycling stability of the cell with the SNFs-Celgard120ppm separator (94.3% after 100 cycles) is better than that of the cells with the Al$_2$O$_3$ ceramic-grafted separator (85.6% after 100 cycles) (Jiang et al., 2017) and the HAP/CF separator (92.3% after 100 cycles) (Li et al., 2017a). Moreover, the cell with the SNFs-Celgard120ppm separator showed the best rate performance compared with the other separators (Figure S27B). At 5.0 C, the capacity of the cell with the SNFs-Celgard120ppm separator is 58 mA h g$^{-1}$, which is 46.03% of the capacity at 0.1 C. Instead, the capacity retention of the cell with the Celgard separator is only 29.66%. Moreover, the
SNFs-Celgard 120ppm separator could evidently enhance the safety of Li ion batteries according to the OCV curves and the photographs of the separators after the OCV test (Figure S28).

To further assess usefulness of the SNFs-Celgard 120ppm separator in Li ion batteries, the LiFePO₄/graphite pouch cells with a high areal electrode loading of 2.0 mA h cm⁻² (15.4 mg cm⁻²) were tested (Figure 6). The capacity decay of the cell was 20.7% with increasing the rate from 0.1 to 2.0 C, whereas that of the cell with the Celgard separator reached 40.4%. The punch cell with the SNFs-Celgard 120ppm separator also showed much better cycling stability with a capacity decay of 21.4% at 1.0 C over 150 cycles and lower resistance.

In addition, the SNFs-Celgard separator has a chance of being acceptable to the battery industry, as the cost of the SNFs layer is only ~0.11 USD m⁻² (Table S5).

**DISCUSSION**

A superLEphilic/superhydrophobic and thermostable SNFs-Celgard separator was prepared by the growth of SNFs onto the Celgard separator. The superLEphilicity, LE uptake and retention rate, Li⁺ conductivity, superhydrophobicity, and moisture uptake of the separator are closely related to the microstructure of the SNFs, which can be controlled simply by the water concentration in toluene. The wettability of the separator is significantly different from all the reported separators. The separator has high superLEphilicity, fast LE diffusion, high LE uptake, LE retention rate, and Li⁺ conductivity. The separator also has high superhydrophobicity and low moisture uptake, making Li metal battery assembly simpler. Additionally, the separator has high thermostability. Consequently, the Li/LiFePO₄ cells show high cycling stability, Coulombic efficiency, rate performance, and safety, as the separator could efficiently eliminate the side reactions at the interface of Li anode triggered by trace water and could reduce resistance of the cells. In addition, the separator outperforms the commercial ceramic-coated separators in the Li/LiFePO₄ cells. Moreover, the separator could improve performance of the other Li metal batteries with high-voltage cathodes and the LiFePO₄/graphite pouch cells. We believe that this work provides an avenue for designing advanced separators for Li batteries and other metal batteries. This study also opens up a new field of application of bioinspired superwetting surfaces, like oil/water separation did a decade ago.
Limitations of the Study

The application of bioinspired superwetting surfaces on separators of Li metal batteries has not been well understood. Further in-depth study about the effects of superwetting separators on the performance of Li batteries should be carried out. In addition, the performance of the SNFs-Celgard separators was studied by using Li/LiFePO4 coin cells as opposed to pouch cells. Moreover, the O2-plasma activation technique may reduce the mechanical strength of polyolefin separators. Thus, new approaches for activation of polyolefin separators without sacrificing their inherent properties remain to be developed.

METHODS

All methods can be found in the accompanying Transparent Methods supplemental file.

SUPPLEMENTAL INFORMATION

Supplemental Information can be found online at https://doi.org/10.1016/j.isci.2019.06.010.

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AUTHOR CONTRIBUTIONS

Y.Y. and J.Z. conceived the concept. Y.Y. performed most of the experiments; B.L. and L.L. performed the wettability tests. All authors have thoroughly discussed the analysis of the data. Y.Y., S.S., and J.Z. wrote the manuscripts with contributions from all authors. J.Z. designed and supervised the work.

DECLARATION OF INTERESTS

The authors declare no competing interests.

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Supplemental Information

A SuperLEphilic/Superhydrophobic and Thermostable Separator Based on Silicone Nanofilaments for Li Metal Batteries

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Figure S1. SEM images of the (A) Celgard and (B) O$_2$-plasma activated Celgard separators, related to Figure 1.

Figure S2. SEM images of the SNFs-Celgard$_{120ppm}$ separator, related to Figure 1B.

Figure S3. (A) Cross-sectional SEM images and (B) elemental maps of the SNFs-Celgard$_{120ppm}$ separator, related to Figure 1 and Figure 5.
Figure S4. Photographs of the separators, related to Figure 1.

Figure S5. Synthesis of the SNFs-Celgard separator, related to Figure 1D-F.

Figure S6. Variation of $\theta_{\text{CA}_{\text{water}}}$ of the $O_2$-plasma activated Celgard separator with storage time (shown as means ± SD, n = 6), related to Figure 2F.
Figure S7. Variation of LE retention rate of the separators with storage time in room conditions, related to Figure 2K.

Figure S8. Photographs of the separators with absorbed LE after kept in room conditions for 1 h, related to Figure 2K.

Figure S9. Impedance plots of the cells with different separators, related to Figure 2.
Figure S10. The characteristic of Li$^+$ transference number ($t_{li}$), related to Figure 2.

Figure S11. Photographs of wetting behavior of three commonly used LEs with different surface tensions on the surface of the Celgard and SNFs-Celgard$_{120ppm}$ separators, related to Figure 2P.
Figure S12. CA_{water} and sliding angle of water on the separators, related to Figure 3A.

Figure S13. Schematic illustration of the device for measuring the moisture uptake of the separators, related to Figure 3C.
Figure S14. SEM images of the Li anode surface in the Li symmetric cells with (A) Celgard and (B) wet Celgard separators at a current density of 1.0 mA cm$^{-2}$, related to Figure 3D.

Figure S15. SEM images of the Li anode surface in the Li symmetric cells with (A) SNFs-Celgard$_{120}$ppm and (B) wet SNFs-Celgard$_{120}$ppm separators at a current density of 1.0 mA cm$^{-2}$, related to Figure 3F.
Figure S16. Charge/discharge curves of the Li/LiFePO$_4$ cells with (A) SNFs-Celgard$_{50\text{ppm}}$ and (B) SNFs-Celgard$_{200\text{ppm}}$ separators, related to Figure 4A.

Figure S17. Voltage hysteresis of the Li/LiFePO$_4$ cells with cycle number, related to Figure 4B-C.
Figure S18. Electrochemical performances of the Li symmetric cells with different separators, related to Figure 4A. (A) Voltage-time curves. SEM images of the Li anode surface in the Li symmetric cells with (B) the Celgard and (C) SNFs-Celgard120ppm separator. The amount of plated Li is 1.0 mAh cm$^{-2}$, and the current density is 1.0 mA cm$^{-2}$ in each cycle. (D, E) Schematic illustrations of dendrite Li growth with different separators.

Figure S19. (A) SEM images of the SNFs-Celgard$_{120ppm}$ separator after 350 cycles and (B) photographs of 10 μL water droplets on the SNFs-Celgard$_{120ppm}$ separator after 350 cycles, related to Figure 4.
**Figure S20.** Linear sweep voltammetry profiles of the Celgard and SNFs-Celgard\textsubscript{120ppm} separators, related to Figure 4.

**Figure S21.** Nyquist plots of the Li/LiFePO\textsubscript{4} cells with different separators (A) before cycling and (B) after 100 cycles, related to Figure 4A.
Figure S22. Electrochemical performances of the Li/LiNi_{0.5}Mn_{1.5}O_{4} cells, related to Figure 4. (A) Cycling stability at 1.0 C (1.0 C = 140 mA h g\textsuperscript{-1}), Nyquist plots (B) before cycling and (C) after 100 cycles, and (D) rate performance. The insets in (A) show discharge/charge profiles.
Figure S23. Electrochemical performances of the Li/Li$_{1.2}$Mn$_{0.34}$Ni$_{0.3}$Co$_{0.3}$O$_2$ cells, related to Figure 4. (A) Cycling stability at 1.0 C (1.0 C = 360 mA h g$^{-1}$), Nyquist plots (B) before cycling and (C) after 100 cycles, and (D) rate performance. The insets in (A) show discharge/charge profiles.
**Figure S24.** Electrochemical Performances of the Li/LiFePO$_4$ cells with the SNFs-Celgard$_{120ppm}$ and the ceramic coated separators, related to Figure 4. (A) Cycling stability at 1.0 C (1.0 C = 160 mA h g$^{-1}$), (B) CA$_{\text{water}}$ on the ceramic coated separators (shown as means ± SD, n = 6), Nyquist plots of the cells (C) before cycling and (D) after 100 cycles. We chose four commercial ceramic coated separators: (1) SEMCORP (one side Al$_2$O$_3$ coated PE membrane with a coating thickness of 4 ± 0.1 μm, Yunnan Energy New Material Co., LTD, China), (2) SH216D1 (one side Al$_2$O$_3$ coated PP membrane with a coating thickness of 4±1 μm, Shenzhen Senior Technology Material Co., LTD, China), (3) SK-1 (one side Al$_2$O$_3$ coated PE membrane with a coating thickness of 4 ± 0.1 μm SKinnovation, Korea) and (4) SK-2 (double side Al$_2$O$_3$ coated PE membrane with a coating thickness of 2 μm on each side, SKinnovation, Korea).
Figure S25. Dimension of the separators before and after heat treatment at different temperature for 1 h, related to Figure 5A.

Figure S26. TGA curves of the separators, related to Figure 5.
**Figure S27.** (A) Cycling stability and (B) rate performance of the LiFePO$_4$/graphite cells with different separators (1.0 C = 133 mA h g$^{-1}$), related to Figure 6.

**Figure S28.** (A) OCV curves of the LiFePO$_4$/graphite cells with different separators at 170 °C. (B) Photographs of the separators after the OCV test, related to Figure 6.
Table S1. Surface tension of various LEs (shown as means ± SD, n = 12), related to Figure 2 and Figure 3.

| LEs          | Carbonates | Ethers | PC        |
|--------------|------------|--------|-----------|
| Surface tension / mN m⁻¹ | 27.79 ± 0.06 | 26.56 ± 0.35 | 31.35 ± 0.16 |

Table S2. Atomic ratio of O, C and Si on the surface of the SNFs-Celgard₁₂₀ppm separator, related to Figure 1E and F.

| Elements | O  | C  | Si  |
|----------|----|----|-----|
| Atomic ratio / % | 31.55 | 46.78 | 21.67 |

Table S3. Physical and electrochemical parameters of the separators, related to Figure 2.

| Separators | Celgard | SNFs-Celgard₁⁰⁰ppm | SNFs-Celgard₁₂₀ppm | SNFs-Celgard₂₀₀ppm |
|------------|---------|--------------------|--------------------|--------------------|
| Porosity / % | 44.9    | 45.7               | 51.9               | 47.9               |
| LE uptake / % | 91.3    | 165.5              | 287.8              | 196.9              |
| Conductivity / mS cm⁻¹ | 0.727 | 0.740 | 1.02 | 0.832 |
Table S4. Wettability of the previously reported separators and the SNFs-Celgard\textsubscript{120ppm} separator, related to Figure 2 and Figure 3.

| Separators                                | CA\textsubscript{LE} / ° | CA\textsubscript{water} / ° | Ref.       |
|-------------------------------------------|---------------------------|-----------------------------|------------|
| PVDF/ZSM-Si(Al) coated PE                 | - \textsuperscript{a}    | 14.5                        | Mao et al., 2017 |
| (PEI/SiO\textsubscript{2}) modified PE   | -                         | 24.6                        | Wang et al., 2015 |
| PE-SiO\textsubscript{2}@PDA               | -                         | 36                          | Dai et al., 2016 |
| (PAA/ZrO\textsubscript{2})\textsubscript{3} modified PE | -                         | 38                          | Xu et al., 2015 |
| Polydopamine coated PE                    | -                         | 39                          | Ryou et al., 2011 |
| N-SiO\textsubscript{2} coated PE         | -                         | 51.3                        | Cho et al., 2017 |
| PAA/PEO@PP                                | 27.8                      | 71.7                        | Li et al., 2015 |
| Tannic acid coated PP                     | -                         | 72                          | Pan et al., 2015 |
| SiO\textsubscript{2} grafted PE          | -                         | 79                          | Zhu et al., 2015 |
| TiO\textsubscript{2} grafted PE          | -                         | 89                          | Zhu et al., 2016 |
| Al\textsubscript{2}O\textsubscript{3}/LPMA64 coated PE | -                         | 95                          | Na et al., 2016 |
| Al\textsubscript{2}O\textsubscript{3}/PI coated PE | 0 Hydrophilic \textsuperscript{b} | refurbished            | Shi et al., 2016 |
| SiO\textsubscript{2}-PMMA coated PE      | 6.1                       | hydrophilic                | Yang et al., 2015 |
| SiO\textsubscript{2}/WCDA coated PE      | 8                         | hydrophilic                | Chen et al., 2016 |
| Al\textsubscript{2}O\textsubscript{3}/CGS grafted PE | 21                       | hydrophilic                | Jiang et al., 2017 |
| Hydroxyapatite/cellulose fibers           | 0                         | hydrophilic                | Li et al., 2017 |
| PU                                       | 5                         | hydrophilic                | Kim et al., 2016 |
| Chitin nanofibers                         | 9.2                       | hydrophilic                | Zhang et al., 2017 |
| Poly(p-phenylene benzobisoxazole)         | 20                        | hydrophilic                | Hao et al., 2016 |
| PPy@NCFs/NCFs                            | 0                         | hydrophilic                | Wang et al., 2017 |
| SH216D1                                  | 4                         | 0                           | tested \textsuperscript{c} |
| SEMCORP                                  | 0                         | 62.6                        | tested |
| SK-1                                     | 0                         | 71.1                        | tested |
| SK-2                                     | 8.3                       | 68.8                        | tested |
| **SNFs-Celgard\textsubscript{120ppm}**   | 0                         | **167.4**                   | This work |

\textsuperscript{a} “-” means not mentioned.

\textsuperscript{b} “hydrophilic” means that the material for modification of the separators is hydrophilic.

\textsuperscript{c} “tested” means that the CA of LE and water was measured at 25 °C using 10 μL droplets on a Contact Angle System OCA 20.
Table S5. Cost of the SNFs layer on the SNFs-Celgard separator, related to Figure 1.

| Cost of TCMS                        | Cost of O2-plasma treatment | Cost of the SNFs layer on the SNFs-Celgard separator |
|-------------------------------------|-----------------------------|------------------------------------------------------|
| 152.5 USD for 2 kg (ABCR)           | 0.03 USD m⁻²                | 0.58 USD m⁻²                                         |
| 144.0 USD for 2 kg (Gelest)         |                             | 0.55 USD m⁻²                                         |
| 10430 USD for 1000 kg (block transaction) | 0.03 USD m⁻²               | 0.11 USD m⁻²                                         |
TRANSPARENT METHODS

Materials

Toluene, ethanol and $n$-hexadecane were purchased from China National Medicines Co., Ltd. TCMS (98%) was purchased from Gelest. LiFePO$_4$, carbon black, graphite, $N$-methyl-2-pyrolidone and PVDF were purchased from Shenzhen Kejing Star Technology Co., Ltd., China. All the LEs were purchased from Zhangjiagang Guotai Huarong Chemical New Material Co., Ltd., China. LiNi$_{0.5}$Mn$_{1.5}$O$_4$ and Li$_{1.2}$Mn$_{0.54}$Ni$_{0.3}$Co$_{0.3}$O$_2$ were provided by Lanzhou University of Technology, China. All chemicals were used as received without further purification.

Preparation of SNFs-Celgard Separators

First, the polyolefin separator (Celgard 2400) was activated with O$_2$-plasma (HARRICK PLASMA PDC-002, USA) at an O$_2$ flow rate of 60 sccm and a power of 15 W for 1 min. The SNFs-Celgard separators were prepared using a similar method described in our previous papers (Zhang and Seeger, 2011; Zhang et al., 2014). In brief, a fresh solution containing 80 mL of toluene with certain water concentrations (50, 120, and 200 ppm) and 50 μL of TCMS was prepared in a media bottle. Subsequently, a piece of the O$_2$-plasma activated Celgard separator (68.75 cm$^2$) was immersed in the solution at room temperature. 6 h later, the SNFs-Celgard separator was successfully prepared. The separator was successively rinsed with 10.0 mL of toluene, 10.0 mL of ethanol and 10 mL of water/ethanol mixture (1:1, v/v), and then dried at 30 °C.

Measurements of Wetting Behaviors

To investigate wettability of the separators, the CA of water and LEs was collected at 25 °C using 10 μL droplets on a Contact Angle System OCA 20 (Dataphysics, Germany). It should be noted that the LE refers to the carbonates based LE (1 M LiPF$_6$ in 1:1 (v/v) EC and DMC) if not specified. The surface tension of various LEs was measured at 25 °C using 10 μL droplets on a Contact Angle System DSA100 (KRÜSS,
Germany). The dynamic wetting behavior of the separators was tested at 4000 fps using a high-speed digital camera (FASTCAM Mini UX100, Photron, Japan).

Measurements of LE Uptake and Moisture Uptake

The LE uptake of the separators was measured by soaking the separators in the LE for 2 h. Subsequently, the separators were taken out of the LE, and the excess LE on the surface of the separator was removed by wiping with filter paper. The LE uptake was calculated using formula (Dai et al., 2016):

\[
\text{LE uptake} (\%) = \frac{m_2 - m_1}{m_1} \times 100\% \quad (1)
\]

where \( m_1 \) and \( m_2 \) are the weight of the separators before and after LE absorption, respectively.

To measure the moisture uptake of the separators, the separators were dried at 60 °C for 24 h in a vacuum oven to a constant weight. Subsequently, the separators were put into a chamber with a constant relative humidity of 92.6% at 25 °C for 7 days (Figure S13). The moisture uptake was calculated using formula (Mihranyan et al., 2004; Peng et al., 2013):

\[
\text{Moisture uptake} (\%) = \frac{m_4 - m_3}{m_3} \times 100\% \quad (2)
\]

where \( m_3 \) is the weight of the dry separators, and \( m_4 \) is the weight of conditioned separators (termed as wet ones). In order to study the effect of moisture uptake on performance of the separators, the separators after moisture uptake test were immediately used for assembly of Li symmetric cells.

Electrode Preparation

To prepare the LiFePO\(_4\) cathode, the LiFePO\(_4\) powder was mixed with 10 wt% PVDF and 10 wt% super P in N-methyl-2-pyrrolidone to form the active material slurry. The slurry was coated on Al foil by the tape casting method. The cathode was dried in a vacuum oven at 60 °C for 24 h, compressed, and cut into circular disks. The content of the active material in each cathode circular disk is 2.6 mg cm\(^{-2}\). The high voltage LiNi\(_{0.5}\)Mn\(_{1.5}\)O\(_4\) and Li\(_{1.2}\)Mn\(_{0.54}\)Ni\(_{0.3}\)Co\(_{0.3}\)O\(_2\) cathodes were prepared via a similar process. The LiNi\(_{0.5}\)Mn\(_{1.5}\)O\(_4\) and Li\(_{1.2}\)Mn\(_{0.54}\)Ni\(_{0.3}\)Co\(_{0.3}\)O\(_2\) contents in the
cathodes are 2.0 mg cm$^{-2}$. The graphite anode was prepared via a similar process, except that the carboxymethylcellulose was used as a binder and the slurry was coated on copper foil. The content of graphite in each anode circular disk is 4.5 mg cm$^{-2}$.

**Cell Assembly and Electrochemical Tests**

CR2032 coin cells were used for all cell assembly and electrochemical tests. 50 μL of the LE was used in each cell. All the procedures were carried out in an Ar-filled glovebox with O$_2$ and water contents below 0.1 ppm. The Li symmetrical cells were assembled by sandwiching a separator between two Li electrodes. The performance of the Li symmetric cells was recorded using a CT2001A battery test system (LAND Electronic Co., Ltd. China) at 1 mA cm$^{-2}$ and the amount of plated Li is 1.0 mA h cm$^{-2}$.

For the Li metal cells, the LiFePO$_4$, LiNi$_{0.5}$Mn$_{1.5}$O$_4$ and Li$_{1.2}$Mn$_{0.54}$Ni$_{0.3}$Co$_{0.3}$O$_2$ cathodes, and the separators were dried at 60 °C for 2 h in a vacuum oven prior to cell assembly, and the cells were assembled using different cathodes and Li anode with the separators. The LiFePO$_4$/graphite cells were assembled using LiFePO$_4$ cathode and graphite anode with the separators. The pouch cells were assembled using LiFePO$_4$ cathode and graphite anode. The areal electrode loading and size of the cathode were 15.4 mg cm$^{-2}$ (2.0 mA h cm$^{-2}$) and 20 cm$^2$ (4 cm $\times$ 5 cm), respectively. The assembled cells were aged at room temperature for 24 h before testing. The discharge/charge and cycling data were recorded using a CT2001A battery test system with a certain voltage window at various cycling rate. The voltage window is 2.7-4.2 V for the Li/LiFePO$_4$ cells, 3.0-4.9 V for the Li/LiNi$_{0.5}$Mn$_{1.5}$O$_4$ cells, 2.4-4.8 V for the Li/Li$_{1.2}$Mn$_{0.54}$Ni$_{0.3}$Co$_{0.3}$O$_2$ cells and 2.4-3.7 V for the LiFePO$_4$/graphite cells.

The electrochemical stability of the separators was evaluated using linear sweep voltammetry (CHI660E, Chenhua Instruments Co., China) from 3.0 to 5.0 V (vs. Li/Li$^+$) at a scan of 1 mV s$^{-1}$. The cell was assembled by sandwiching a separator between stainless steel (working electrode) and Li metal (reference and counter electrodes). The Li$^+$ conductivity of the separators was calculated by the electrochemical impedance spectroscopy (EIS). The cells were assembled by sandwiching a separator
between two stainless steel blocking electrodes. The EIS measurements were carried out using an impedance analyzer (CHI660E) at open circuit potential with a constant perturbation amplitude of 5 mV in the frequency range of 0.1-100 KHz, and was calculated using formula (Yang and Zhang, 2018):

$$\sigma = \frac{L}{(R_b \times A_1)}$$  \hspace{1cm} (3)

where $\sigma$ is the Li$^+$ conductivity (mS cm$^{-1}$), $L$ is the thickness of the separator (cm), $R_b$ is the bulk resistance ($\Omega$), and $A_1$ is the area of the stainless steel electrode (cm$^2$).

The Li$^+$ transference number ($t_{Li}$) of the separators was measured by a potentiostatic polarization method with a constant potential at 20 mV for 1000 s, and was calculated using formula (He et al., 2018):

$$t_{Li} = \frac{I_s (\Delta V - I_o R_o)}{I_o (\Delta V - I_s R_s)}$$  \hspace{1cm} (4)

where $\Delta V$ is the potentiostatic potential (V); $I_o$ and $I_s$ are the current at initial and steady state (mA), respectively; $R_o$ and $R_s$ are the resistance before and after the potentiostatic polarization ($\Omega$), respectively.

In order to study the safety performance of the cells with different separators at high temperature, the open circuit voltage (OCV) measurement was carried out. The cells were assembled using LiFePO$_4$ cathode and Li anode or graphite anode with different separators. The cell was charged to 4.0 V at 25 °C, and then put into an oven at certain temperature. Subsequently, variation of the voltage with time was monitored using an electrochemical working station (CHI660E).

**Characterization**

Surface morphology of the separators was observed via field emission scanning electron microscopy (SEM, JSM-6701F, JEOL). Fourier transform infrared (FTIR) spectra of the separators were collected using a Nicolet NEXUS FTIR spectrometer using KBr pellets. X-ray photoelectron spectra (XPS) of the separators were recorded using a VG ESCALAB 250 Xi spectrometer with a monochromated Al K$_\alpha$ X-ray radiation source and a hemispherical electron analyzer. The spectra were collected in the constant pass energy mode with a value of 100 eV, and all binding energies were calibrated using the C 1s peak at 284.6 eV as the reference. The porosity of the
separators was measured by soaking the separators in \( n \)-hexadecane for 2 h, and supposing that the pore volume of the separator is equal to the volume of the absorbed \( n \)-hexadecane by the separator (Dai et al., 2016). The excess \( n \)-hexadecane on the surface of the separator was removed by wiping with filter paper. The porosity was calculated using formula 5:

\[
\text{Porosity (\%)} = \frac{\Delta m}{\rho V_o} \tag{5}
\]

where \( \Delta m \) is the mass difference of the separator before and after immersion in \( n \)-hexadecane, \( V_o \) is the total volume of the separator, and \( \rho \) is the density of \( n \)-hexadecane.

In order to study thermostability of the separators, the thermal shrinkage was measured based on the area change of the separator (2.83 cm\(^2\) circle) before and after heat treatment at certain temperature (120-200 °C) for 1 h, and was calculated using formula 6:

\[
\text{Thermal shrinkage (\%)} = \frac{A_1-A_2}{A_1} \times 100\% \tag{6}
\]

where \( A_1 \) and \( A_2 \) are the areas of the separator before and after heat treatment, respectively. The thermostability was also analyzed by differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) at a heating rate of 10 °C min\(^{-1}\) from 20 to 500 °C in O\(_2\) atmosphere.
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