**Supporting Information**

A gel polymer electrolyte with IL@UiO-66-NH2 as fillers for high-performance all-solid-state lithium metal batteries

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**1．Other Experimental Sections:**

***1.1 Material Characterization***

In order to identify the crystalline structure of synthesized samples, the X-ray diffraction (XRD) patterns have been tested at room temperature between 5° and 50° (Bruker-D8 Advance). The overall morphologies of UiO-66-NH2 pellets and GPEs membranes were examined by field-emission scanning electron microscope (FESEM, FEI-Quanta FEG 250). The N2 adsorption / desorption isothermal was performed. The energy dispersive spectrometer (EDS) mapping was adopted to observe the distribution of different elements (F, S, Zr, N).

***1.2 Electrochemical Measurement***

Symmetrical blocking cells (SS / GPE /SS) were prepared for AC impedance testing at different temperatures with an electrochemical work station (CHI-660E). The ionic conductivity of polymer electrolyte can be obtained by the analysis and calculation of alternating current impedance (AC impedance). The scanning frequency range is 10-1 Hz ~ 106 Hz, the scanning rate is 10 mV, and the test temperature range is 30-90 ℃, all tests were conducted after 2 hours of insulation. The measurement of ionic conductivity (*σ*, S⋅cm-1) is calculated according to **Equation (S1)**:

**(S1)**

**where** *R* (Ω) is the resistance value of the bulk electrolyte, *L* (cm) is the thickness of the electrolyte membrane, and *S* (cm2) is the cross-sectional area of the SS electrodes.

The typical electrochemical window of the GPE membrane is measured using a linear sweep voltammetry at the scan rate of 1 mV s-1 with the GPE membrane sandwiched between the lithium foil as the reference and counter electrode and the stainless steel sheet as working electrode at room temperature in the voltage range of 2-6 V. To determine lithium-ion transference number (tLi+), the symmetric lithium cells were assembled for the chronoamperometry test at an applied DC voltage of 10 mV at 60 ℃. Electrochemical impedance spectroscopy (EIS) was also performed before and after the DC polarization with the frequency ranging from 106 Hz to 10-1 Hz. The tLi+ value was calculated by **Equation (S2)** as follows:

**(S2)**

**where** *△V* is the polarization voltage, *I0*is the initial current, *Iss* is the steady state current, *R0* is the initial total resistance, and *Rss* is the steady state total resistance.

***1.3 Cell assembly and Test***

Symmetric stainless steel / electrolyte / stainless steel cells were assembled for EIS measurements in the pouch cell configuration. Cyclic voltammetry (CV) measurements were performed in lithium (Li) / GPE / LiFePO4 (LFP) in the coin CR2032 cells at 60 ℃ at a voltage range of 2.6 - 4.0 V. The LFP cathode was prepared by a blade-coating method with slurring the active material (70 wt% LFP, 20 wt% carbon black, 10 wt% Polyvinylidene fluoride (PVDF)) in *N*-methyl-2-pyrrolidone (NMP) and coating onto the aluminium (Al) foil substrate, following which was dried at 120 ℃ overnight in a vaccum oven and then the electrode was punched with a diameter of 14 mm. All the cells were tested between 2.6 - 4.0 V without liquid electrolyte at 60 ℃ by the LAND battery tester system.

**Supplementary Figures.**

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**Fig. S1.** SEM images of various wt% IL@MOFs nanocomposites.

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**Fig. S2.** N2 absorption/desorption isotherm of UiO-66-NH2 (without IL).



**Fig. S3.** Temperature-dependent EIS spectroscopy curves for UPP-0, UPP-3, and UPP-4 GPEs.



**Fig. S4.** Nyquist plots of symmetric Li/UPP-5/Li cells before cycling (black) and after 30 cycles (red) at 0.1 mA cm−2 at 60℃; the inset is the equivalent circuit.

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**Fig. S5.** Nyquist plots of (a) UPP-0 and (b) UPP-5 batteries before cycling (black) and after 100 cycles (red) at 0.1 mA cm−2 at 60℃; the inset is the equivalent circuit.

**Supplementary Tables.**

**Table S1.** N2 absorption/desorption results of MOFs with different wt% of IL

|  |  |
| --- | --- |
| wt% of IL | Total Surface area(*S*BET)(m2/g) |
| 0% | 809.45 |
| 30% | 402.34 |
| 40% | 55.00 |
| 50% | 53.56 |

**Table S2.** Lithium-ion transference number () and corresponding test values of UPP-5 at 60℃

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Sample | *I*0 / A | *I*ss / A | *R*0 / Ω | *R*ss / Ω | *t*Li+ |
| UPP-0 | 0.00003291 | 0.00001658 | 116.2 | 122 | 0.259 |
| UPP-5 | 0.0002294 | 0.0001446 | 15.811 | 15.826 | 0.52 |