Enhanced Electrochemical Performance of Poly(ethylene oxide) Composite Polymer Electrolyte via Incorporating Lithiated Covalent Organic Framework

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Abstract

The lithiated covalent organic framework (named TpPa-SO₃Li), which was prepared by a mild chemical lithiation strategy, was introduced in poly(ethylene oxide) (PEO) to produce the composite polymer electrolytes (CPEs). Li-ion can transfer along the PEO chain or across the layer of TpPa-SO₃Li within the nanochannels, resulting in a high Li-ion conductivity of 3.01×10^{-4} S/cm at 60 °C. When the CPE with 0.75 wt.% TpPa-SO₃Li was used in the LiFePO₄||Li solid-state battery, the cell delivered a stable capacity of 125 mA·h/g after 250 cycles at 0.5 C, 60 °C. In comparison, the cell using the CPE without TpPa-SO₃Li exhibited a capacity of only 118 mA·h/g.

Keywords Lithiated covalent organic framework · Composite polymer electrolytes · Poly(ethylene oxide) · Solid-state lithium-ion batteries

Introduction

As the demand for power sources continues to increase, various types of high-performance energy storage devices are developing rapidly [1–3]. Solid electrolytes are the key part of solid-state lithium-ion battery (SSLIB), which is believed as one of the next-generation battery systems with high energy density and superior safety [4]. Composite polymer electrolytes (CPEs), such as poly(ethylene oxide) (PEO), are the most promising candidate material for commercial SSLIB [5, 6]. However, the low ionic conductivity that resulted from high crystallinity still cannot be satisfied for application. To solve this problem, inorganic particles

such as oxides and sulfides were widely used as fillers to decrease the crystallinity of PEO or construct extra Li-ion conductive pathways [7, 8]. Traditional efficient fillers have some shortcomings: (1) oxides usually need a high-temperature treatment, such as Li₇La₃Zr₂O₁₂ (> 900 °C) [9]; (2) most oxides and sulfides are sensitive to water and air [10, 11]; (3) the high weight content of fillers hinders the improvement in the overall battery's energy density. Therefore, great efforts in finding better fillers are needed for practical applications.

Covalent organic frameworks (COFs) are a new kind of porous materials with advantages such as highly adjustable structures, light mass, high specific surface area, and unique one-dimensional channel structures [12, 13]. Although these features are suitable for use as fillers, COFs are rarely applied in CPEs due to their poor ionic conductivity [14–16]. To enhance the intrinsic Li-ion conductivity of COFs, this study prepared a lithiated COF (named TpPa-SO₃Li) by a mild chemical lithiation strategy. The obtained TpPa-SO₃Li was selected as the active filler in the CPE for SSLIB. Compared with other fillers without Li-ion conductivity, the TpPa-SO₃Li provides a rapid Li-ion transfer via the –SO₃Li groups as Li-ion conducting sites in the nanochannels, which work as the expressway between the PEO chains, leading to enhanced Li-ion conductivity. Moreover, the extra advantages of high chemical stability and low density provide the potential for practical application. Results show that the

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TpPa-SO₃Li serves as promising filler in CPE and enhances the electrochemical performances of LiFePO₄||Li SSLIB.

Experiment Section

TpPa-SO₃Li was prepared by solvothermal and chemical lithiation methods [13]. TpPa-SO₃Li, PEO (molecular weight $M_w \approx 6 \times 10^5$), and LiClO₄ were dissolved in anhydrous acetonitrile with a certain weight ratio of EO:Li = 18:1. The homogenized suspension was cast into a polytetrafluoroethylene mold and dried at room temperature for 24 h. After further drying at 55 °C for another 12 h under vacuum, the CPE membrane (named (PEO)₁₈LiClO₄/TpPa-SO₃Li(*x*), *x* is the mass fraction of TpPa-SO₃Li) was obtained. The CPE without TpPa-SO₃Li was denoted as (PEO)₁₈LiClO₄.

Results and Discussions

Figure 1a shows the chemical structure of TpPa-SO₃H, which was synthesized by the Schiff base condensation reaction of 2,4,6-trihydroxybenzene-1,3,5-tricarbaldehyde (Tp) and 2,5-diaminobenzenesulfonic acid (Pa-SO₃H). The enol-imine form converted to keto-enamine form after condensation. It was lithiated by Lewis acid–base reaction using lithium acetate. As shown in Fig. 1b, the Fourier transform

infrared (FT-IR) peaks of TpPa-SO₃H at 1240, 1575, and 3400 cm^{−1} represent the C–N, C=C, and enamine N–H bonds, respectively. The peak at 3200 cm^{−1}, which corresponds to O–H bonds in sulfonates, is found in TpPa-SO₃H. After being lithiated, this peak significantly weakened, indicating that the H atoms in the –OH groups are replaced by Li atoms. Meanwhile, the O–Li bonds form and show a characteristic peak at 1750 cm^{−1}, which overlaps with the characteristic peak of C=O bonds. X-ray photoelectron spectroscopy (XPS) spectra (Fig. 1c and Fig. S1) also confirm the lithium substitution. Due to the splitting of the spin–orbit, double peaks appear in the S 2p spectrum and shift to higher binding energy after being lithiated. It confirms that the environment of the S atom has changed, which is attributed to the substitution of H atoms in the sulfonates by Li atoms [17].

Scanning electron microscopy (SEM) images show that the TpPa-SO₃H and TpPa-SO₃Li have similar stacked particle structures (Fig. 1d, e). These particles have an average diameter of less than 100 nm and are formed by stacking porous nanosheets. The X-ray diffraction (XRD) pattern of TpPa-SO₃H (Fig. 1f) shows the characteristic peaks at $2\theta = 4.6^\circ$ and 26.2° that correspond to (100) and (001) planes, respectively. This confirms the ordered pores with a pore size of 1.88 nm and an interlayer distance of 3.4 Å. This indicates that the lithiation process has basically no effect on the layered structure and morphology. The crystalline structure of TpPa-SO₃Li can be verified by the transmission

Fig. 1 **a** Chemical structure of TpPa-SO₃X (X=H, Li). **b** FT-IR spectra of TpPa-SO₃H and TpPa-SO₃Li. **c** XPS spectra of S 2p in TpPa-SO₃H and TpPa-SO₃Li. SEM images of **(d)** TpPa-SO₃H and **(e)** TpPa-SO₃Li. **f** XRD patterns of TpPa-SO₃H and TpPa-SO₃Li

electron microscopy (TEM) image (Fig. S2) as well. The Li content obtained by the inductively coupled plasma optical emission spectrometer is about 1.53 wt.%, which is a little lower than the theoretical value of 2.33 wt.%.

TpPa-SO₃Li can be uniformly dispersed in the casting solution without sedimentation (Fig. S3). As shown in Fig. 2a and Fig. S4, the CPEs are flexible with a thickness of ~50 μm and have a uniform surface without visible defects or pellets (Fig. 2b, c). In addition, there is no obvious difference in the surface morphology of CPEs with or without TpPa-SO₃Li. The uniform dispersion of TpPa-SO₃Li in PEO can be demonstrated by the cross-sectional energy-dispersive spectrometer (EDS) mapping of S (Fig. 2d). The XRD characterization was performed to study the crystallinity of CPEs in Fig. 2e, indicating that the introduction of TpPa-SO₃Li with various ratios has no effect on the crystallinity of CPEs either [5]. After adding 0.75 wt.% TpPa-SO₃Li, the melting enthalpy of CPEs changes from 88.03 J/g to 91.88 J/g. (Fig. 2f). Correspondingly, the crystallinity of CPEs increased from 41.19 to 42.99%, which suggests that the crystallinity of CPEs is hardly affected.

To study the influence of TpPa-SO₃Li on the ionic conductivity, this work assembled SS|CPE|SS cells (SS represents stainless steel) and performed electrochemical impedance spectroscopy (EIS). Figure 3a shows the typical spectra of (PEO)₁₈LiClO₄/TpPa-SO₃Li(0.75) at different temperatures. The resistance decreases rapidly with the increase in temperature. At 50 °C and above, the semicircle disappears,

indicating a decreased interface resistance because of the improved interface interaction. As shown in Fig. 3b, with the increase in the TpPa-SO₃Li content, the ionic conductivity shows a trend of initially rising and then falling with inflection points at 0.75 wt.% TpPa-SO₃Li content. Taking the curve at 60 °C as an example, the ionic conductivity ranges from 1.62×10^{-4} to 3.01×10^{-4} S/cm as the filling amount increases from 0 to 0.75 wt.%. When the content is further increased and exceeds the threshold, the conductivity drops rapidly to even lower than that of (PEO)₁₈LiClO₄. This phenomenon can be explained by the percolation behavior. It is attributed to aggregation, phase separation, and bubbles caused by excess TpPa-SO₃Li, which goes against ion conduction. Moreover, due to the low density and high specific surface area of TpPa-SO₃Li, the ionic conductivity can be improved at a very low content, and the threshold of the percolation behavior is only about 0.75 wt.%.

To study the effect of the lithiation sites, (PEO)₁₈LiClO₄/TpPa-SO₃H(0.75) was prepared with the same method, and its ionic conductivity was tested at different temperatures. As shown in Fig. 3c, the ionic conductivity of (PEO)₁₈LiClO₄/TpPa-SO₃H(0.75) is significantly lower than that of (PEO)₁₈LiClO₄. Since TpPa-SO₃H does not have Li-ion conductivity, its uniform dispersion in CPEs may form micro-domains that are not conducive to the Li-ion. In addition, the H-ions that dissociated from the sulfonates hinder the Li-ions from entering the nano-channels of TpPa-SO₃H by steric hindrance and Coulomb

Fig. 2 a Digital photographs of (PEO)₁₈LiClO₄/TpPa-SO₃Li(0.75). SEM images of (b) (PEO)₁₈LiClO₄ and (c) (PEO)₁₈LiClO₄/TpPa-SO₃Li(0.75). d Cross-sectional SEM image and S EDS mapping of

(PEO)₁₈LiClO₄/TpPa-SO₃Li(0.75). e XRD patterns of the CPEs. f DSC traces of (PEO)₁₈LiClO₄ and (PEO)₁₈LiClO₄/TpPa-SO₃Li(0.75)

Fig. 3 **a** EIS spectra of (PEO)₁₈LiClO₄/TpPa-SO₃Li(0.75) at different temperatures. **b** Ionic conductivity of CPEs at different temperatures and TpPa-SO₃Li contents. **c** Arrhenius plot for the ionic conductivity of CPEs with TpPa-SO₃H or TpPa-SO₃Li. **d** EIS spectra of

(PEO)₁₈LiClO₄/TpPa-SO₃Li(0.75) before and after polarization (inset shows the corresponding $I-t$ curve). **e** Schematic illustration of Li-ion conductive mechanism of (PEO)₁₈LiClO₄/TpPa-SO₃Li(0.75)

interaction, which further increases the Li-ion diffusion energy barrier. The chemical lithiation method can replace H-ions with Li-ions, introduce evenly distributed Li-ion jumping conduction sites, and construct low-resistance transmission channels.

In addition to the high ionic conductivity, sulfonates in TpPa-SO₃Li serve as single Li-ion conduction sites, which is beneficial to increase the Li-ion transference number (t_{Li^+}) [13]. Chronoamperometry and EIS were carried out at 60 °C to measure the t_{Li^+} using Li|CPE|Li cells. As shown in Fig. 3d and Fig. S5, (PEO)₁₈LiClO₄/TpPa-SO₃Li(0.75) delivers a t_{Li^+} of 0.300, while (PEO)₁₈LiClO₄ shows a t_{Li^+} of 0.258.

The improvements in the ionic conductivity and t_{Li^+} benefit from the structure and composition of TpPa-SO₃Li. As shown in Fig. 3e, the unique one-dimensional channel structure provides rapid Li-ion transfer and shortens the transfer distance. Meanwhile, lithiation sites in the channels significantly reduce the Li-ion diffusion barrier.

The linear sweep voltammetry (LSV) measurement was performed at 60 °C to study the electrochemical stability window of the CPEs (Fig. 4a). The result shows that (PEO)₁₈LiClO₄ and (PEO)₁₈LiClO₄/TpPa-SO₃Li(0.75) are electrochemically stable at the voltage range of 1.0–4.5 V. Within the operating voltage range of LiFePO₄, both PEO and TpPa-SO₃Li can be kept stable.

Li symmetric cells were characterized by charge/discharge measurements at 60 °C, 0.1 mA/cm², and 0.1 mA·h/cm² to study the interfacial stability. As shown in Fig. S6, the overpotential of Li|(PEO)₁₈LiClO₄/TpPa-SO₃Li(0.75)|Li is much smaller than that of Li|(PEO)₁₈LiClO₄|Li. Moreover, Li|(PEO)₁₈LiClO₄|Li is short-circuited after cycling for 80 h, which signifies that (PEO)₁₈LiClO₄/TpPa-SO₃Li(0.75) has a more stable interface with lithium than (PEO)₁₈LiClO₄.

To explore the practical application of the CPEs, this work assembled LiFePO₄|CPE|Li cells and measured their electrochemical performance at 60 °C and 0.5 C with activation at 0.1 C for five cycles. As shown in Fig. 4b, the polarization voltage of LiFePO₄|(PEO)₁₈LiClO₄|Li significantly increases with the cycle process, while LiFePO₄|(PEO)₁₈LiClO₄/TpPa-SO₃Li(0.75)|Li exhibits a stable polarization voltage of 0.11 V (Fig. 4c). This proves that it has the potential to be applied in SSLIB.

As shown in Fig. 4d, LiFePO₄|(PEO)₁₈LiClO₄|Li delivers initial and stable discharge capacities of 151.2 and 118 mA·h/g in the first 250 cycles, respectively. On the other hand, LiFePO₄|(PEO)₁₈LiClO₄/TpPa-SO₃Li(0.75)|Li shows initial and stable discharge capacities of 154.7 and 125 mA·h/g, respectively. The unstable Coulombic efficiency may be due to the side reaction caused by the trace solvent in the CPEs. The Coulombic efficiency of LiFePO₄|(PEO)₁₈LiClO₄|Li

Fig. 4 **a** LSV profiles of (PEO)₁₈LiClO₄ and (PEO)₁₈LiClO₄/TpPa-SO₃Li(0.75). **b** Charge/discharge curves of LiFePO₄/(PEO)₁₈LiClO₄/Li. **c** Charge/discharge curves of LiFePO₄/(PEO)₁₈LiClO₄/TpPa-SO₃Li(0.75)/Li. **d** Cycling per-

formance of LiFePO₄/CPE/Li cells at 0.5 C and 60 °C. **e** EIS spectra of LiFePO₄/(PEO)₁₈LiClO₄/Li. **f** EIS spectra of LiFePO₄/(PEO)₁₈LiClO₄/TpPa-SO₃Li(0.75)/Li

was basically stable after 75 cycles. The unlithiated sulfonate in TpPa-SO₃Li will be electrochemically lithiated, leading to a fluctuating Coulombic efficiency of LiFePO₄/(PEO)₁₈LiClO₄/TpPa-SO₃Li(0.75)/Li. To test the stability of LiFePO₄/CPE/Li cells to temperature, the cells were cooled to room temperature for 24 h after 250 cycles and then tested at 60 °C and 0.5 C again (Fig. S7). The stable discharge capacities of LiFePO₄/(PEO)₁₈LiClO₄/Li and LiFePO₄/(PEO)₁₈LiClO₄/TpPa-SO₃Li(0.75)/Li decayed to 100 and 113 mA·h/g, respectively. The corresponding capacity retention rates before and after cooling were 84.7% and 90.4%, respectively, indicating that LiFePO₄/(PEO)₁₈LiClO₄/TpPa-SO₃Li(0.75)/Li was more stable to temperature.

EIS spectra at the reduction state were tested to study the interfacial stability. As shown in Fig. 4e, LiFePO₄/(PEO)₁₈LiClO₄/Li shows two overlapped semicircles in the middle- and high-frequency range. Moreover, the impedance increases rapidly during cycling, which means a serious interface reaction between (PEO)₁₈LiClO₄ and electrodes. After three cycles, LiFePO₄/(PEO)₁₈LiClO₄/TpPa-SO₃Li(0.75)/Li shows only one semicircle (Fig. 4f), and the corresponding impedance is smaller than that of the initial state. Therefore, the addition of TpPa-SO₃Li effectively improved the interface stability between the CPE and electrodes.

Conclusions

The TpPa-SO₃Li was prepared via a mild chemical lithiation strategy and applied as active filler in the PEO-based CPE. The -SO₃Li groups in TpPa-SO₃Li work as Li-ion conducting sites in the nanochannels, providing an expressway between the PEO chains. Therefore, high ionic conductivity of 3.01×10^{-4} S/cm was obtained at 60 °C. When the CPE with only 0.75 wt.% TpPa-SO₃Li was assembled in the SSLIB, it delivered a reversible capacity of 125 mA·h/g after 250 cycles at 0.5 C and 60 °C. This strategy provides a convenient method to prepare Li-ion conducting COFs and provides a new path for lightweight CPEs.

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1007/s12209-021-00300-z>.

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Declarations

Conflict of interests The authors declare that there is no conflict of interest.

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