“Polymer-in-Ceramic” Membrane for Thermally Safe Separator Applications
Lin Luo, Zhihao Gao, Zongmin Zheng,* and Jianmin Zhang*

ABSTRACT: In this work, a facile casting method was utilized to prepare “polymer-in-ceramic” microporous membranes for thermally safe battery separator applications; that is, a series of composite membranes composed of silicon dioxide (SiO$_2$) as a matrix and polyvinylidene fluoride (PVDF) as a binder were prepared. The effects of different SiO$_2$ contents on various physical properties of membranes such as the porosity, electrolyte absorption rate, electrochemical stability, and especially thermal stability of the SiO$_2$/PVDF composite membranes were systematically studied. Compared with a commercial polypropylene separator, the SiO$_2$/PVDF membrane has a higher porosity (66.0%), electrolyte absorption (239%), and ion conductivity (1.0 mS·cm$^{-1}$) and superior thermal stability (only 2.1% shrinkage at 200°C for 2 h) and flame retardancy. When the content of SiO$_2$ in the membrane reached 60% (i.e., PS6), LiFePO$_4$/PS6/Li half-cells exhibited excellent cycle stability (138.2 mA h·g$^{-1}$ discharging capacity after 100 cycles at 1C) and Coulombic efficiency (99.1%). The above advantages coupled with the potential for rapid and large-scale production reveal that the “polymer-in-ceramic” SiO$_2$/PVDF membrane has prospective separator applications in secondary lithium-ion batteries.

1. INTRODUCTION
Lithium-ion batteries (LIBs) are widely used in electric vehicles (EVs), aerospace, robotics, national security, and other fields due to their advantages of high energy density, high energy efficiency, long cycle life, no memory effect, rapid charge and discharge, low self-discharge rates, and a wide operating temperature range. Battery separators with good safety and reliability and a long service life have been extensively studied.$^{1-3}$

From a structural point of view, LIBs are mainly composed of four parts: anode, cathode, separator, and electrolyte.$^{4,5}$ As the core component of LIBs, the separator can separate the positive and negative electrodes of LIBs to avoid short circuits. Meanwhile, the porous structure of the separator allows ions to pass selectively and freely so that the reactions inside the battery are reversible.$^5$ At present, polyolefin microporous membranes, especially polyethylene (PE), polypropylene (PP), and sandwich PP/PE/PP, have become the most widely used separator products in LIBs because of their low price, good mechanical strength, and excellent chemical and electrochemical stability.$^7$ At present, problems regarding polyolefin separators such as weak electrolyte affinity, low porosity, poor wettability, and poor thermal stability lead to low energy density and inferior rate and cycling performances in LIBs.$^8$ Especially, poor thermal stability makes the separator shrink severely in high-temperature situations, eventually leading to thermal runaway or even explosion, which greatly hinders the application of LIBs in next-generation EVs.$^9$ Thus, it is of great importance to develop separators with high thermal stability for next-generation thermally safe LIBs.

To improve the thermal stability and flame retardancy of battery separators, researchers have tried to find alternative materials for separators to balance the structure, properties, and production cost. Polyvinylidene fluoride (PVDF) is widely

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studied as a separator material for LIBs due to its superb electrochemical stability and strong thermal stability. Meanwhile, the β crystalline phase (TTTT molecular configuration) of semicrystalline PVDF shows a high dielectric constant and polarity, which is beneficial for lithium-ion dissociation and transportation in the electrolyte, hence higher ionic conductivity is achievable.\textsuperscript{10,11} Besides, several kinds of ceramic nanoparticles (SiO\textsubscript{2}, Al\textsubscript{2}O\textsubscript{3}, TiO\textsubscript{2}, ZrO\textsubscript{2}, etc.) have been studied as low-content additive fillers or coatings for composite membranes to improve their thermal stability. Among them, SiO\textsubscript{2} nanoparticles have the advantages of non-toxicity, non-pollution, low cost, and strong electronegativity.\textsuperscript{12} Different techniques have been explored to prepare the SiO\textsubscript{2} composite membrane, including (1) blending SiO\textsubscript{2} with polymers as fillers to form membranes by phase inversion or stretching processes,\textsuperscript{8,13} (2) the electrospinning method,\textsuperscript{14,15} and (3) coatings on PP or PE separators.\textsuperscript{16} For instance, Zhu et al.\textsuperscript{16} used an electron beam irradiation method to prepare a SiO\textsubscript{2}-grafted PE separator, which improved the thermal stability of the separator (only 20% shrinkage at 180 °C). Xu et al.\textsuperscript{14} prepared a SiO\textsubscript{2}/PVDF-HFP nanofiber separator by electrospinning. It had excellent thermal stability at 200 °C with almost no dimensional change. Although previous studies have improved the thermal stability of membranes to some extent, significant enhancement has not been achieved due to a relatively low SiO\textsubscript{2} content (no more than 10%). The thermal properties of these “ceramic-in-polymer” membranes are still greatly influenced by the polymer matrix with low thermal stability. In addition, these “ceramic-in-polymer” membranes exhibit other disadvantages such as coating fall-off, complicated procedures, and most importantly, the inability to realize the flame-retardant function.

To tackle the above-mentioned problems, we herein proposed a facile casting method to fabricate novel “polymer-in-ceramic” SiO\textsubscript{2}/PVDF composite membranes, and a series of composite membranes composed of SiO\textsubscript{2} as the matrix and PVDF as the binder were prepared. The effects of different SiO\textsubscript{2} nanoparticle contents on the morphology, electrolyte affinity, thermal stability, flame retardancy, and ionic conductivity of these membranes were systematically studied. The composite membranes were employed to assemble the LiFePO\textsubscript{4}/separator/Li half-cell (Li as the negative electrode and LiFePO\textsubscript{4} as the positive electrode). The rate and cycling performances of the cells with these composite membranes were evaluated and compared with cells employing a PP separator. The mechanism of improvements of the above properties was discussed in detail. The development of SiO\textsubscript{2}/PVDF composite membranes with a high SiO\textsubscript{2} content by this facile process will not only enable a rapid and large-scale production but also eliminate the above-mentioned problems and provide enhanced electrolyte wettability, thermal stability, and flame retardancy for LIB separators.

2. EXPERIMENTAL SECTION

2.1. Materials. SiO\textsubscript{2} nanoparticles with a particle size of 30 nm were obtained from Shanghai Aladdin Co. Ltd. PVDF powders (Solef 6010) were purchased from Solvay Co. (Germany). N-Methyl-2-pyrrolidone (NMP, AR) and 1 mol/L LiPF\textsubscript{6} (in EC/DEC = 1:1 vol/vol) were bought from Suzhou Doduo Chemical Technology Co. Ltd. All chemicals were used without further purification and modification.

2.2. Preparation of Composite Membranes. Composite membranes were prepared by a simple casting technique, as shown in Figure 1a. First, appropriate amounts of PVDF and SiO\textsubscript{2} were added into a mortar and ground at 60 °C for 10 min. Then, NMP was added and ground for another 10 min to form a blended slurry. Finally, the blended slurry was cast uniformly on a flat aluminum foil using a doctor blade (300 μm). The SiO\textsubscript{2}/PVDF composite membranes were obtained after drying in a vacuum oven at 120 °C for 12 h. Membranes with different mass ratios (i.e., \( M_{SiO2}/M_{PVDF} = 5:5, 6:4, 7:3 \)) were denoted as PS5, PS6, and PS7, respectively. Figure 1b shows a flexibility demonstration of the PS6 membrane. After wrapping on a glass rod, a composite membrane with 60 wt % SiO\textsubscript{2} exhibited excellent flexibility, with no fracture, indicating that the composite membrane has sufficient flexibility for the assembly of pouch or cylindrical batteries.\textsuperscript{22}
2.3. Characterizations. The morphologies and microstructure of composite membranes were examined using a scanning electron microscope (JSM-6390LV, Japan) with an energy-dispersive spectroscope at an accelerating voltage of 15 kV. Contact angles were determined by the sessile drop method with the electrolyte (5 μL) on a contact angle meter (Theta Flex, Sweden). The electrolyte uptake was examined by measuring the weight of membranes before and after soaking in an electrolyte for 2 h. The uptake ratio was then calculated using eq 1.

\[ \eta = \frac{M_2 - M_1}{M_1} \times 100\% \]  

where \( M_1 \) and \( M_2 \) are the weights of the membrane before and after soaking, respectively. The porosity of membranes

Figure 2. SEM images (top surface) of (a) PS5 and (b) PS7 and (c) EDS mapping of the PS6 membrane with Si, O, and F elements.

Figure 3. (a) Contact angle test; (b) electrolyte absorption test; (c) porosity and electrolyte uptake ratio of different membranes; and (d) schematic of lithium-ion transport between SiO\(_2\) nanoparticles.
measured by the n-butanol soaking method was calculated according to eq 2.

\[ P = \frac{M_2 - M_1}{\rho \times A \times D} \times 100\% \]  

(2)

where \( \rho \) is the density of the n-butanol solvent; \( M_1 \) and \( M_2 \) are the weights of the membrane before and after soaking for 2 h, respectively; and \( A \) and \( D \) are the area and thickness of the membrane, respectively.

Thermogravimetry (TG, STA8000, USA) was used to analyze the thermal decomposition behavior of membranes by heating from room temperature to 800 °C at a heating rate of 10 °C·min\(^{-1} \) under a nitrogen atmosphere. Thermal shrinkage behavior was investigated by heating these membranes at different temperatures for 2 h. The shrinkage ratio was then calculated using eq 3.

\[ \text{TSR} = \frac{S_0 - S_1}{S_0} \times 100\% \]  

(3)

where \( S_0 \) and \( S_1 \) are the area of the membrane before and after heat treatment, respectively.

2.4. Electrochemical Measurements. The LiFePO\(_4\), PVDF, and Super P powders were mixed in an NMP solvent with a weight ratio of 8:1:1 to obtain cathode materials. CR2032 coin cells were used to assemble LiFePO\(_4\)/separator/Li half-cells to evaluate their electrochemical performance with different membranes. The electrolyte in this work was 1 mol/L LiPF\(_6\) (in EC/DMC = 1:1 vol/vol). All coin cells were assembled in an argon-filled glovebox (moisture < 0.01 ppm, oxygen < 0.01 ppm). The charge–discharge cycling performance and C-rate capability were tested at a voltage range of 2.5–4.2 V using a Neware Battery Testing System (BTS-4000, China). All electrochemical measurements were carried out at 25 °C.

Linear sweep voltammetry (LSV) was conducted to check the electrochemical stability of membranes. Membranes sandwiched between the stainless steel (SS) working electrode and lithium metal counter electrode were tested at a scan rate of 0.1 mV·s\(^{-1} \).

The bulk resistance \( R_b \) of the SS/membrane/SS cell was measured by electrochemical impedance spectroscopy (EIS) in a frequency range of 0.1–500 kHz with a voltage amplitude of 5 mV at 25 °C. The ionic conductivity (\( \sigma \)) was then calculated using eq 4

\[ \sigma = \frac{D}{R_b \times A} \]  

(4)

where \( D \) is the thickness of the membrane, \( A \) is the surface area, and \( R_b \) is the bulk resistance, respectively.

3. RESULTS AND DISCUSSION

The surface and cross-sectional microstructure of SiO\(_2\)/PVDF composite membranes were characterized by scanning electron microscopy (SEM) (Figures 2 and S1). Composite membranes present a dense microporous structure with a pore size ranging from 0.1 to 0.5 μm on their surface (Figure S3). When the content of SiO\(_2\) was 50%, the average pore size of the membrane was 0.2 μm. As the SiO\(_2\) content increased, the average pore size became smaller. When the content of SiO\(_2\) was too high (e.g., 70%), severe agglomeration would occur, which caused a decrease in the porosity of the PS7 membrane (Figure 3c). Highly connected interstitial spaces were formed...
between the ceramic particles, providing a dense microporous structure to improve liquid absorption and promote ion transportation. Furthermore, the surface and cross-sectional energy-dispersive spectroscopy (EDS) element mappings in Figures 2c and S2, respectively, show homogeneous distributions of Si, O, and F in the PS6 composite membrane, indicating that SiO$_2$ nanoparticles and the PVDF binder were well dispersed.

Membranes should have excellent electrolyte wettability to facilitate lithium-ion transport between the cathode and anode. The contact angle measurements were used to evaluate the electrolyte wettability of different membranes (Figure 3a). The nonpolar PP membrane has intrinsically poor wettability with electrolytes, so it was hardly wetted by the electrolyte (contact angle: 52.8°), which exhibited almost no change after 10 s. As expected, composite membranes had much lower contact angles. The contact angle reduced with an increase in SiO$_2$ content due to more polar Si–O bonds. To verify the electrolyte absorption capacities of different membranes, they were immersed vertically in the electrolyte, and the penetration heights of the electrolyte through membranes after immersing for 2 h are shown in Figure 3b. The penetration heights in composite membranes were significantly higher than those in PP membranes. They gradually increased with an increase in SiO$_2$ content, which is consistent with contact angle results, thanks to better affinity between more polar Si–O bonds and organic solvents (EC and DEC). Figure 3c compares the porosity and electrolyte uptake ratio of different membranes. When the SiO$_2$ content increased in the membranes, the porosity and electrolyte uptake ratio also increased. Among these composite membranes, PS6 with 60 wt % SiO$_2$ exhibited a highest porosity of 66.3% and an electrolyte uptake ratio of 239.1%, which are much higher than those values of the PP membrane. However, when the SiO$_2$ content was too high (e.g., PS7 with 70 wt % SiO$_2$), the porosity of the membrane reduced from 66.3 to 52.7%, which could be attributed to the agglomeration phenomenon due to the large amount of SiO$_2$ and partial pore blockage. More importantly, the presence of a large number of polar groups on the surface of SiO$_2$ nanoparticles could accelerate lithium-ion dissociation and transportation, therefore reducing interfacial resistance between the electrolyte and separator. The electronegativities of M$_m$O$_n$ oxide can be calculated according to eq 5:

$$\chi_{M,O} = [(\chi_M)^m(\chi_O)^n]^{1/(m+n)}$$

where $\chi_M$ and $\chi_O$ are the element electronegativities. SiO$_2$ nanoparticles have high electronegativity (2.82). Therefore, these nanoparticles will attract electropositive lithium ions in the electrolyte, prompting these ions to hop between electronegative groups through nanoparticle gaps (as shown in Figure 3d), hence improving the electrochemical kinetics of lithium-ion transport.

The thermal stability of membranes is closely related to the safety of batteries. Whether the battery can work safely and continuously at elevated temperatures largely depends on whether the separator can maintain dimensional stability. To investigate the thermal stability of membranes, they were heated and held at different temperatures (150, 180, and 200 °C) for 2 h, and the thermal shrinkage ratios were then measured (Figure 4a). The PP membrane shrunk almost completely at 180 °C and completely melted at 200 °C. By
contrast, SiO$_2$/PVDF membranes hardly shrank, and the shrinkage ratio of the PS6 membrane was only 2.1% at 200 °C for 2 h (Figure 4c). As expected, the shrinkage ratio of composite membranes gradually decreased as the SiO$_2$ content increased (Table S1). The combustion behaviors of the PS6 and PP membranes were examined and are shown in Figure 4b. Once the PP membrane got close to the fire, it immediately curled up and lost its original shape. In contrast, the PS6 membrane was not easy to burn when placed on the fire, and its original shape was still maintained after 10 s. When it was removed from the fire, combustion ceased immediately. The superior thermal stability and flame retardancy of the SiO$_2$/PVDF membrane can be exploited in battery separator applications. It is proposed that when the thermal runaway of the battery occurs, the composite separator can still play a role in blocking the contact between positive and negative electrodes, therefore preventing further deterioration of thermal runaway. The thermal decomposition behavior of membranes was evaluated by TG (Figure 4d). The TG curves reveal the weight loss of various membranes during heating up to 800 °C in a nitrogen atmosphere. The PP membrane decomposed at 450 °C and had no weight residue beyond 470 °C. In the TG curves of composite membranes, the weight loss below 400 °C was usually related to the removal of the adsorbed solvent (NMP and water), and the PVDF binder decomposed at 500 °C. The remaining residual weight ratio was in good consistency with the preparation procedure, indicating that SiO$_2$ nanoparticles in composite membranes have a fairly uniform distribution.

The oxidative decomposition of electrolytes on the electrode can cause safety issues in LIBs, and the voltage that the battery can withstand is evaluated by measuring the electrochemical window. The electrochemical stability of PP and PS6 membranes was evaluated by LSV (Figure 5a). An increased current in the high-voltage range is generally known to be caused by the decomposition of liquid electrolytes. The PP membrane became unstable at 4.1 V, whereas the PS6 membrane remained stable up to 4.6 V, which was ascribed to the good electrolyte compatibility of SiO$_2$/PVDF membranes. Moreover, SiO$_2$ nanoparticles in composite membranes could stabilize liquid electrolytes by absorbing PF$_6$ and water generated by the decomposition of LiPF$_6$.

The bulk resistance $R_b$ of the SS/separator/SS cells was measured by EIS (Figure 5b). $R_b$ is the intercept on the X axis of the Nyquist plot in a low-frequency range. With increasing SiO$_2$ content, the $R_b$ of composite membranes gradually decreased and their ionic conductivity gradually increased (Table 1) because the microporous structure formed by SiO$_2$ nanoparticles could improve electrolyte absorption and the electronegative SiO$_2$ nanoparticles could facilitate ion conduction by their interaction with lithium salts.

The AC impedance spectra of LiFePO$_4$/separator/Li half-cells assembled with PP, PS5, PS6, and PS7 membranes were utilized to investigate the compatibility between separators impregnated with liquid electrolytes and electrode materials. All the Nyquist plots in Figure 5c show semicircles in the midfrequency range, which represent the charge transfer resistance ($R_{ct}$) in the interfacial regions. $R_{ct}$ of these cells with different membranes after fitting is shown in Table 1. The PS6 membrane has a relatively low $R_{ct}$ due to its higher porosity and superior electrolyte wettability. A lower $R_{ct}$ could improve the compatibility between the electrode and separator, facilitating the transport efficiency of lithium ions between the electrode and electrolyte.

To analyze the C-rate capability of cells, charge–discharge measurements were conducted at 0.1, 0.2, 0.5, and 1C, respectively (Figure 5d). The discharge capacity of half-cells gradually decreased with an increase in the C-rate due to the influence of ohmic polarization and interfacial resistance on ionic transportation. The discharge capacities of the LiFePO$_4$/PS6/Li half-cell (156.8, 154.1, 148.2, and 139.8 mAh g$^{-1}$ at 0.1, 0.2, 0.5, and 1C, respectively) were all higher than those of the cell with the PP membrane (154.6, 152.5, 146.6, and 138.1 mAh g$^{-1}$, respectively). When the current density returned to 0.1C, the discharge capacity of the cell returned to 154.4 mAh g$^{-1}$, and the capacity retention rate at this time was 98.5%.

The cycling performance of the LiFePO$_4$/Li half-cells assembled with different membranes was evaluated at 1C for 100 cycles. As shown in Figure 5e, the composite membrane-based cells displayed good cycling properties, and the Coulombic efficiency of the cell was almost 99% (Figure 5f). In Figure 5e, the LiFePO$_4$/PS6/Li half-cell showed a slight increase in capacity in the initial dozens of cycles, which could be attributed to the improved wetting behavior of separator and electrode materials during charge–discharge cycling tests. As a result, the cell with the PS6 membrane exhibited a more stable cycling performance.

4. CONCLUSIONS

In summary, a facile casting method was utilized to successfully prepare “polymer-in-ceramic” microporous membranes for thermally safe battery separator applications. Compared with the PP membrane, the porosity, electrolyte uptake ratio, and ionic conductivity of the SiO$_2$/PVDF composite membrane have been significantly improved. Particularly, the thermal stability and flame retardancy of the composite membrane were much superior to those of the PP membrane. The shrinkage ratio of PS6 (with 60 wt % SiO$_2$) was only 2.1% (at 200 °C for 2 h). Moreover, it can maintain the original shape during combustion, which is preferable in a thermal runaway situation. The electrochemical tests of LiFePO$_4$/Li half-cells with the PS6 membrane showed good rate capacity, excellent cycle stability (138.2 mAh g$^{-1}$ discharging capacity after 100 cycles at 1C), and high Coulombic efficiency (99.1%). The above advantages coupled with the potential for rapid and large-scale production reveal that the “polymer-in-ceramic” SiO$_2$/PVDF membrane is a prospective separator candidate in secondary LIBs.

**Table 1. Resistance and Ionic Conductivity of Half-Cells with Different Membranes**

| sample | $R_b$ (Ω) | $D$ (μm) | $σ$ (mS cm$^{-1}$) | $R_{ct}$ (Ω) |
|--------|--------|--------|---------------|--------|
| PP     | 1.6    | 25     | 0.8           | 265.1  |
| PS5    | 2.3    | 23     | 0.5           | 229.4  |
| PS6    | 1.2    | 25     | 1.0           | 239.2  |
| PS7    | 1.1    | 40     | 1.8           | 310.0  |

**ASSOCIATED CONTENT**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c03689.
Cross-sectional SEM images and EDS mappings of the 
PS6 membrane with Si, O, and F elements; pore size 
distributions; and shrinkage rate of different membranes 
(PDF)

AUTHOR INFORMATION

Corresponding Authors
Zongmin Zheng — College of Mechanical and Electrical 
Engineering, Power & Energy Storage System Research 
Center, Qingdao University, Qingdao 266071, China; 
National Engineering Research Center for Intelligent 
Electrical Vehicle Power System (Qingdao), Qingdao 
266071, China; orcid.org/0000-0002-0259-1540; 
Email: zmzheng@qdu.edu.cn

Jianmin Zhang — College of Mechanical and Electrical 
Engineering, Power & Energy Storage System Research 
Center, Qingdao University, Qingdao 266071, China; 
National Engineering Research Center for Intelligent 
Electrical Vehicle Power System (Qingdao), Qingdao 
266071, China; orcid.org/0000-0003-2552-7485; 
Email: zhangjm@qdu.edu.cn

Authors
Lin Luo — College of Mechanical and Electrical Engineering, 
Power & Energy Storage System Research Center, Qingdao University, Qingdao 266071, China
Zhihao Gao — College of Mechanical and Electrical Engineering, Power & Energy Storage System Research Center, Qingdao University, Qingdao 266071, China

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.2c03689

Notes
The authors declare no competing financial interest.

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