

MOF/Poly(Ethylene Oxide) Composite Polymer Electrolyte for Solid-state Lithium Battery

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Abstract: Solid polymer electrolytes (SPEs) with high flexibility and processability enable the fabrication of leak-free solid-state batteries with varied geometries. However, SPEs usually suffer from low ionic conductivity and poor stability with lithium metal anodes. Here, we propose nano-sized metal-organic framework (MOF) material(UiO-66) as filler for poly(ethylene oxide) (PEO) polymer electrolyte. The coordination of UiO-66 with oxygen in PEO chain and the interaction between UiO-66 and lithium salt significantly improve the ionic conductivity (3.0×10^{-5} S/cm at 25 °C, 5.8×10^{-4} S/cm at 60 °C) and transference number of Li^+ (0.36), widen the electrochemical window to 4.9 V (vs Li^+/Li), enhance the stability with lithium metal anode. As a result, the as-prepared Li symmetrical cells can continuously operate for 1000 h at $0.15 \text{ mA} \cdot \text{cm}^{-2}$, 60 °C. The results show that UiO-66 filler is effective to improve the electrochemical performance of polymer electrolyte.

Key words: composite electrolyte; poly(ethylene oxide); metal-organic framework material; lithium metal battery

Lithium-batteries technology can be enhanced by replacing the liquid electrolytes currently in use with solid polymer electrolytes (SPEs), enabling the fabrication of flexible, compact, laminated solid-state structures free from leaks and available in varied geometries^[1]. The SPEs explored for these purposes are ionically conducting polymer membranes formed by complexes between lithium salt (LiX) and high molecular weight polymer containing Li^+ coordinating groups, such as poly(ethylene oxide) (PEO). In PEO polymer electrolytes, with the polymer in amorphous state, Li^+ is fast transported along with local relaxation and segmental motion of polymer chain^[2-3], but the PEO tends to crystallize below 60 °C. So the conductivity of PEO polymer electrolytes reaches practically useful values (of the order of 10^{-4} S/cm) only at the temperature above 60 °C. Numerous attempts for diminishing the polymer crystallinity were made to improve the conductivity of the polymer electrolytes, including mixing with other co-polymers^[4], adding plasticizers^[5] and doping inorganic particles^[6-7]. Incorporating inorganic materials into polymer matrix is the most

successful approach, which improves ionic conductivity as well as electrochemical stability and mechanical properties. These inorganic materials mainly include nonconductive materials, such as SSZ-13^[8], Al_2O_3 ^[1], SiO_2 ^[9], and conductive materials, such as $\text{Li}_{0.33}\text{La}_{0.57}\text{TiO}_3$ ^[10], $\text{Li}_{6.75}\text{La}_3\text{Zr}_{1.75}\text{Ta}_{0.25}\text{O}_{12}$ ^[11], and $\text{Li}_{1.5}\text{Al}_{0.5}\text{Ge}_{1.5}(\text{PO}_4)_3$ ^[12]. Investigations showed that nanoparticles with Lewis acidic surface properties can more efficiently boost the dissociation of lithium salt and reduce the crystallinity of PEO, thus improving the ionic conductivity^[1, 13]. However, the poor contact between inorganic nanoparticle and PEO for the surface energy gap usually leads to inhomogeneous dispersion. Ceramic fillers grafted with molecular brushes^[14] and modified with dopamine^[15] are endowed with inorganic-organic properties. They are expected to enhance the miscibility with PEO, future improving the ionic conductivity and stability of polymer electrolytes.

Metal-organic frameworks (MOFs) consisting of metal ion clusters and organic linkers are typical nanoporous materials, which possess inorganic-organic hybrid

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property and high specific surface area, thus being ideal fillers to polymer electrolytes. In 2013, Yuan, *et al.*^[16] used $\text{Zn}_4\text{O}(\text{1,4-benzenedicarboxylate})_3$ metal-organic framework(MOF-5) as filler for PEO electrolyte obtaining high ionic conductivity of $3.16 \times 10^{-5} \text{ S}\cdot\text{cm}^{-1}$ (25 °C) due to the uniformly dispersion. But the weak metal-organic coordination bonds of MOF-5 are easy to be attacked, leading to crystal transition or structure collapse and poor stability for lithium battery.

In this work, nano-sized UiO-66, one of the extensive investigated MOFs, was introduced as filler into PEO electrolyte. The UiO-66 with outstanding hydrothermal and chemical stability does not contain transition metals which provide redox-active centers, so the electronic conduction can be avoided when contact with metallic Li.

1 Experimental

1.1 Synthesis of nano-sized UiO-66

Nano-sized UiO-66 was synthesized according to the reported two-step synthesis^[17]. (1) 207 mg ZrCl_4 (98%, Aladdin) was dissolved in 40 mL *N,N*-dimethylformamide (DMF) (99.9%, Aladdin) under stirring, and the solution was heated to about 120 °C for 2 h. Then 1 mL acetic acid was added and stirred for additional 0.5 h at 120 °C. (2) 147 mg 1,4-benzenedicarboxylic acid (H_2BDC) (99%, Aladdin) was added into the solution. And the resulting mixture was introduced into a 50 mL Teflon-lined stainless-steel autoclave and placed in an oven at 120 °C for 24 h. After cooling to room temperature, the resulting precipitates were centrifuged, washed with DMF, purified in methanol and then dried at 60 °C under vacuum for 24 h.

1.2 Preparation of UiO-66/PEO composite polymer electrolytes (CPEs)

PEO ($M_w = \sim 600,000$, 99.9%, Aladdin) was dried at 50 °C, and lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) (99%, Aladdin) was dried at 100 °C for 24 h under vacuum and stored in an Ar-filled glove box. Firstly, LiTFSI was dissolved in anhydrous acetonitrile, and UiO-66 and PEO were added under magnetic stirring to afford homogeneous solution, in which the molar ratio of $\text{EO} : \text{Li}^+$ was kept 16 : 1, and the content of nano-sized UiO-66 fillers was designed to be 0, 5%, 10%, 15%, 20%, 25%, naming the corresponding electrolytes as SPE, CPE-(5%, 10%, 15%, 20%, 25%). Afterwards, the solution was cast on polytetrafluoroethylene template to volatilize the solvent at ambient temperature. Finally, the membranes were dried at 60 °C for 12 h under vacuum to volatilize the residual solvent.

1.3 Sample characterization

The crystalline structures of ingredients were collected from X-ray diffraction (XRD) with Cu-K α radiation ($\lambda = 0.1542 \text{ nm}$) at room temperature ($2\theta = 5^\circ - 50^\circ$) with the step of 0.1 (°)/s. The structure morphologies of UiO-66 and CPE were revealed by the scanning electron microscopy (SEM, Hitachi, S-3400N).

1.4 Electrochemical measurement and cells assembly

The ionic conductivity was measured at temperature from 25 to 80 °C in symmetric cell with stainless steel (SS) electrodes by the AC impedance analysis (Autolab, Model PGSTAT302N) in the frequency range from 1 Hz to 1 MHz and at an amplitude of 50 mV. Linear sweep voltammetry (LSV) was employed to examine the electrochemical window in SS/electrolyte/Li cells, conducting from 3 to 5.5 V at a scan rate of 10 mV/s. The transference number of Li^+ (t_+) was tested in Li/electrolyte/Li cells and calculated according to $t_+ = \frac{I_\infty(\Delta V - I_0 R_0)}{I_0(\Delta V - I_\infty R_\infty)}$,

where ΔV is the applied DC polarization voltage (10 mV), I_0 and I_∞ are the initial and steady current values during polarization, respectively. R_0 and R_∞ are the resistance values before and after polarization, respectively. For inhibition ability of lithium dendrites growth test, a symmetric cell with solid electrolyte sandwiched between two lithium metal electrode was assembled, and the test was carried out at 60 °C.

2 Results and discussion

UiO-66 ($[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{BDC})_6]$, where BDC^{2-} is 1,4-benzenedicarboxylic acid radical) with a face-centered cubic (fcc) lattice structure (Fig. 1(a)) consisting of $\text{Zr}_6\text{O}_4(\text{OH})_4$ clusters and BDC linkers possesses 1.2 nm octahedral and 0.75 nm tetrahedral cages^[18]. Fig. 1(b) is the SEM image of as-prepared UiO-66 where the crystals are spherical shape with 80–150 nm in size. The UiO-66 was incorporated into PEO-LiTFSI polymer electrolyte to fabricate composite electrolyte by simple solution-cast method. A smooth surface of composite electrolyte is observed in Fig. 1(c), indicating that the nano-sized UiO-66 fillers are uniformly distributed in PEO matrix due to the inorganic-organic hybrid property of UiO-66.

The phase purity of as-prepared UiO-66 crystals was confirmed by the XRD pattern which matches well with the simulated one based on the reported lattice parameters, as shown in Fig. 2(a), indicating the successful synthesis of nanostructure of UiO-66. The content of UiO-66 in polymer electrolyte was optimized to achieve high ionic conductivity. Arrhenius plots for PEO electrolytes with different UiO-66 contents are shown in Fig. 2(b).

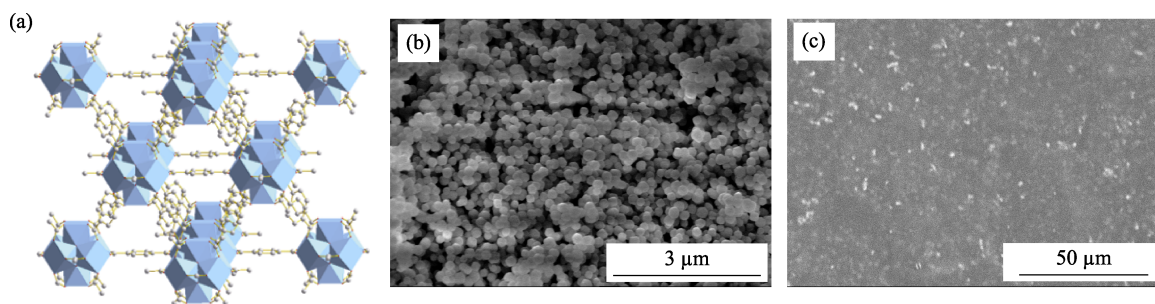


Fig. 1 (a) Crystal structure of UiO-66, and SEM images of (b) nano-sized UiO-66 and (c) UiO-66/PEO composite polymer electrolyte

It is clear that higher ionic conductivity is obtained with the addition of the nano-sized UiO-66 into PEO electrolyte. As the coordination of $[\text{Zr}_6\text{O}_4(\text{OH})_4]^{12+}$ with oxygen in PEO reduces the crystallinity of PEO chain to promote the segmental motion of polymer chain, which is proved by the XRD pattern of CPE-10% compared with PEO (Fig. 2(a)). Moreover, the interaction between $[\text{Zr}_6\text{O}_4(\text{OH})_4]^{12+}$ and TFSI⁻ promotes the dissociation of lithium salt. The increase of UiO-66 fillers content below a certain value is accompanied by the promotion of ionic conductivity. However, the further increase of fillers reduces ionic conductivity owing to dilution and block effects. The CPE-10% shows the highest ionic conductivity (3.0×10^{-5} S/cm at 25 °C, 5.8×10^{-4} S/cm at 60 °C), while the ionic

conductivity of SPE is only 5.0×10^{-6} S/cm at 25 °C and 1.7×10^{-4} S/cm at 60 °C. The conducting properties of CPE-10% at the temperature from 25 to 80 °C were also investigated by AC impedance spectroscopy, and the Nyquist plots are presented in Fig. 2(c). It shows that the impedance value decreases with the temperature increasing.

The effect of UiO-66 on the electrochemical window of PEO electrolyte was investigated by LSV at 60 °C. As shown in Fig. 2(d), the steady platform of CPE-10% at about 4.9 V is higher than that of SPE, owing to the coordination of UiO-66 with oxygen which promotes the oxidation voltage of PEO and the fact that Zr(IV) in UiO-66 is difficult to be reduced. Thus, it is expected

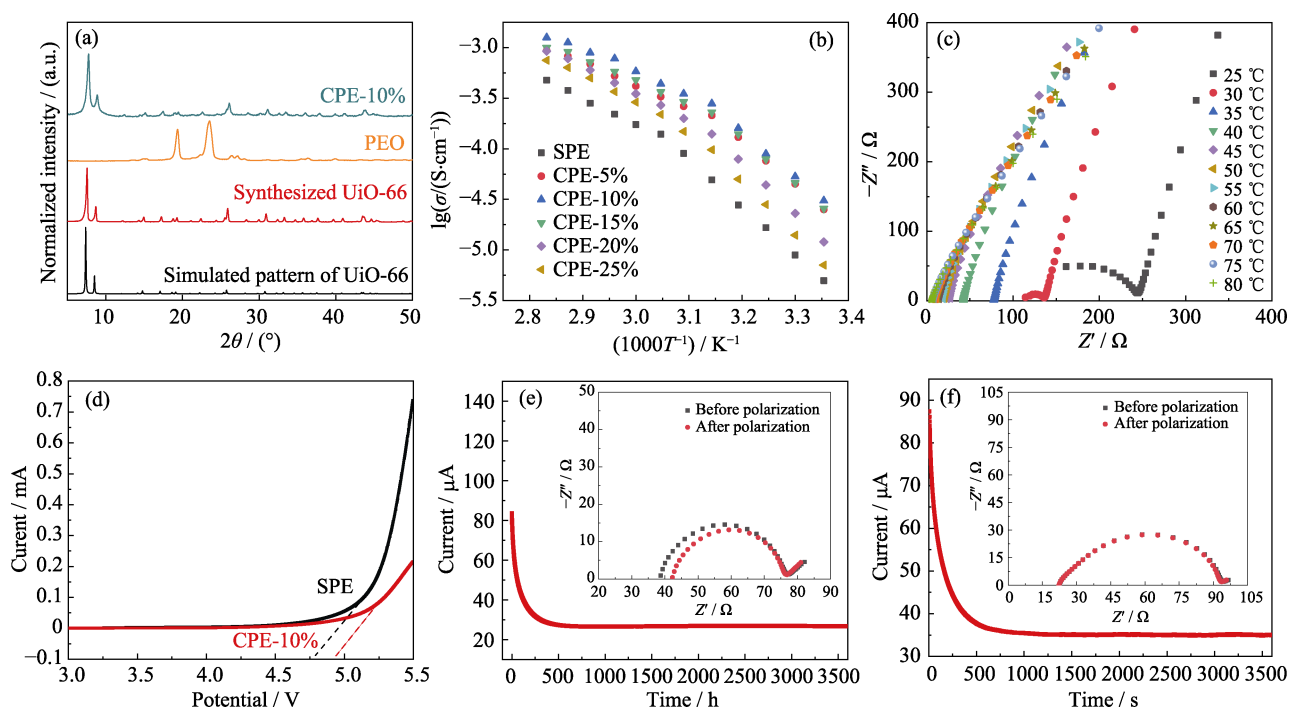


Fig. 2 (a) XRD patterns of simulated UiO-66, synthesized nano-sized UiO-66, PEO, and CPE-10%; (b) Arrhenius plots for the ionic conductivities of PEO electrolytes with different contents of UiO-66; (c) Nyquist plots within frequency of 1 Hz-1 MHz for the CPE-10% at the temperature from 25 to 80 °C; (d) LSV curves of SPE and CPE in SS/electrolyte/Li cells at 60 °C; (e) DC polarization profile of symmetric Li/SPE/Li cell at an applied voltage of 10 mV at 60 °C; (f) DC polarization profile of symmetric Li/CPE-10%/Li cell at an applied voltage of 10 mV at 60 °C. Insets in (e,f): AC impedance spectra of the corresponding symmetric cells before and after DC polarization

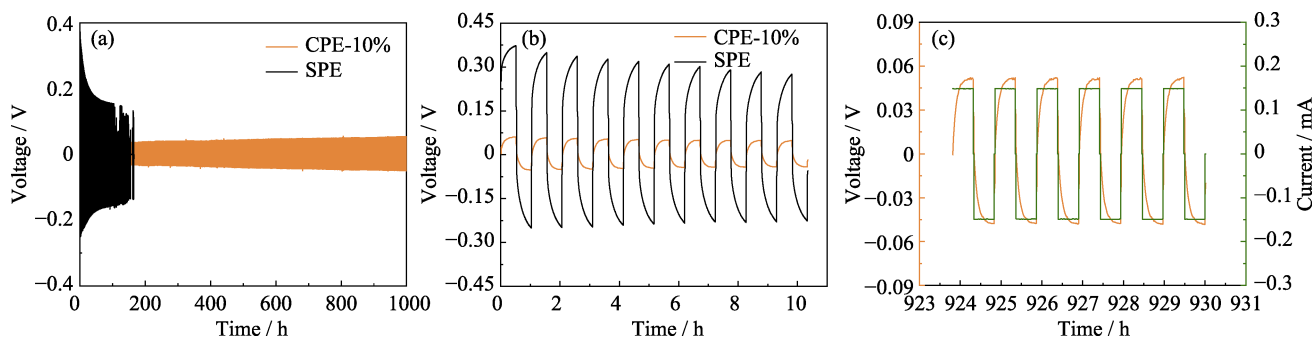


Fig. 3 (a) Galvanostatic cycles with a constant current density of $0.15 \text{ mA}\cdot\text{cm}^{-2}$ for symmetric Li/CPE-10%/Li and Li/SPE/Li cells at $60 \text{ }^\circ\text{C}$, (b) magnification of galvanostatic cycles of Li/CPE-10%/Li and Li/SPE/Li cells at 1–10 cycle, and (c) magnification of galvanostatic cycles of Li/CPE-10%/Li cell at 895–900 cycle

that the CPE is suitable for a lithium battery matching with high-voltage positive cathode. The transference number of Li^+ is an important parameter providing information about the rate capability contribution of Li^+ in solid state electrolyte. Time-current curves following 10 mV of DC polarization for SPE and CPE-10% are presented in Fig. 2(e-f). The t_+ of CPE-10% is 0.36 and higher than that of SPE (0.25). It is due to the fact that the coordination of $[\text{Zr}_6\text{O}_4(\text{OH})_4]^{12+}$ with the oxygen of PEO in CPEs weakens the coordination of oxygen with Li^+ deriving the transfer of Li^+ , and a fraction of anions are immobilized by $[\text{Zr}_6\text{O}_4(\text{OH})_4]^{12+}$.

The long-term electrochemical stability against lithium anode is one important feature of solid-state electrolyte, which could be measured by galvanostatic lithium plating and stripping in symmetric Li/electrolyte/Li cells. Fig. 3(a) shows a voltage window with a constant current density of $0.15 \text{ mA}\cdot\text{cm}^{-2}$ for 1 h each cycle at $60 \text{ }^\circ\text{C}$. In Fig. 3(b), the symmetric Li/CPE-10%/Li cell shows a charge-discharge voltage range between -0.058 and 0.06 V in the first cycle and then slightly decreases to -0.048 – 0.053 V after 900 cycles, indicating the good electrochemical stability between CPE and lithium metal and the excellent CPE ability to block lithium dendrite growth. This ability can be ascribed to the following factors: (1) the improved mechanical strength; (2) a fraction of anions immobilized by $[\text{Zr}_6\text{O}_4(\text{OH})_4]^{12+}$ boosting the uniform Li plating and stripping^[11,19]. In contrast, the charge-discharge voltage of symmetric Li/SPE/Li cell ranges from -0.25 to 0.37 V in the first cycle (Fig. 3(b)), and the battery shows short circuit after 104 h. Such poor cycle performance could be blamed for uneven Li plating and stripping, which results from the low t_+ of SPE possessing plenty of free anions.

3 Conclusions

In summary, the PEO-based electrolyte with UiO-66

as filler was fabricated *via* solution-casting technique. The as-obtained CPE-10% shows high ionic conductivities of $3.0\times 10^{-5} \text{ S/cm}$ at $25 \text{ }^\circ\text{C}$ and $5.8\times 10^{-4} \text{ S/cm}$ at $60 \text{ }^\circ\text{C}$, which are attributed to the following factors: (1) the low crystallinity of PEO owing to the coordination of $[\text{Zr}_6\text{O}_4(\text{OH})_4]^{12+}$ with oxygen in PEO chain; (2) the interaction between TFSI^- and $[\text{Zr}_6\text{O}_4(\text{OH})_4]^{12+}$ promoting the dissociation of lithium salt. The higher transference number of Li^+ (0.36) is due to the immobility of a fraction of anion which also benefits the ability to suppress lithium dendrite growth of the CPE. The improved mechanical strength and excellent electrochemical stability of CPE against lithium metal endow the effective suppression of lithium dendrite growth, enabling a long cycle life for lithium metal batteries (over 1000 h cycling at $0.15 \text{ mA}\cdot\text{cm}^{-2}$, $60 \text{ }^\circ\text{C}$).

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固态锂电池用 MOF/聚氧化乙烯复合聚合物电解质

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摘要: 固态聚合物电解质具有柔韧性好和易于加工的优势, 可制备各种形状的固态锂电池, 杜绝漏液问题。但固态聚合物电解质存在离子电导率低以及对锂金属负极不稳定等问题。本研究以纳米金属-有机框架材料 UiO-66 为聚合物电解质的填料, 用于改善电解质的性能。UiO-66 与聚氧化乙烯(poly(ethylene oxide), PEO)链上醚基的氧原子的配位作用以及与锂盐中阴离子的相互作用, 可显著提高聚合物电解质的离子电导率(25 °C, 3.0×10^{-5} S/cm; 60 °C, 5.8×10^{-4} S/cm), 并将锂离子迁移数提高至 0.36, 电化学窗口拓宽至 4.9 V。此外, 制备的 PEO 基固态电解质对金属锂具有良好的稳定性, 对称电池在 60 °C、 $0.15 \text{ mA} \cdot \text{cm}^{-2}$ 电流密度下可稳定循环 1000 h, 锂电池的电化学性能得到显著改善。

关键词: 复合电解质; 聚氧化乙烯; 金属-有机框架材料; 锂金属电池

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