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Selective Permeable Lithium-ion Channels on Lithium Metal for Practical Lithium–Sulfur Pouch Cells

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Abstract: Lithium metal batteries are considered a promising candidate for high-energy-density energy storage. However, the strong reducibility of lithium and highly reactivity when contacting oxidants, such as lithium polysulfides in lithium-sulfur batteries, caused by the serious "shuttle effect" and leads to low Coulombic efficiency. Herein we design selectively permeable lithium-ion channels on lithium metal surface, which allow lithium ions to pass through by electrochemical overpotential, while the polysulfides are effectively blocked due to the much larger steric hindrance than lithium ions. The selective permeation of lithium ions through the channels is further elucidated by the molecular simulation and visualization experiment. Consequently, a prolonged cycle life of 75 cycles and high Coulombic efficiency of 99% are achieved in a practical Li-S pouch cell with limited amounts of lithium and electrolyte, confirming the unique role the selective ion permeation plays in protecting highly reactive alkali metal anodes in working batteries.

Introduction

Lithium metal anode with an ultralow electrochemical potential (–3.04 V *vs.* standard hydrogen electrode) is taken as the promising candidate for high-energy-density energy storage. Lithium metal anodes have been widely applied in solid-state lithium batteries, lithium–sulfur batteries, and lithium–air batteries.^[1] However, lithium metal anode is intrinsically highly reactive to oxidants,^[2] such as lithium polysulfides that are abundant in lithium–sulfur batteries, resulting in severe "shuttle effect"^[3] and low Coulombic efficiency.^[4] The spontaneously formed solid electrolyte interphase (SEI) between lithium anode and electrolyte is an electronic insulator and affords ion channels for lithium ions (Li⁺) transportation.^[5] The diffusion velocity of Li⁺

is intuitively related to the pathways in bulk electrolyte;^[6] however, the Li⁺ transport in the SEI layer is also important and even more relevant to the lithium plating/stripping behaviors.^[7] Disordered lithium-ion channels are generated on the lithium surface due to the parasitic reactions that hinders the transportation of ions and induces the corrosion of electrode.^[8] Therefore, constructing the ion-selective ordered channels to allow rapid diffusion of Li⁺ through the working interface while blocking the large volume of corrosive anions is highly expected.^[4, 9]

Among the materials for ordered channels, porous anodic aluminum oxide templates^[10] is an inappropriate choice due to the micrometer-scale channels. Solid state electrolyte (SSE), like Garnet-type or sulfide-based electrolyte, has intrinsic ordered channels to selectively permeate Li*.[11] However, a conformal and ultrathin SSE pellet is hard to fabricate to fully cover Lithium anodes. Furthermore, the chemical and interfacial stability of SSE to lithium or polysulfides remains challenging, leading to complicated evolution of interfacial behavior and consumption of active materials.^[12] An alternative way is to choose stable materials with inherent ordered nanoscale channels as the selectively permeable layer. The zeolites or metal-organic frameworks (MOFs), a class of crystalline materials that consist of nanoscale channels, has been chosen as a filter for its selective permeability to certain molecules, cations, and anions.^[13] The special porous structure of zeolites and MOFs opens a new avenue in designing the selective permeable pathway of Li+ [14] Nevertheless, a defect-free two-dimensional plane consisting of zeolites or MOFs has been hardly realized yet to completely conceal the lithium metal surface.^[15] Additionally, there is weak chemical interaction between a zeolite or a MOF and lithium metal, resulting in weak specific adsorption and easy exfoliation.[5b, 13a] Consequently, randomly packed zeolite or MOF crystals in the protective film result in disordered orientation of pore structure

and further lead to a large barrier for Li⁺ passing through.^[16] An alternative strategy is to employ polymer layers, of which high ionic conductivity and strong chemical resistance to polysulfides can effectively improve the stability of lithium metal.^[17] However, this strategy still cannot solve the dilemma of polysulfides penetrating through SEI to consume lithium if the ion channels in polymer film are uncontrolled.^[18] Hence, a selectively permeable interphase with high chemical stability to improve the interface integrity and to protect lithium metal is highly expected.



Figure 1. The selective permeable interphase in a working battery. Schematic illustration of the diffusion behaviour of lithium ions through polymer interphases. The polysulfides are rejected by the (a) ordered selective permeable polymer interphase but accepted by (b) disordered polymer interphase in a working cell. The ATR-FTIR spectra of (c) selective and (d) non-selective permeable polymer interphases. The red dashed circle indicates the peaks of residual AT-PDMS on Li foil after repeated washing.

In this contribution, the selectively permeable lithium-ion channels are created on lithium metal surface in a practical lithium-sulfur battery. Polydimethylsiloxane terminated with lithiophilic end groups of aminopropyl (AT-PDMS) functionally regulates the organization of polymer chains and diminishes the free volume of macromolecular chains at the interface of lithium anode, attaining selectively permeable lithium-ion channels. The ordered channels allow Li⁺ to pass through by electrochemical overpotential, meanwhile the polysulfides are effectively blocked owing to the much larger gyration volume than Li⁺ (Figure 1a). In contrast, disordered channels in polymer are unable to hinder the polysulfides (Figure 1b). The selective lithium-ion channels enable a high Coulombic efficiency and excellent capacity retention in lithium-sulfur pouch cells. The shuttle current of the protected cell is one tenth that of an unprotected cell. This strategy is practicable and efficient in selectively blocking polysulfides and as well, demonstrates a universal concept to build selective permeable lithium-ion channels in protecting highly-reactive alkali metal anodes in working batteries.

Results and Discussion

The selectively permeable channels

PDMS is one of the ideal polymer interphases due to its high electrochemical and chemical stability as well as high ionic conductivity induced by suitable swelling ability to electrolyte. Additionally, PDMS exhibits weak adsorption capability to polysulfides.[19] The selectivity of interphase is achieved by regulating the organization of polymer chains. Aminopropylterminated PDMS reacts with lithium via end group to achieve chemical grafting.^[20] The selectivity of interphase is regulated by the organization of polymer chains. AT-PDMS reacts with lithium via the lithiophilic end group to achieve chemical grafting.^[20] Classic polymer brush theory predicts that grafted polymer spontaneously forms ordered structure driven by entropy.^[21] The free volume is also diminished due to crowded polymer chains. Therefore, the organization of polymer chains is effectively regulated by chemically functionalizing the PDMS with end groups exhibiting different reactivates. In this contribution, AT-PDMS is selected to build selective-permeable interphase (SPI) and methyl-terminated PDMS (MT-PDMS) with similar molecular weight to AT-PDMS for unselective-permeable interphase (UPI). Herein the lithium anodes with SPI and UPI are denoted as SP-Li and UP-Li, respectively.

AT-PDMS and MT-PDMS were coated on the surface of lithium anodes by a facile solution method. As indicated in **Figure S1**, both SP-Li and UP-Li reveal shiny surface. The smooth surface was characterized by scanning electron microscope (**Figure S1a, e**). The thickness of interphase is around 5 µm (**Figure S1b, f**). Energy dispersive spectrometer (EDS) reveals that the SPI contains Si, C, O, and N. However, there is no N in the UPI. Both SPI and UPI exhibit similar morphology (**Figure S1c, d, g, h**). Fourier transform infrared (FTIR) spectroscopy of AT-PDMS and MT-PDMS are highly similar, which confirms the end group is relatively rare in amount (**Figure S2**).

1,2-dimethoxyethane (DME) was applied to wash SP-Li and UP-Li repeatedly. The PDMS backbone is, in principle, without strong interaction with lithium metal and therefore, PDMS can be fully removed upon washing. Nevertheless, SP-Li still reveals characteristic peaks of Si-O and Si-C at 1050/800 cm⁻¹ and 1250 cm⁻¹, respectively, indicating the presence of residual PDMS on lithium metal (Figure 1c). In contrast, no signal of PDMS is observed on the surface of UP-Li (Figure 1d). Through the above comparison, the lithiophilic end groups present in AT-PDMS are recognized as the key to enhance the adhesion of PDMS-based protective layer on lithium metal. Such an enhancement is ascribed to the strong interactions enabled by chemical bonds between lithium and aminopropyl.^[22] As a consequence of chemical immobilization, the anchored AT-PDMS forms ordered organization of polymer chains. The free volume is smaller than that of entanglement organization of polymer chain due to greater crowding effect. Direct characterization of such structure is challenging due to the high reactivity of Li metal. Fortunately, the extensive fundamental research in polymer physics on grafted polymer has built solid theoretical basis for understanding the interfacial behavior. Grafted surface exhibites a higher degree of

crowding.^[23] Besides, it was found that long PDMS chains, which are chemically attached to the surface, undergo uniaxial reorientations around the direction normal to the solid-polymer interface, revealing the ordered organization of polymer chain near the surface.^[24] In lithium-sulfur batteries, we ignore the influence of solvation structure because the grafted monolayer polymer chain of lithium anode have insufficient space to accommodate the solvated groups.[25] This indicates the desolvation has been completed when get through the polymer chain. Soluble polysulfides are usually composed of four to eight sulfur atoms in the chain and two lithium atoms at the ends, whose radius of gyration is three times larger than de-solvated Li* (Figure S3). When Li⁺ and polysulfides diffuse through the polymer brush layer with narrow space between polymer chains (e.g. AT-PDMS), polysulfides with larger volume exhibit high diffusion impedance but Li⁺ does not.^[26] A loose chain structure (e.g. MT-PDMS), on the other hand, has limited ability to stop polysulfide from penetrating the interphases. Therefore, a selectively permeable interphase is achieved with a chemical modified polymer layer (Figure 1a, b).

Polysulfides blocking

Fading tests were employed to qualitatively understand the variance among different interphases in the ability of blocking polysulfides in ether solvent. The schematic illustration of fading test is shown in Figure 2a. The oxidative polysulfides are immediately consumed by the reductive metallic lithium once they contact with each other, resulting in the fading of the solution. The color of 1,3-dioxolane (DOL)/DME solution with 0.67 mM Li₂S₆ (4 mM [S]) was recorded every eight hours and normalized by adjusting the lightness of the picture to make red and green value equal to 150 (Figure S4). Then the blue value quantifies the extent that the solution color is closed to transparent. The color of solution soaking SP-Li remained yellow after 50 hours, however, the other two solution faded after 20 and 35 hours, respectively, indicating that the SPI covered on the lithium anode owns the ability to defend the aggression of polysulfides (Figure 2b). In addition, shuttle currents for SP-Li were reduced by five and ten times compared with UP-Li and bare lithium foils (Figure 2c). The average Coulombic efficiency of 50 cycles increases from 82% of bare lithium and 84% of UP-Li to 91% of SP-Li with LiNO3-free DOL/DME electrolyte at 0.5 C in lithium-sulfur batteries (Figure 2d and Figure S5). Therefore, the SPI renders remarkable ability to chemically and electrochemically resist polysulfides.

The PDMS layer still stayed on the top of lithium anode after 70 cycles, which is confirmed by the attenuated total Reflection-Fourier transform infrared (ATR-FTIR) spectra of cycled lithium anodes. (Figure S6), indicating the stable interaction between AT-PDMS to Li. The PDMS interphase is able to regulate the stripping and plating process everlastingly. Although the voltage hysteresis is stable and similar with each other (Figure S7), bare lithium is covered with a highly porous dead lithium layer (Figure S8a and S9a). The disordered morphology and large thickness are attributed to continuous reactions between polysulfides and lithium metal, as well as highly uneven deposition behavior. The thickness of dead lithium layer decreases from 90 µm to 65 µm with UPI or 25 µm with SPI when the lithium metal is coated with a PDMS layer (Figure S8b, c). In sharp contrast, SP-Li reveals dendrite-free morphology due to a better resistance to oxidants (Figure S8 and S9).



Figure 2. Characterization on lithium-ion channels and selective permeability. (a) Schematic illustration of corrosion behavior with/without selective permeable interphase. (b) Comparison between the color of 4 mM [S] (Li₂S₆)/DOL/DME solution socking pristine Li, unselective-permeable Li, and selective permeable Li. (c) The shuttle currents test in Li-S cell with LiNO₃-free ether electrolyte. (d) Average Coulombic efficiency of 50 cycles of Li–S coin cell with LiNO₃-free ether electrolyte at 0.5 C.

The electrochemical impedance spectra were conducted to evaluate the electrochemical impedance of Li-Li symmetrical cells in polysulfide-containing electrolyte. The results were fitted with equivalent circuit model (Figure S10 and S11). The interfacial impedance of symmetrical cell with SP-Li is as large as 764 ohms before cycling, which is much larger than that of 375 ohms of UP-Li. The larger impedance demonstrates the higher charge transfer barrier for ion selective permeable layer. We can find the impedance of the cell gets much lower after first cycling (Figure S11b), according to the activation process of the interface. The interfacial impedance remains stable at around 7 ohms after 20 cycles, exhibiting excellent interfacial stability and few parasitic reactions. However, the interfacial impedance of UP-Li illustrates distinctly fluctuation. Besides the inconstant of interfacial impedance, the bulk resistance is also unstable. Obviously, the semicircle keeps shifting to the right, indicating continuous electrolyte consumption and "dead lithium" accumulation (Figure S12). The Tafel plots are presented in Figure S13. Tafel slope of bare lithium, SP-Li, and UP-Li resemble with each other at around 0.09 mV dec⁻¹, indicating that a PDMS interphase has limited side effect on reaction kinetics.^[27] To conclude, SPI exhibits excellent compatibility property with polysulfide-contained electrolyte.

Mechanistic investigations

To further complement the experimental observations, we conducted dissipative particle dynamics (DPD) simulation to probe the selective permeability on particles with different sizes. Initially, beads of Li⁺ or polysulfides are positioned closely on the top of the simulation box, and the polymer chains are tethered on a fixed wall with various graft densities (**Figure 3a, b**). Herein the graft density, σ , is the ratio of the number of polymer chains to wall beads. Both the numbers of Li⁺ and polysulfides were set to 700 to get the same concentration gradient. After releasing the initial constraints, both the Li⁺ and polysulfides diffuse to the

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polymer chains due to the concentration gradient. As shown in **Figure 3c**, **d**, at low graft density ($\sigma = 0.01$), polymer chains are disordered and freely stretch so that the local chain concentration is relatively low, which is a reference state for physical modified swelling polymer layer. Li⁺ and polysulfides are able to diffuse through this polymer layers with low impedance. The chain concentration near the surface is higher due to tethered state at a medium graft density ($\sigma = 0.03$). Li⁺ can still go through polymer layer but most polysulfides are blocked, which is similar with what we observed in experiment. However, at high graft density ($\sigma = 0.1$), even tiny Li⁺ are partially blocked. This extremely high graft density is usually achieved by surface-initiated polymerization.

Figure 3e quantitatively reveals the comparison between polysulfides and Li⁺ on the diffusion time versus grafting density. Obviously, the diffusion time of polysulfides is much more sensitive on grafting density, indicating the fact that the diffusion of polysulfides could be easily regulated through the control of graft density whereas Li⁺ possesses the ability to diffuse through ions channels made of the same polymer without large resistance.



Figure 3. Diffusion behavior of polysulfides and lithium ions through chemical modified polymer interphase with varied graft density using DPD simulation. Initial state of polymer chain and particles of (a) lithium ions and (b) polysulfides. The final configurations of (c) lithium ions and (d) polysulfides interacting with polymer chains after 2000 τ with graft density of 0.01 (left), 0.3 (middle), 0.1 (right). (e) Diffusion duration of lithium ions and polysulfides versus presupposed graft density.

The ordered organization of polymer chains renders AT-PDMS an excellent ability to block polysulfides but allow Li⁺ to pass through rapidly. The size effect contributes to polysulfides blocking and the difference in interfacial electrochemical potential is taken as the driving force for rapid transportation of Li⁺. Such a driving force can be confirmed by the interfacial impedance at different overpotential in Li–Li symmetric cells (**Figure S14**). After normalization, the relative interfacial impedance of SP-Li rises slowly when the overpotential is lower than 30 mV (**Figure 4a**). When the overpotential reaches to 40 mV, the interfacial impedance has a sudden drop to around 0.75 to that at 0 mV and keeps 0.25 at 100 mV. As the overpotential increases, the impedance continues to lessen, indicating that the interfacial potential difference drives the continues movement of Li⁺. In contrast, the interfacial impedance of pristine Li remains a slight decrease when the overpotential lower than 80 mV (**Figure 4b**). The trends in impedance of symmetric cells confirm the SP-Li depends more on the overpotential than pristine Li. This phenomenon may come from conformation transition induced by lithium ion flow to form ordered Li⁺ channels.

The pouch cell application



Figure 4. Overpotential-depended regulated Li ion channels in polymer interface and their electrochemical cycle performance in practical Li-S cells. The relative variation of interfacial impedance versus different overpotential in (a) pristine Li and (b) selective-permeable Li. Insert figure in (b) is schematic illustration of overpotential-depended lithium-ion channels. (c) The cycle life and CE of Li–S pouch cells at 0.1 C with 1.7-fold excess lithium metal and E/S at 5:1. (d) The charge and discharge voltage profiles at the different cycles in practical Li-S pouch cells.

In order to better present the advantage of the ordered Li* channels on lithium surface, Li-S pouch cells were configured in Figure 4. Demanded for high practical energy density, lithium metal anodes in pouch cell work in tougher conditions than coin cells such as limited lithium sources (1.7-fold excess), low electrolyte/sulfur ratio of 5:1, and high loading of sulfur (3.6 mg cm⁻²). As a consequence, the concentration of polysulfides becomes extremely high, leading to rapid failure.^[28] Typical cycle performance of Li-S pouch cell with bare Li is shown in Figure 4c. Although the specific capacity is around 1000 mAh g⁻¹ at 0.1 C. the lifespan is just 33 cycles and the Coulombic efficiency is lower than 80%. Rampant side reaction induced by polysulfides seriously limits the lifespan of a Li-S pouch cell in this case. The SP-Li containing pouch cell maintains much improved 80% capacity retention and the Coulombic efficiency of more than 99% until around 80th cycle, revealing excellent stability in harsh and practical environment. Therefore, the parasitic reaction is effectively inhibited by the ordered organization of polymer chains, meanwhile, rapid ions transport is guaranteed due to ordered lithium-ion channels. In detail, typical double platform chargedischarge curve is observed for pouch cell with SP-Li with similar curve at 5th and 50th cycles (Figure 4d). However, the pouch cell with pristine lithium metal anodes experiences severe overcharge at 45th cycle and causes low Coulombic efficiency even if the

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charge-discharge window has been narrowed (**Figure S15**). Moreover, better performance and longer lifespan are also observed compared with UP-Li and bare Li in a coin cell with 2.5fold lithium excess SP-Li, further confirming the universal function of the selectively permeable Li⁺ channels (**Figure S16**).

Conclusion

A selectively permeable interphase on lithium anode, created by aminopropyl-terminated polydimethylsiloxane anchored on lithium metal via direct reaction, was reported here. Ordered organization of polymer chains driven by entropy diminished the free volume of polymer to selectively block larger polysulfides under stronger spatial hindrance but to allow Li* to pass through. The shuttle current of in Li-S cell was reduced by 90% and the Coulombic efficiency was increased from 82% to 91% without the addition of lithium nitrate passivating agent in the electrolyte. The suitable graft density was identified as the key for the polymer protective layer to enable selective ion permeation through a sizesieving effect. In practical pouch cells, interphases with selectivepermeable property effectively prolonged lifespan of Li-S pouch cells with limited lithium and electrolyte and high-loading sulfur cathodes to 75 cycles. A high Coulombic efficiency of 99% was achieved. This work presented an efficient way in selectively blocking polysulfides by ordered organization of polymer chains through appropriate chemical modification. This also sheds a fresh light on configuration design of polymer interphase to protect highly reactive alkali metal anodes in working batteries.

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The selectively permeable lithium-ion channels on lithium metal surface were created by aminopropyl-terminated polydimethylsiloxane anchored on lithium metal by directly reaction, which allow lithium ions to get through by electrochemical dynamics, while the polysulfides to be effectively blocked due to the much larger volume than lithium ions. The selective lithium ion channels enable a prolonged cycle life and a high Coulombic efficiency of 99% in a practical Li–S pouch cell.

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Selective Permeable Lithium-ion Channels on Lithium Metal for Practical Lithium–Sulfur Pouch Cells