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Protection of Lithium Anode by a Highly Porous PVDF Membrane for High-Performance Li-S Battery

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Abstract

The Li-S battery is considered as the next-generation energy storage solution largely because of its high energy density. However, the lithium metal anode has suffered from the “shuttle effect” of soluble polysulfide species and the formation of dendrites that cause quick performance decay and safety issues. Here, a polyvinylidene fluoride (PVDF) membrane that contains a hierarchical porous structure was introduced as a protection layer to insulate the lithium anode from polysulfide shuttling and dendrite formation. The PVDF protected Li-S battery showed a capacity of around 850 mAh g⁻¹ and Coulombic efficiency of 98% over 200 cycles at 0.5 C. Both performances are significantly improved from the normal Li-S batteries. The PVDF membrane is stable, easy to coat, and scalable, which offers a convenient, affordable, yet effective strategy for achieving commercialization of high energy density and safe Li-S batteries.

KEYWORDS: Li-S battery, PVDF membrane, shuttling effect, dendrite formation, Li anode protection.
Introduction

With the global electrification process, it is commonly acknowledged that building a modern world requires high-performance rechargeable batteries. The lithium-ion battery (LIB), developed in 1991, has been widely utilized and occupied the majority of the energy storage market.\textsuperscript{1,2} However, the demand for higher battery capacity has kept growing, and the state-of-art LIB cannot satisfy the request.\textsuperscript{3-5} Thus, the high capacity lithium-sulfur (Li-S) battery has caught great attention in recent years.\textsuperscript{6-8} This attractive advantage depends mostly on the utilization of lithium metal as an anode material because it is not only the most lightweight metal but also containing an extremely high theoretical specific capacity (~3,860 mAh g\textsuperscript{-1}) and a low redox potential (-3.04 V).\textsuperscript{9-11}

Despite the benefits, however, there are several issues that hinder the practical application of lithium metal in Li-S batteries. The first is the formation of uncontrollable dendrites on the lithium anode surface during the dissolution/deposition processes, which may penetrate the separator and cause a battery short circuit.\textsuperscript{12} Also, unlike the graphite anode, the solid electrolyte interphase (SEI) formed on lithium surface will be continuously destroyed by the consumption of lithium anode and electrolyte, leading to poor cycling performance.\textsuperscript{13, 14} Moreover, the cross-over of the soluble polysulfides caused by the so-called “shuttle effect” during cycling will lead to the deposition of insulating species (i.e., Li\textsubscript{2}S and Li\textsubscript{2}S\textsubscript{2}) on the anode surface that will quickly decrease the electrical capacity and the Coulombic efficiency (CE).\textsuperscript{15, 16} To overcome these issues, various techniques have been utilized. One method is to modify the separator by carbon, metal oxides, polymers, or two-dimensional materials, to suppress the shuttle effect.\textsuperscript{17-20} However, this approach cannot sufficiently restrict lithium dendrites. Recently, a more straightforward yet efficient strategy has been developed. By directly protecting the lithium anode with an artificial layer or SEI, the lithium surface can be insulated from the polysulfide intermediates, and the formation of dendrites can be minimized.
as well.\textsuperscript{21-24} However, most reported methods involved either complicated processes or hazardous and expensive materials, which is not well suitable for practical applications. A low cost, stable, and easily processable layer is thus highly desirable.

Polyvinylidene difluoride (PVDF) is known to have excellent electrochemical and thermal stability and has been used as a universal binder in lithium/lithium-ion batteries.\textsuperscript{25, 26} In our previous work, we developed a novel “mixed solvent phase separation” (MSPS) method to prepare highly porous PVDF membranes.\textsuperscript{27} The membrane has an ultrathin skin layer containing a super high density of uniform surface pores with pore size around 30 nm and a sponge-like bulk layer with pore size in hundreds of nanometers. Such an asymmetric porous structure is formed in one process and has a great advantage in separation since it meets the requirements for both high selectivity and high permeability. The unique porous structure also stimulates us to apply it as a protection layer for lithium anode in Li-S battery. It is expected that the porous PVDF membrane can block the deposition of polysulfide species and inhibit the growth of lithium dendrites. While from the other hand, the highly porous structure, particularly the high-density surface pores, will allow fast transport of lithium ions, which ensure high rate cyclability. As expected, a high specific capacity of around 850 mAh g\textsuperscript{-1} over 200 cycles under 0.5 C with a Coulombic efficiency of 98\% is reported here for Li-S battery.

**Results and discussions**

The SEM images of the PVDF membrane are shown in Figure 1a and Figure 1b. It can be seen that the membrane surface contains a high density of circular pores with a narrow pore size distribution centered at 30 nm (Figure S1). The surface porosity is more than 20\%. However, the bulk of the membrane has a sponge-like porous structure with pore size in hundreds of nanometers that is much bigger than the surface pores. The surface layer is very thin and interconnected with the bulk layer. The asymmetric porous structure is formed in one-
step through the novel MSPS process. The detail membrane preparation procedure and the pore-forming mechanism can be found in previous work.\textsuperscript{27}

The Fourier transform infrared spectra (FTIR) in Figure 1c revealed that the PVDF membrane contained $\alpha$, $\beta$, and $\gamma$ three types of crystalline phases.\textsuperscript{28} Figure 1d shows the uptake curve of the PVDF membrane versus time with the electrolyte of 1 M LiTFSI in DOL/DME. The electrolyte uptake ratio increased with time and reached a saturated capacity of 700\% after 30 min. This value is substantially higher than other hosts benefitting from the highly porous sponge-like structure and a high electrolyte uptake is beneficial for achieving a high conductivity.\textsuperscript{29,30} Figure 1e and 1f show that the PVDF membrane has a contact angle of 84.3\textdegree for water and 28.6\textdegree for electrolytes. This is expected as PVDF is well known to be hydrophobic and oleophilic. The wettability is critical for the battery’s electrochemical performance because a poor wettability will increase the internal resistance and reduce the rate capability.\textsuperscript{31} A low contact angle to electrolyte indicates that the electrolyte can easily penetrate through the membrane, which can guarantee the fast transport of lithium ions.

**Figure 1.** (a) Surface and (b) cross-section SEM images of the prepared PVDF membrane, while the thickness of the membrane is about 19.08 $\mu$m. (c) FTIR spectra of the PVDF
membrane. (d) Electrolyte uptake plots of the PVDF membrane. The contact angles of the membrane with (e) water and (f) liquid electrolyte.

To investigate the reversibility of lithium during the deposition/dissolution process, two symmetric cells assembled with bare lithium electrodes and PVDF protected lithium electrodes were cycled at 1 mA cm\(^{-2}\). Figure 2a shows the voltage vs. time profiles of the two cells, while the magnified profiles of 2-10 h and 100-110 h (which equal to about 1-15 and 181-200 cycles) are shown in Figure 2b and 2c. Initially, both cells displayed a decreased voltage trend, but the cell with PVDF/Li exhibited a little lower polarization than the pristine cell. For the pristine cell, the overpotential varied significantly during the Li migration process, especially when reaching around 25 h (which equals to about 40 cycles), indicating poor reversibility and uneven growth of the ‘dead’ Li. In clear contrast, the PVDF/Li cell maintained a steadily decreased potential for more than 250 h, which is equivalent to more than 450 cycles, proving its superiority in suppressing the formation of Li dendrite. Moreover, it is more evident to see the superior performance of the PVDF/Li cell than the bare Li one when a commercial electrolyte (1 M LiPF\(_6\) in EC/DEC) was used (Figure S2), which is in agreement with the previous report.\(^{32}\) Furthermore, the PVDF/Li cell demonstrated a much lower Li migration voltage and better retention performance than the pristine cell. This result also indicates the stability of the PVDF membrane in different environments and its applicability in commercial LIBs.
Figure 2. (a) Galvanostatic charge-discharge voltage profiles for pristine Li and PVDF protected Li symmetric cells at a constant current density of 1 mA cm$^{-2}$. Magnified voltage profiles from (b) 2-10 h and (c) 100-100 h.

The Li-S battery electrochemical performance was studied with coin cells assembled with the simple sulfur/carbon composite cathode and the lithium anode with and without PVDF membrane. As shown in Figure 3a, the battery cycling performance distinguishes significantly under 0.5 C (1 C=1675 mAh g$^{-1}$). For the pristine battery, the initial discharge capacity was only 601 mAh g$^{-1}$ and dropped to 194 mAh g$^{-1}$ after 200 cycles. Such a quick capacity decay is normal for Li-S batteries that have no protection, attributing to the severe shuttle effect of the polysulfide species. As a comparison, the battery with PVDF/Li delivered an initial capacity of 968 mAh g$^{-1}$. After 200 cycles, the capacity slowly decreased to 850 mAh g$^{-1}$, and a high CE of around 98% was maintained. The enhanced battery capacity and excellent cycling stability of the PVDF/Li battery demonstrate that the PVDF membrane has effectively suppressed the shuttle effect as well as lithium dendrites. Figure 3b shows the galvanostatic charge-discharge profiles of the first cycle. Both batteries exhibited two characteristic reduction peaks at $\sim$2.3 V and $\sim$2.0 V, which are associated with the reduction of the elemental...
sulfur to dissoluble long-chain polysulfides ($\text{Li}_2\text{S}_n$, $4 \leq n \leq 8$) and further to short-chain insulating polysulfides (i.e., $\text{Li}_2\text{S}_2$ and $\text{Li}_2\text{S}$). These peak voltage values are consistent with the reported results.\textsuperscript{33, 34} The result also proves that the PVDF membrane did not react inside the battery or hinder the lithium diffusion process. It is further noticed that the second stage of the charge-discharge curve of the pristine battery is much shorter, which indicates that the polysulfide species have migrated to the anode side and could not undergo further reactions.

![Graph](image)

**Figure 3.** (a) Cycling performance comparison of Li-S cells with PVDF coated Li and bare Li anode at 0.5 C and relative (b) 1\textsuperscript{st} cycle charge-discharge curves. (c) SEM images of bare Li foil surface before cycling. SEM image and EDS mapping of sulfur element for (d, e) bare Li and (f, g) PVDF protected Li after 200 cycles in Li-S batteries. The scar bar is 2 µm.

The cycled Li-S batteries were further disassembled, and the anodes were characterized by SEM and EDS (Figure 3c-g). The pristine anode displayed a rough morphology with congregated dendrites (Figure 3d) and was full of polysulfide deposition (Figure 3e). In contrast, the PVDF protected lithium anode is relatively smooth (Figure 3f) and remained similar to the uncycled one (Figure 3c). The formed dendrites were small and hardly visible. Moreover, the EDS results indicated a much less deposition of sulfur element than the
unprotected one (Figure 3g). These observations confirm that the PVDF membrane can efficiently inhibit the Li dendrite growth and suppress the polysulfide shuttling.

To investigate the battery rate capability in-depth, the batteries were cycled from 0.1 C to 2.5 C, and each C rate tests were followed by electrochemical impedance spectroscopy (EIS) measurements (Figure 4). As cycling from low to high rates, the battery with PVDF/Li anode delivered a capacity of 1390, 1137, 1015, 883, and 660 mAh g⁻¹ under the rate of 0.1 C, 0.25 C, 0.5 C, 1 C, and 2.5 C, respectively. The one with pristine Li, however, decreased almost linearly at the first five cycles under 0.1 C and exhibited less than half value of the capacity compared to that of the PVDF/Li battery. The relative galvanostatic charge-discharge curves are shown in Supplementary Figure S3. The excellent rate capability and cycle stability confirm that the PVDF membrane can effectively enhance battery performance. Furthermore, after each five rate tests, EIS measurements were conducted for the two cells, shown in Figure 4b and 4c, and the relative equivalent circuits are shown in Supplementary Figure S4. The intercept of the compressed semicircle with the x-axis at the high-frequency range corresponds to the ohmic resistance (Rₑ), which value (around 5 Ω) was very close to the batteries with and without the PVDF protective layer before cycling, demonstrating that the thin PVDF layer (around 20 μm) does not introduce much internal resistance. Based on the impedance results, the ionic conductivity was calculated using relation \( \sigma = \frac{L}{RA} \), where \( \sigma \) is the ionic conductivity, R is the intercept of the semicircle with the real Z’ axis, L is the distance between the electrode, and A is the contact area. The distance between the electrode, L, was assumed equal to the thickness of the separator or the thickness of the separator plus the thickness of the PVDF membrane. The glass fiber separator used is around 190 μm and the PVDF membrane is around 20 μm. The contact area of the electrode is 1.13 cm². After cycling under 0.1 C, the R values for the pristine and the PVDF protected batteries were 7.99 Ω and 9.19 Ω, respectively, and the calculated relative ionic conductivities were \( 2.1 \times 10^{-3} \) S cm⁻¹ and \( 2.02 \times 10^{-3} \) S cm⁻¹,
respectively. The ionic conductivity value of the pristine cell was almost the same as that of the PVDF protected cell, suggesting that there was almost no effect by the PVDF membrane. With the rising of the C rate and cycles, the pristine cell demonstrated an increasing $R_e$. It has a noticeable change when reached 0.5 C, the $R_e$ value increased to around 7 Ω and an extra semicircle has appeared from 1 C (Figure 4b). The addition of the $R_e$ comes from the redistribution of the insulating sulfur during the charge-discharge process, and the appearance of the second semicircle suggests a much higher charge transfer resistance and the formation of an SEI film, represented as $R_{sl}$ in Figure S4b. The insulating polysulfides migrated and deposit on the surface of the cathode and the anode during the reduction/oxidation process, which formed the SEI. In comparison, the PVDF/Li anode showed a small interfacial resistance even at high rate cycling, implying that the PVDF membrane functioned as a stable and less resistive protective layer that facilitated the lithium ion transfer at the interfaces during cycling. No additional semicircle also indicates that the insulating polysulfides during the charge/discharge process were suppressed effectively, further proving the capability of suppressing the shuttle effect of the PVDF membrane.
Figure 4. (a) Rate capabilities of Li-S batteries with PVDF coated Li and bare Li anode tested at 0.1 C, 0.25 C, 0.5 C, 1 C and 2.5 C. 1 C = 1,675 mAh g\(^{-1}\). Nyquist plots for cells using (b) pristine Li and (c) PVDF coated Li after every five cycles of rate tests.

Conclusion

In conclusion, we have developed a novel porous PVDF membrane as a Li anode protection layer in Li-S battery. The PVDF membrane can restrain the Li dendrite and block the polysulfide deposition on the anode. It also exhibits high chemical and physical stability during the battery cycling process. With the help of the protective layer, the Li-S battery enhanced greatly in Coulombic efficiency and electrochemical stability, with an 850 mAh g\(^{-1}\) capacity and 98% CE after 200 cycles at 0.5 C. The preparation of the PVDF membrane is easy, scalable, and cheap, which make it a promising approach to improve the Li-S battery performance.

Associated Content

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: xxxxx.

Experimental Section and Supplementary Figures; Figure S1; Figure S2; Figure S3; Figure S4.

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Notes
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