Supporting Information

Multiscale Optimization of Li-ion Diffusion in Solid Lithium Metal Battery via Ion Conductive Metal-organic Frameworks

Qi Zhang, ‡[a] Dixiong Li, ‡[a] Jia Wang,[b] Sijia Guo,[a] Wei Zhang,[a] Dong Chen,[a] Qi Li,[a] Xianhong Rui,[a] Liyong Gan[c] and Shaoming Huang*[a]

[a] Guangzhou Key Laboratory of Low-Dimensional Materials and Energy Storage Devices, School of Materials and Energy, Guangdong University of Technology, Guangzhou, 510006, China

[b] Institute of Materials Chemistry, Technische Universität Wien, Vienna, 1060, Austria

[c] Institute for Structure and Function and Department of Physics, Chongqing University, Chongqing, 400030, China

***Corresponding author.** E-mail address: *smhuang@gdut.edu.cn*

‡ These authors contributed equally to this work.

Experiment section

Materials: Zircomiun tetrachloride (99.9%, Sigma-Aldrich), 1,2,4,5-Benzenetetracarboxylic acid (99.9%, Sigma-Aldrich), 1,2,4-Benzenetetracarboxylic acid (99.9%, Sigma-Aldrich), dimethylformamide (DMF) (99.9%, Sigma-Aldrich), formic acid (99.9%, Sigma-Aldrich), bis(trifluoromethanesulfoneimide) lithium salt (LiTFSI) (99.99%, Aladdin), 1-ethyl-3-methylimidazolium-bis(trifluoromethyl-sulfnyl) imide ([EMIM][TFSI]) (97.0%, Aladdin), polyvinylidenefluoride-co-hexafluoropropylene (PVDF-HFP) (Mw = 400 000, Sigma-Aldrich), polyvinylidene difluoride (PVDF), propylene carbonate (PC) (99.9%, Sigma-Aldrich) were used as-purchased without further purification.

Synthesis of nanoparticles of MOFs: UiO-66-SO_3H was synthesized as former reported.[1] A mixture of $ZrOCl_2 \cdot 8H_2O$ (1.0 g, 3.1 mmol), sodium 2,5-dicarboxybenzenesulfonate (BDC-SO_3Na, 0.83 g, 3.1 mmol) was dissolved in a mixture of formic acid (11.7 mL) and N,N-dimethylacetamide (DMA) (30 mL). This solution was then placed in a 100 mL autoclave and heated at 150 °C for 24 h. After centrifugation and drying, the powder was collected.

UiO-66-2OH was synthesized as former reported.[2] A mixture of $ZrCl_4$ (250 mg, 1.08 mmol), 2,5-dihydroxyterephthalic acid (294 mg, 1.5 mmol) was dissolved in a mixture of hydrochloric acid (2 mL) and DMF (30 mL). This solution was then introduced in a 50 mL autoclave and heated at 100 °C for 12 h. The powder was collected by centrifuge and washed with DMF and ethanol for 3 times.

UiO-66 was synthesized as former reported.[3] A mixture of $ZrCl_4$ (0.93g, 4 mmol), 1,4-benzenedicarboxylic acid (H_2BDC) (1.32g, 8mmol) was dissolved in a mixture of hydrochloric acid (0.67 mL) and DMF (24 mL). This solution was then introduced in a 50 mL autoclave and heated at 220 °C for 16 h. The white powder was collected by centrifuge and washed with DMF and ethanol for 3 times.

UiO-66-CO_2H was synthesized as former reported. A mixture of $ZrCl_4$ (1.2g, 5 mmol), 1,2,4-Benzenetetracarboxylic acid (2.2g, 10mmol) was dissolved under stirring in 25 mL of distilled water at room temperature. This solution was then heated at 100 °C under reflux for 24h. After centrifugation and drying, the powder was collected.

Synthesis of LCMOFs: LCMOF is obtained by adding 100 mg MOFs in 15 mL of 1 M LiTFSI solution in PC, and keeping the mixture in a shaker for 6 hours to adsorb Li^+ in pores. The solid is collected by centrifugation and washed with PC slightly to remove the LiTFSI on surface. At last the solid is dried at 100 °C to obtain LCMOFs.

Preparation of LCMOF/PVDF-HFP/Li-IL solid electrolyte: Li-IL is obtained by adding 574.18 mg LiTFSI in 2 mL [EMIM][TFSI] and heated at 120 °C overnight before use. Different ratios of LCMOF and Li-IL were first stirred to form a homogenous mixture. A prepared solution of PVDF-HFP in DMF (75 mg/mL) was then added. The mass ratio between LCMOF and PVDF-HFP was adjusted by the added volume of PVDF-HFP solution. After magnetically stirring for 24 h, the mixture was casted onto cleaned petri dishes and prebaked for half an hour under infrared lamp. Then the mixture was further dried at 60 °C under vacuum for 12 h to completely remove the DMF solvent. The obtained flexible membranes were stored in an argon filled glove box($\leqslant$1 ppm H_2O and O_2). The solid electrolyte was activated in 1 M LiTFSI solution of PC for 2 minutes and dried before test.

Computational calculation: All calculations were carried out with the spin-polarized Perdew-Burke-Ernzerhof generalized gradient approximation implemented in Vienna Ab-Initio Simulation Package.1-3 A plane-wave basis set within a cutoff energy of 500 eV and a Monkhorst-pack 3× 3 × 3 k-mesh were used. The structures were allowed to relax with a force convergence criteria of 0.01 eV/Å. The van der Waals interactions were considered using the empirical correction of Grimme (D2).4 The climbing image nudged elastic band method5 was used to calculate the minimum energy paths of Li^+ diffusion in UiO-66 ($Zr_6O_4(OH)_4(BDC)_6$), UiO-66-CO_2H ($Zr_6O_4(OH)_4$(BDC-$CO_2H)_6$) and UiO-66-2CO_2H ($Zr_6O_4(OH)_4$(BDC-2$CO_2H)_6$).[4-8]

Characterization results

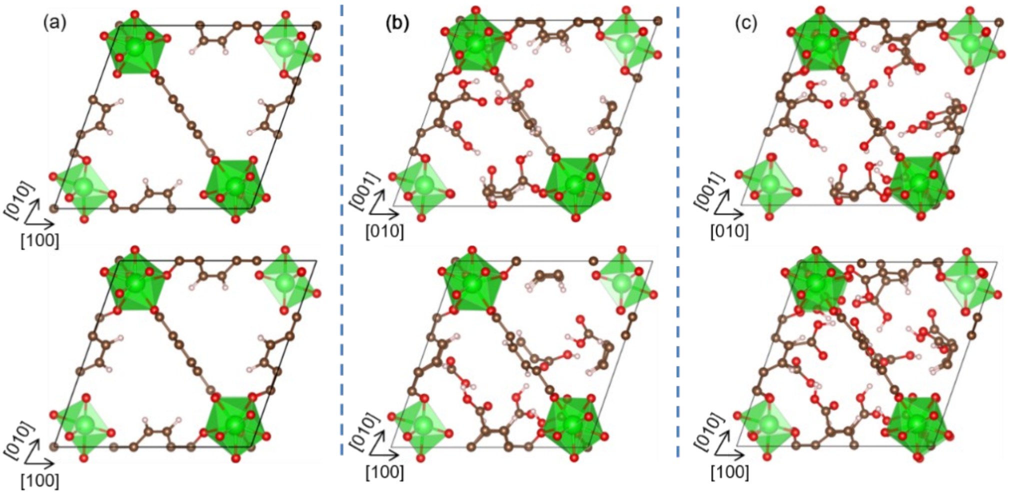


Fig. S1 Top (upper panel) and side (lower panel) views for UiO-66 (a) UiO-66-CO_2H (b) and UiO-66-2CO_2H (c). Red, gray and green balls indicate O, C and Zr atoms respectively.

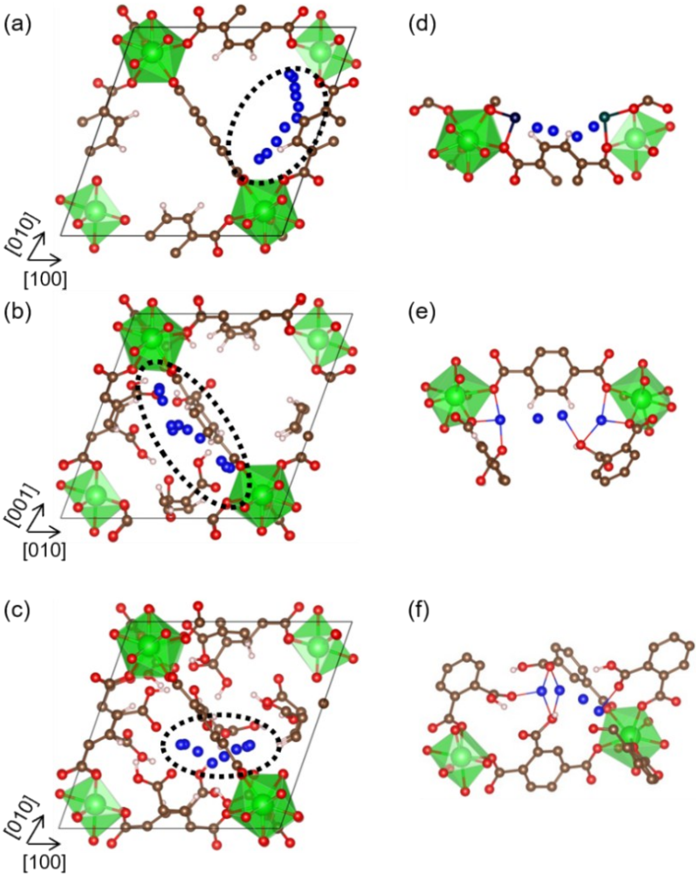


Fig. S2 (a, b, c) Corresponding views of Li^+ diffusion in UiO-66, UiO-66-CO_2H and UiO-66-2CO_2H respectively. Blue, red, gray and green balls indicate Li, O, C and Zr atoms, respectively. (d, e, f) Corresponding zoomed structure of the circled region in pathways for UiO-66, UiO-66-CO_2H and UiO-66-$2CO_2H$, respectively.

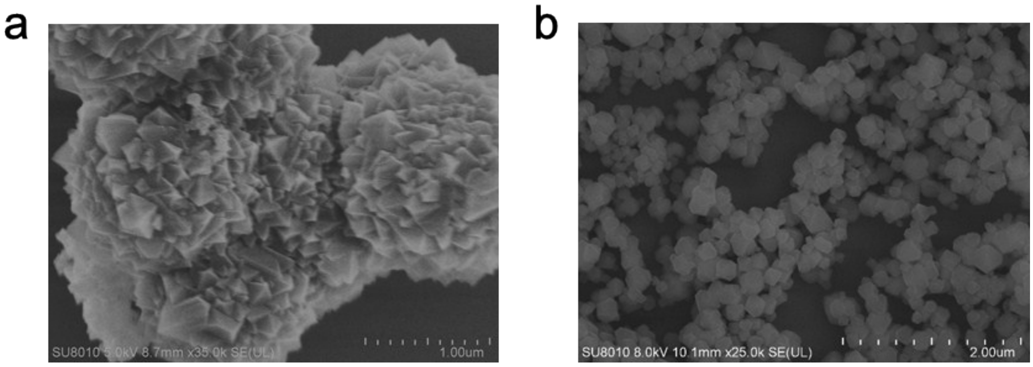


Fig. S3 SEM morphology for the conglobate polycrystal and UiO-66-$2CO_2H$-NDP.

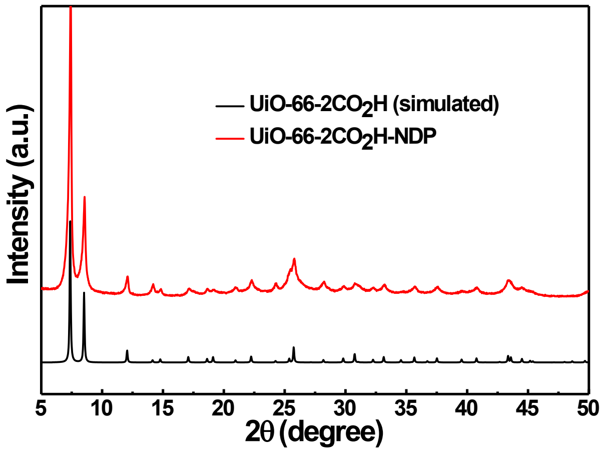


Fig. S4 PXRD of simulated UiO-66-$2CO_2H$ simulated and UiO-66-$2CO_2H$-NDP.

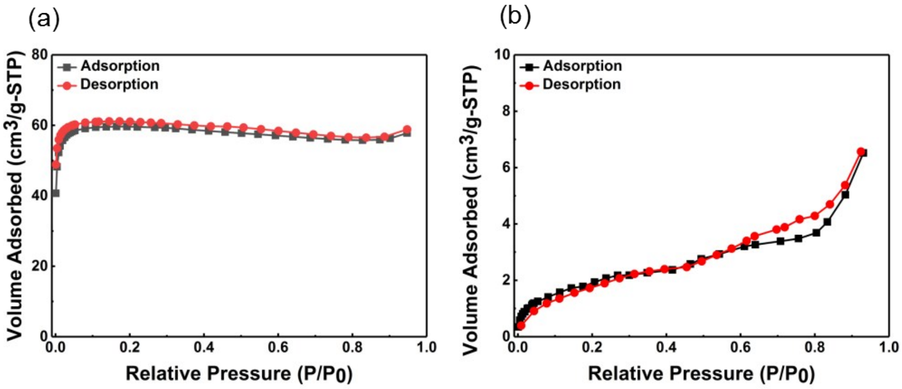


Fig. S5 (a) BET of UiO-66-$2CO_2H$-NDP. (b) BET of LCMOF-1

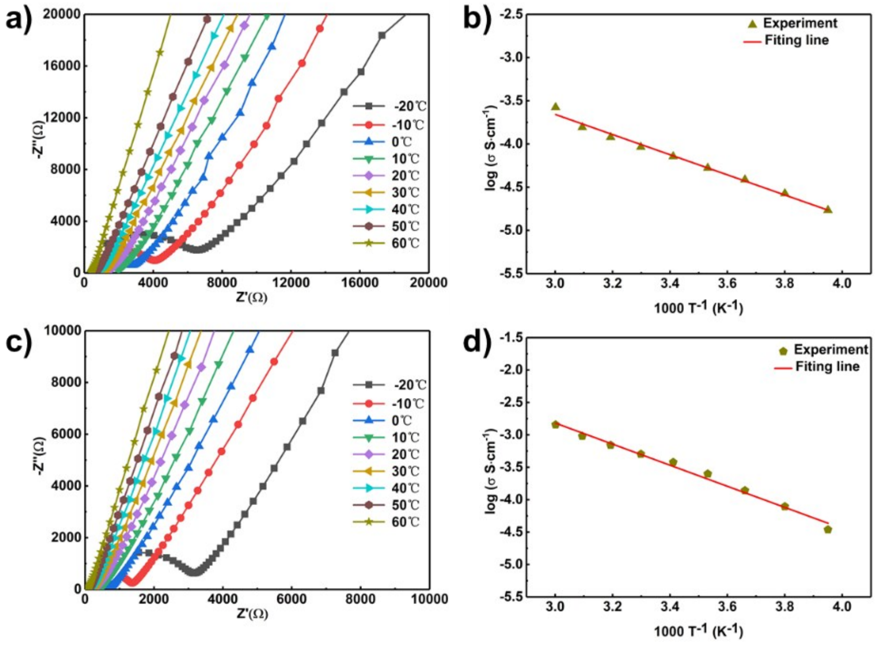


Fig. S6 (a) EIS of Li^+ inserted UiO-66 powder from -20 to 60 °C. (b) Corresponding Arrhenius plot of the SE based on Li^+ inserted UiO-66 powder. (c) EIS of LCMOF-1 from -20 to 60 °C. (d) Corresponding Arrhenius plot of the ionic conductivity of LCMOF-1 based SE.

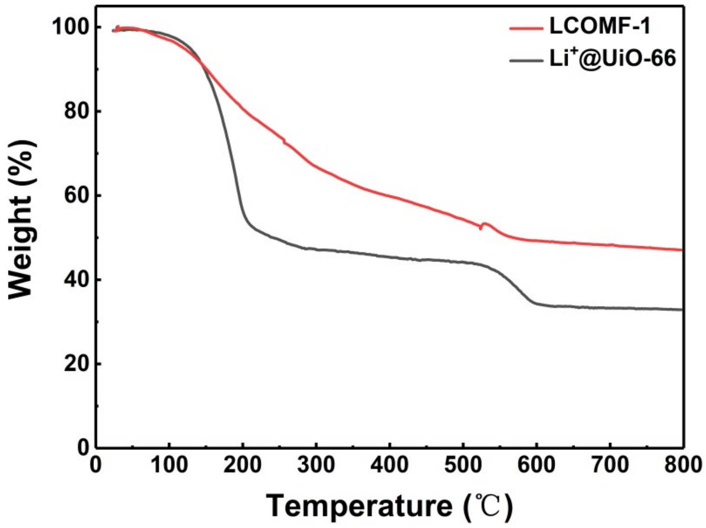


Fig. S7 TGA plot for LCOMF-1 compared to the TGA plot of UiO-66.

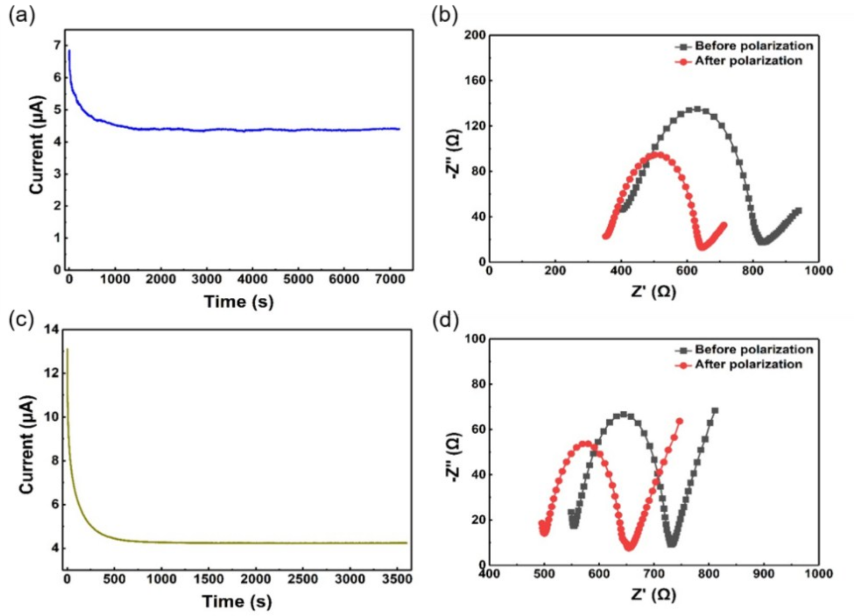
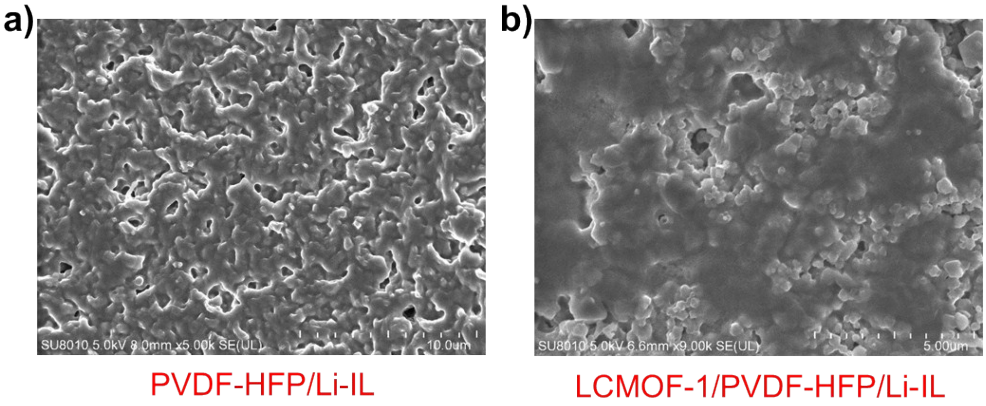


Fig. S8 (a) DC polarization plot of LCOMF-1 powder. (b) the AC impedance spectra before and after polarization of LCOMF-1 powder. (c) DC polarization plot of Li@UiO-66 powder. (d) the AC impedance spectra before and after polarization of Li@UiO-66 powder.



PVDF-HFP/Li-IL

LCMOF-1/PVDF-HFP/Li-IL

Fig. S9 A sectional view of the PVDF-HFP/Li-IL membrane and LCMOF-1 derived SE.

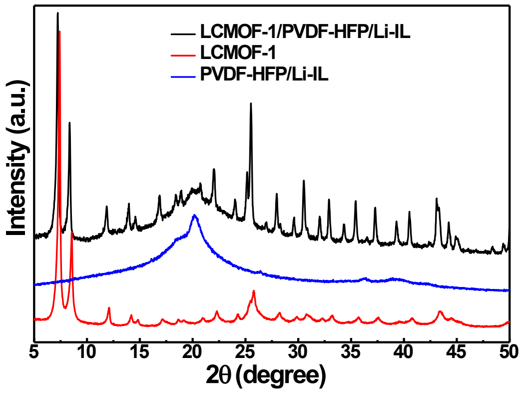


Fig. S10 PXRD of LCOMF-1, PVDF-HFP/Li-IL membrane and LCMOF-1/PVDF-HFP/Li-IL membrane.

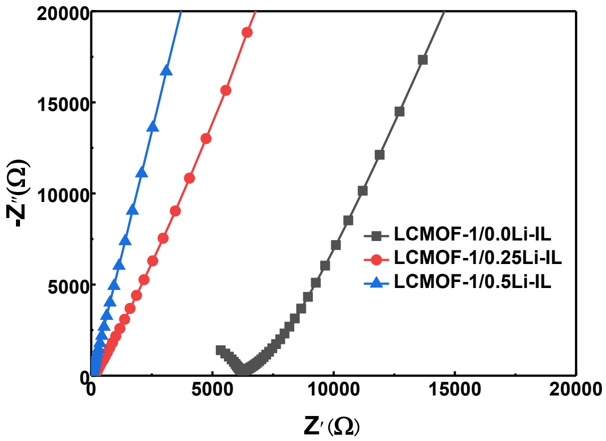


Fig. S11 EIS of LCMOF-1/PVDF-HFP/Li-IL membrane with different amount of Li-IL at room temperature.

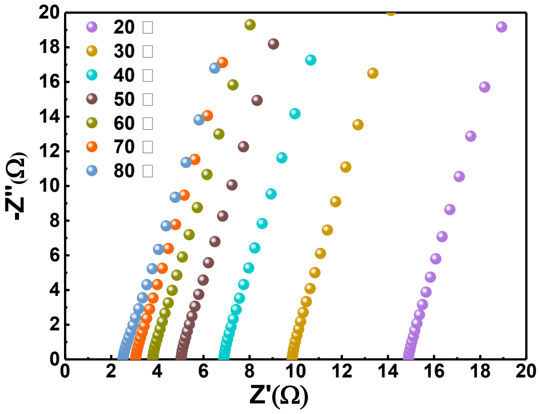


Fig. S12 Enlarged view for the EIS of LCMOF-1 at high-frequency region.

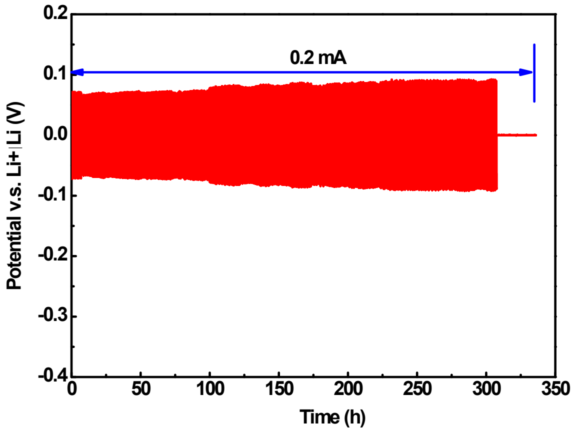


Fig. S13 Li-plating/stripping cycles of the Li|PVDF-HFP/Li-IL|Li symmetric cell at current of 0.2 mA.

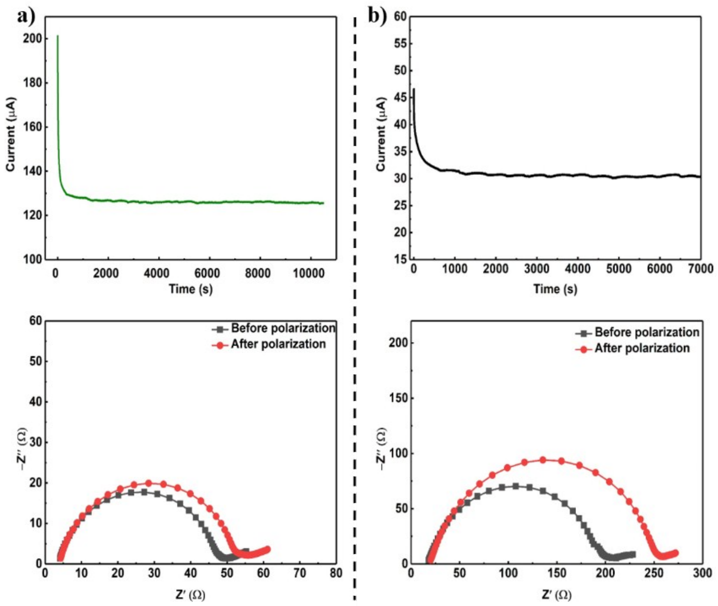


Fig. S14 Potentiostatic measurement (up) and electrochemical impedance spectra (bottom) used to calculate the Li$^+$ transference number of (a) PVDF-HFP/Li-IL, (b) LCMOF-1/PVDF-HFP/Li-IL.

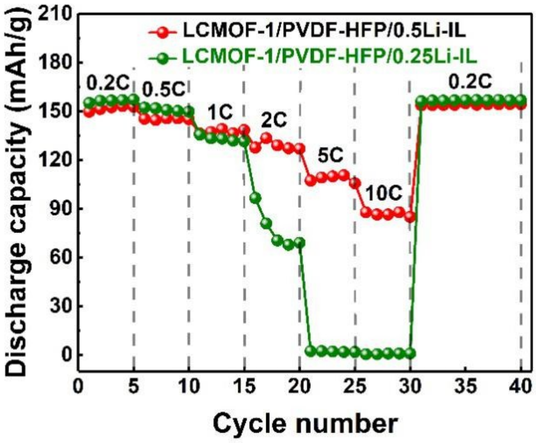


Fig. S15 C-rate performance of LCMOF-1/PVDF-HFP/Li-IL based SSB with different ratio of Li-IL.

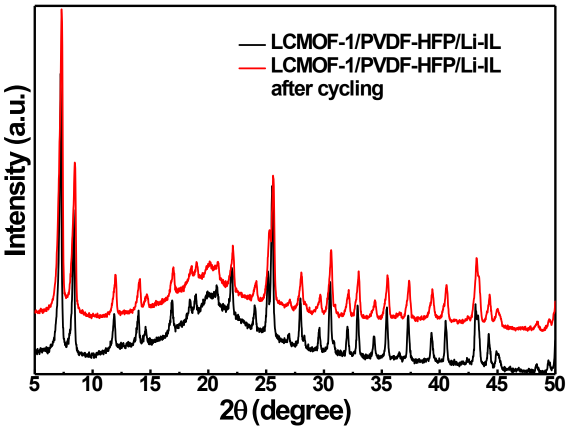


Fig. S16 PXRD of LCMOF-1/PVDF-HFP/Li-IL membrane before and after cycling.

Reference

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