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Effective Suppression of Lithium Dendrite Growth Using Fluorinated Polysulfonamide Containing Single-Ion Conducting Polymer Electrolyte

Yunyun Zhong, Jianwei Zhang, Shuanjin Wang, Dongmei Han, Min Xiao* and Yuezhong Meng*

Lithium metal anode, which is considered as “Holy Grail” anode material, possesses extra-high energy density and extra-low negative electrochemical potential. However, it is hardly applied in lithium batteries owing to lithium dendrite formation and interfacial instability in the electrolyte, resulting in safety problem and poor long-cycle performance. In this connection, we designed and synthesized a novel artificial solid electrolyte interface (SEI) layer which exhibits high ionic conductivity and single-ion conductive characteristic. The SEI layer named as LiSFSI-PET4A-PETMP (LFPP) SEI layer was synthesized by one step click reaction in-situ on the surface of lithium metal using lithium [(4-styrenesulfonyl) (fluorosulfonyl)imide] (LiSFSI), pentaerythritol tetraacrylate (PET4A), and pentaerythritol tetrakis (2-mercaptoacetate) (PETMP). The formed LFPP-SEI layer has a controllable 3D cross-linked network structure. It also exhibits high ionic conductivity and high lithium ion transference number near to unity, which is beneficial to prevent the nucleation of lithium dendrites, so as to suppress the formation of lithium dendrite from the source. The Li/LFP full cells using LFPP 2%-Li anode exhibits a quite high and stable capacity with capacity retention of 75.8% and a high coulombic efficiency of 99.0% at 1 C after 390 cycles. Moreover, the full battery using LFPP 2%-Li anode and LFPP 1%-Li anode at 0.5 C for 250 cycles shows a very good coulombic efficiency of 100.0% and capacity retention of 77.5% and 77.7%, respectively.

Introduction

The application of lithium metal anode has been a research focus for its extra-high energy density of 3,860 mAh g\(^{-1}\) and extra-low negative electrochemical potential of -3.04 V versus standard hydrogen electrode. However, it is hardly applied in lithium batteries owing to lithium dendrite formation and interfacial instability in the electrolyte, resulting in safety problem and poor long-cycle performance. In addition, it suffers from volume expansion during cycle performance which also can weaken the cycle performance. 

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In recent years, many efforts have been devoted to suppressing the lithium dendrite formation,\textsuperscript{2,9} A native solid electrolyte interface (SEI) layer between liquid electrolyte and lithium metal can spontaneously shape up due to the high reactivity of the electrolyte solvent, such as cyclic carbonate (e.g., ethylene carbonate, EC) and cyclic ether (e.g., 1,3-dioxolane, DOL). But the native SEI layer exhibits low ionic conductivity ($4.2 \times 10^{-6}$ S cm$^{-1}$),\textsuperscript{10} structural instability and chemical heterogeneity,\textsuperscript{11} which induces heterogeneous electrodeposition and generate dendrite growth. Many studies have been disclosed to suppress the formation and growth of lithium dendrite, such as using solid electrolyte or gel electrolyte,\textsuperscript{4,8,12-16} constructing artificial solid electrolyte interface (SEI) layer,\textsuperscript{5,17-23,54} designing functionalized separators,\textsuperscript{24-30} and improving the structure of current collectors.\textsuperscript{2,31-37} Constructing an artificial SEI layer is one good solution to solve the challenge of suppressing the formation and growth of lithium dendrite. Many kinds of artificial SEI layers have been reported, such as poly(vinylidene-co-hexafluoropropylene)(PVDF-HFP)/LiF,\textsuperscript{38} Al$_2$O$_3$ sputter coating,\textsuperscript{39} Li polyacrylic acid (LiPAA),\textsuperscript{40} poly(vinylidene difluoride (PVDF),\textsuperscript{41} LLZTO/Li-Nafion dual-phase SEI,\textsuperscript{42} Li polyacrylic acid (LiPAA),\textsuperscript{43} LiAlO$_2$,\textsuperscript{44} poly(ethylene vinyl alcohol-β-acrylonitrile ether) (EVOH-β-OCH$_2$CH=CN, abbreviated as EBC)/lithium bis(trifluoromethyl sulphonate (LiTFSI),\textsuperscript{45} LiPO$_4$,\textsuperscript{46} graphene oxide (GO),\textsuperscript{46} covalent organic framework (COF),\textsuperscript{47} graphene/LiF and so on. The artificial SEI layer mentioned above can stabilize the active lithium metal anode largely, however, most of them exhibit extremely low ionic conductivity or even ionic insulation. The work by Tikekar et al. showed that the stable SEI layer should have the following characteristics: high ionic conductivity under strong bias, large shear modulus of the Interphase and sufficiently small size of the initial nucleates.\textsuperscript{49}

Herein, we report a novel artificial SEI layer (Fig. 1) exhibiting extra high ionic conductivity ($0.0927$ mS cm$^{-1}$) and lithium ion transference number near to unity ($0.91$). The LFPP-SEI can form a uniform film on the surface of Li anode with good flexibility and high mechanical strength. The extra high ionic conductivity and lithium ion transference number of the SEI layer can weaken or even eliminate the anion depletion-induced strong electric fields on the surface of lithium anode to vanish the nucleation of lithium dendrites, so as to suppress the formation of lithium dendrite from the root. The galvanostatic plating/stripping cycling performance of symmetric cell with LFPP 1%-Li exhibits a quite stable over-potential of 0.038 V for over 1000 h, indicating the superior stability of the LFPP SIPE coated Li anode. The full LFP batteries with LFPP-Li anodes exhibit a very high coulombic efficiency of 100.0% on average and capacity retention of 77.7% for 250 cycles.

**Results and Discussion**

1. Ionic Conductivity

In our precious study, the ionic conductivity of LFPP with electrosprun PVDF as standing membrane soaked with DMC/EC (vol. % = 1:1) is up to $5.1 \times 10^{-3}$ S cm$^{-1}$. To further investigate the ionic conductivity of the LFPP artificial SEI layer soaked with solvent, the EIS analysis was carried out in symmetric coin cells assembled by two LFPP coated stainless steel round soaked with DMC/EC/EMC (vol. % = 1:1:1) using PP membrane (Celgard 2500) as separator.\textsuperscript{50}

![Fig. 2 EIS curves of SS/SS cells with LFPP coated SEI layer using DMC/EC/EMC (vol. % = 1:1:1) (a) as solvent, and corresponding ionic conductivity versus concentration of precursors in DMC/EC/EMC (vol. % = 1:1:1) (b).](image)

The LFPP SEI layer was prepared by one-step in-situ click reaction on the surface of stainless steel (SS). A series of LFPP SEI layer with various thickness was fabricated by simply adjusting the mass concentration of precursors, consisting of LiSFSI, PET4A and PETMP in DMC/EC/EMC (vol. % = 1:1:1). The thickness of the LFPP SEI layers are not directly available by scanning electron microscope (SEM), because the section of SS round is too thick and hard to cut off. It was calculated by the thickness of LFPP coated on Cu Foil, which is more accessible. For the LFPP/DMC precursor solution exhibit different diffusibility, the volume dropped on to Li foil and Cu foil are 45 μL and 20 μL respectively. Given that the area of Cu foil and SS foil are identical, LFPP layer on SS round is 2.25 times as thick as that on Cu foil. The thickness of LFPP layer on Cu foil can be obtained in Fig. S1 and Table S1.

The EIS curves and ionic conductivity calculation results are shown in Fig. 2 and Table S1. The ionic conductivity is very high up to $0.0927$ mS cm$^{-1}$ in DMC/EC/EMC (vol. % = 1:1:1), which is much higher than that of reported routine SEIs ($4.2 \times 10^{-6}$ S cm$^{-1}$).\textsuperscript{10} It can be seen that a higher ionic conductivity can be readily achieved by increasing the concentration of precursors as shown in Fig. 2.

2. Electrochemical Stability
The electrochemical stability of electrode material determines the voltage range in lithium-ion batteries. In this work, the electrochemical stability of the LFPP SEI layer in carbon electrode was measured by linear sweep voltammetry (LSV) in 2032 coin cells using stainless steel as cathode and LFPP-Li as anode (LFPP-Li//SS) and using carbon cathode and LFPP-Li as anode (Super P//LFPP-Li). The LSV measurement was carried out from 0 V to 6.0 V at a scan speed of 1 mV/s. As shown in Fig. 3a, the LFPP SEI layer is electrochemically stable up to 5.2 V. To further investigate the electrochemical stability of the LFPP SEI layer applied in carbonate electrolyte, the cyclic voltammetry was performed in a voltage range of 2.5 V - 4.2 V at a scan speed of 1 mV/s as shown in Fig. S4, indicating no obvious redox peak. It is also confirmed that the LFPP SEI layer is electrochemically stable from 2.5 V to 4.2 V, which can then guarantee its extensive application in lithium batteries. When the electrochemical stability of the LFPP SEI layer was tested using stainless-steel foil as working electrode, the resultant electrochemical stability window was always over-estimated. A carbon-based electrode is used in Fig. 3b. The electrochemical stability is up to 5.7 V.31

3. Galvanostatic Li Plating/stripping Cycling Behaviors

To further investigate the influence of the LFPP SEI layer coated on Li metal anode, galvanostatic cycling performance was evaluated in symmetric LFPP-Li cell. The galvanostatic cycling of symmetric LFPP-Li // LFPP-Li cells were tested at a current density of 0.5 mA cm$^{-2}$ with a capacity of 1 mAh cm$^{-2}$. As shown in Fig. 4, the over-potential of the cells with LFPP-Li increases with increasing the concentration of LFPP precursor, owing to the thickness increase of LFPP SEI layer. When the concentration of LFPP precursor is 5% and 2%, the galvanostatic cycling performance is stable at 0.7 V-1.0 V for about 950 h. After about 1100 h, the over-potential bumps up sharply, which can be attributed to lithium dendrites formation and the incrassated SEI layer.40 Moreover, the SFSI anion of LiSFSI salt is uniformly distributed on the surface of lithium anode, which can guide Li$^+$ to distribute and deposit evenly. The symmetric cell with LFPP 1%-Li exhibits the lowest and most stable over-potential at 0.038 V for over 1000 h. The outstanding cycling performance of the symmetric LFPP-Li cells with LFPP 1%-Li SEI layer demonstrates the superior stability and lithium ion transport ability of the LFPP SEI layer.

Furthermore, XPS analysis was operated to explore the stability of the interface enhanced by LFPP SEI layers by investigating the chemical compositions on the surface of the lithium anode. Fig. 5 shows the XPS spectra for the anodes retrieved from symmetric lithium cells based carbonates electrolytes with LFPP-Li. Compared with the anode from symmetric lithium cells with polished Li anode after cycling for 200 h at 0.5 mA cm$^{-2}$ with a capacity of 1 mAh cm$^{-2}$, there are SO$_2$-F(685.9 eV) and more abundant Li-F (684.4 eV), C-O (286.3 eV) on the anode surface, which is in accordance with the chemical composition of LFPP SEI layer.52 It can be seen that C-C, C-H peak (284.8 eV, C 1s), C=O peak (286.3 eV, C 1s), CO$_2$ peak (288.6 eV, C 1s), poly(EC) peak (289.8 eV, C 1s), and Li-F peak (684.4 eV, F 1s) appear on the surface of polished Li in a symmetric lithium cell after cycling, which are the typical composition for the native solvent-induced SEI formation. However, it has been proved that the native SEI layer induced by electrolytes is unstable, which can then tolerate chemical heterogeneity, inducing heterogeneous eletrodeposition and generating dendrite growth.31

4. Battery Performance

The battery performance and cyclic voltammetry curves of Li/LiFePO$_4$ cells with LFPP-Li and polished Li are shown in Fig.6, respectively. Fig. 6a and 6b describe the rate performance of Li/LFP full batteries using LFPP-Li anode and polished Li anode. At a low rate, the LFPP-Li//LFP batteries using LFPP-Li anode exhibit better performance than the Li//LFP batteries using polished Li anode. The battery using LFPP 0.5%-Li as anode exhibits the best performance. This can be attributed to that the LFPP SEI layer behaves good compatibility with liquid electrolyte and has very high lithium ion transference number near to unity, which can weaken or even eliminate the anion depletion-induced strong electric fields on the lithium anode. It is further proved that, by the charge-discharge curves of the initial cycle.
Fig. 6 Battery performance of LiFePO₄ full batteries using LFPP-Li anode and polished Li anode: rate performance (a, b) and the corresponding charge-discharge curves of the initial cycle (c) and the 60th cycle (d); long cycle performance at 0.5 C (e); cyclic voltammetry curves of LFPP 1%-Li/LFP (f, inset is EIS curve before and after CV).

The advantages of LFPP SEI layer becomes much more obvious when subjected to long cycle performance measurement at a rate of 1 C as shown in Fig. 6b and at 0.5 C in Fig. 6e. In Fig. 6b, the long cycle performance at 1 C was performed from the 61st cycle to the 450th cycle. As listed in Table 1, the capacity retention and coulombic efficiency of the cell using LFPP-Li anode is much higher than that using polished Li anode. The cell using LFPP 2%-Li anode exhibits the highest capacity retention of 75.8% and a high coulombic efficiency of 99.0% at 1 C after 390 cycles. During the long cycle performance at 0.5 C in Fig. 6e, the batteries using LFPP 2%-Li anode and LFPP 1%-Li anode exhibit the best performance with a very high coulombic efficiency of 100.0% and capacity retention of 77.5% and 77.7% respectively, indicating the decreased polarization voltage. This is attributed to the improvement of compatibility demonstrated further in the following EIS tests. The EIS measurements were conducted from 100 kHz to 1 Hz at a voltage of 5 mV before and after CV measurements. As shown in Fig. 6f, the interface impedance (the diameter of the semicircle) becomes smaller after 5 cycles, owing to the improvement of compatibility among Li metal, LFPP SEI layer, and liquid electrolyte. The battery performance and CV curves of LFPP-Li applied in Li//NCM full cells are shown in Fig. S2. The cycle stability is inferior than that in Li//LFP batteries.

To further evaluate the effect of the LFPP SEI layer on lithium metal anode on battery performance, the Li//LiFePO₄ cells with LFPP-Li and polished Li were disassembled after 500 cycles, followed by the examination under SEM observation. Fig. 7c and 7d show the top view and side view of polished Li anode after cycling in Li//LiFePO₄ cells for 100 cycles at 0.5 C, depicting obvious cracks from the top view and numerous lithium dendrite and dead lithium from the cross section. Compared with the polished Li anode, the LFPP-Li anode (Fig. 7a) presents relatively smooth top surface with very few defects. From the cross section in Fig. 7b, it found that there are almost no dead lithium and very few lithium dendrites, demonstrating the advantage of LFPP-Li anode.

Table 1 Coulombic efficiency and capacity retention of the long cycle performance of Li//LiFePO₄ full cells using LFPP-Li anode and polished Li anode at 1 C and 0.5 C.

|                | 1 C after rate performance | 0.5 C |
|----------------|----------------------------|-------|
|                | CE*                       | CR*   | CE   | CR   |
| LFPP 5%-Li     | 99.7%                     | 69.1% | 98.9%| 70.0%|
| LFPP 2%-Li     | 99.0%                     | 75.8% | 100.0%| 77.5%|
| LFPP 1%-Li     | 98.8%                     | 57.9% | 100.0%| 77.7%|
| LFPP 0.5%-Li   | 99.6%                     | 71.0% | 98.5%| 70.2%|
| Polished-Li    | 95.8%                     | 55.0% | 99.8%| 59.9%|

* CE: Coulombic efficiency on average; CR: Capacity retention.
effectively suppressing lithium dendrite formation of LFPP SEI layer.

Conclusions

In conclusion, we report a novel artificial SEI layer which exhibits high ionic conductivity and single-ion conductive characteristic. The LFPP SEI layer showed a very high ionic conductivity up to 0.0927 mS cm⁻¹. Furthermore, its lithium ion transference number is 0.91, which is quite high near to unity. These characteristic natures can weaken or even eliminate the anion depletion-induced strong electric fields on the lithium anode to prevent the nucleation of lithium dendrites, finally to suppress the formation of lithium dendrite from the source. The SEI layer also shows very good electrochemical stability from 0 to 5.2 V. The symmetric cell with LFPP 1%-Li exhibits a very small over-potential of 0.038 V for over 1000 h at current densities of 0.5 mA cm⁻² with a capacity of 1 mAh cm⁻². The Li/LFP full cells using LFPP 2%-Li anode gives the most stable capacity with the highest current retention of 75.8% and an extra high coulombic efficiency of 99.0% at 1 C after 390 cycles. During the long cycle performance at 0.5 C, the batteries using LFPP 2%-Li and LFPP 1%-Li anodes exhibit the best performance with 100% coulombic efficiency on average and capacity retentions of 77.5% and 77.7%, respectively. Therefore, LFPP SEI layer is an outstanding artificial protective layer for Li metal anode to achieving the object of stability and dendrite-free when applied in lithium metal batteries.

Experimental Section

Chemicals and materials

The super dry solvent purchased from JK Chemical, including acetonitrile, N, N-dimethylformamide were made no pretreatment before use. 2-Dimethoxy-2-phenylacetophenone (DMPA) (Aladdin), sodium p-styrenesulfonate (Aladdin), and thionyl chloride were also used as-purchased. Super P (MTI Kejing), PVDF (Arkema), and LiFePO₄ (MTI Kejing) were dried at 50 °C under high vacuum before use. All liquid reagents, such as pentaerythritol tetraacrylate (PET4A, Aladdin), sodium p-styrenesulfonate (PET4A, Aladdin), and thionyl chloride were also used as-purchased. Super P (MTI Kejing), PVDF (Arkema), and LiFePO₄ (MTI Kejing) were dried at 50 °C under high vacuum before use. All liquid reagents, such as pentaerythritol tetraacrylate (PET4A, J&K) and Pentaerythritol tetraacrylate (PETA, Aldrich) were dried with 3 Å molecule sieves and stored in glove box. As control groups, batteries using polished bare Li metal as anode were assembled in standard CR2025 coin cells with LFPP-Li as anode in a glove box. As control groups, batteries using polished bare Li metal as anode were assembled. Battery performance tests were performed in a voltage range between 2.5 V and 4.0 V at 28 °C. The Li/LFP cells using LFPP-Li anode and polished Li anode were performed at a current density of 0.5 mA cm⁻² with a capacity of 1 mAh cm⁻².

Preparation process of LFPP-Li anode

Precursor solution was prepared by LiFSI, PETA4A, and PETMP using dimethyl carbonate (DMC, J&K Chemical, super dry) and DMPA as solvent and initiator respectively. 70 μL precursor solution was dropped onto the top surface of polished lithium metal foil. The polished lithium metal foil was obtained by two steps, including removing the surface oxidation layer of commercial lithium foil by a blade and rolling out by a glass rod. After a thiol-ene click polymerization under 365 nm UV light for 30 min, the LFPP SEI layer took shape on the lithium foil. Although DMC is very easy to volatilize, the LFPP-Li was completely dried under high vacuum at room temperature for 30 min to remove residual solvent.

Electrochemical measurements

LFPP coated stainless steel (LFPP-SS) was prepared by the same method of LFPP-Li. Afterwards, symmetric coin cells were assembled with two LFPP coated stainless steel round electrode with a diameter of 15.5 mm, using PP (Celgard 2500) membrane as separator and 20.0 μL DMC/EC/EMC (vol.%=1:1:1) as solvent. Electrochemical impedance spectroscopy (EIS) was performed in the symmetric coin cells using a Solartron 1220 frequency response analyzer from 0.1 MHz to 1 Hz at an amplitude of 5 mV at 25 °C. The ionic conductivity was calculated according to the following formula:

$$\sigma = \frac{l_{SEI+PP}}{(R_b \times A)}$$  \hspace{1cm} (1)

where $l_{SEI+PP}$ is thickness of the SEI layer and PP separator, $R_b$ is bulk resistance of the SEI layer and PP separator soaked with liquid electrolyte, and $A$ is area of the stainless steel. The electrochemical stability of the LFPP SEI layer was tested in a standard 2032 coin cell with LFPP-SS electrode as cathode and LFPP-Li as anode and using carbon cathode and LFPP-Li as anode (Super P/LFP-Li) with 1 M LiPF₆/DMC: EC: EMC, vol.%=1:1:1) as liquid electrolyte. Carbon cathode was made by casting method with a weight ratio of Super P: PVDF=1:1. Linear scanning voltammetry (LSV) was conducted from 0 to 6.0 V (vs. Li/Li⁺) at a scan speed of 1 mV s⁻¹ at room temperature. Cyclic voltammograms (CV) were conducted from 2.5 V to 4.2 V at a scan speed of 1 mV s⁻¹.

Galvanostatic cycling performance of symmetric Li/Li cells with LFPP-Li anode or polished Li anode was performed at a current density of 0.5 mA cm⁻² with a capacity of 1 mAh cm⁻². LiFePO₄ (LFP) cathode was obtained by casting method with the weight ratio of LFP: super P: PVDF=8:1:1. The loading density of LFP is about 1.8 mg cm⁻². Cathode circles ($Φ=12 mm$) were obtained by a cutting machine. The Li/LFP cells were assembled in standard CR2025 coin cells with LFPP-Li as anode in a glove box. As control groups, batteries using polished bare Li metal as anode were assembled. Battery performance tests were performed in a voltage range between 2.5 V and 4.0 V at 28 °C. The Li/LFP cells using LFPP-Li anode and polished Li anode after 100 cycles were taken apart, and then the electrodes were washed by DMC for SEM analysis and XPS analysis.

Lithium nickel cobalt manganese oxide (NCM) cathode was made by casting method with the weight ratio of NCM 523: super P: PVDF=8:1:1. The loading density of NCM is 3.6 mg cm⁻². Then Li/NCM cells were assembled in standard CR2025 coin cells with LFPP-Li as anode using 1 M LiPF₆/DMC: EC: EMC, vol.%=1:1:1) as liquid electrolyte in a glove box. Battery performance tests were performed in a voltage range between 3.0 V to 4.5 V at 28 °C.

Cyclic voltammograms (CV) measurements of Li/LFP cells with LFPP-Li anode or bare-Li anode were operated in a voltage range between 2.5 V to 4.0 V at a scan speed of 0.1 mV s⁻¹ at room temperature. Cyclic voltammograms (CV) measurements of Li/NCM cells was conducted from 3.0 V to 4.7 V at a scan speed of 0.1 mV s⁻¹ at room temperature.
Conflicts of interest
There are no conflicts to declare.

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Polished Li anode

Precursor solution dropped onto polished Li anode

UV light initiation

LFPP-Li anode

Cycling

U⁺ U⁺ U⁺ U⁺ LFPP

cross-linked polymer backbone

185x93mm (300 x 300 DPI)
222x193mm (300 x 300 DPI)
A flexible artificial SEI layer with 3D cross-linked network structure exhibits highly ionic conductivity and single-ion conductive characteristic.