Supplementary Information for

A MOF vertical array enables continuous ion transport pathways with high throughput

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Supplementary Experimental Section

Materials

LiTFSI was kindly provided by Guangzhou Tinci Materials Technology Co. Ltd. Poly(vinylidene fluoride) (PVDF, Mw: 1,000,000 g mol^{-1}) was purchased from Arkema. Polyethylene oxide (PEO, Mw: 600,000 g mol^{-1}), $Co(NO_3)_2 \cdot 6H_2O$ (99%) and 2-methylimidazole were purchased from Macklin. The separator with ceramic coating layer (MA-EN-SE-0D) was purchased from Guangdong Canrd New Energy Technology Co. Ltd.

Synthesis of MOF particle

2.6 g of 2-methylimidazole and 1.17 g of $Co(NO_3)_2 \cdot 6H_2O$ were first dissolved in two 80 mL of deionized water, respectively. After stirring vigorously for 5 min, the above two solutions were mixed quickly and allowed to react for 5 h. Then, the purple powder was obtained by centrifugation with a speed of 10,000 r min^{-1} for 5 min and washed with methanol three times. Finally, the MOF particle was obtained after activation in a vacuum oven at 150 ℃ for 24 h.

Fabrication of MOF particle CSE

First, 0.042 g MOF powder, 0.1 g PVDF, and 0.1 g LiTFSI were added into 1 ml NMP solvent and stirred for 6 h at 50 °C. Then, the above solution was bladed on a clean and smooth glass plate using a 250 μm doctor blade, which was further vacuum dried at 80 °C for 24 h, denoted as PVDF/MOF particle layer. In another solution, 0.01 g MOF powder were added into 1 ml PEO/LiTFSI solution (the molar ratio of [EO]: LiTFSI was 16:1) and stirred for 6 h, which was then coated on the surface of

PVDF/MOF particle layer. The film was then under vacuum dried at 80 °C for 24 h to obtain PVDF/MOF particle/PEO CSE, denoted as MOF particle CSE. Finally, the film was cut into circular disc with a diameter of 19 mm and stored in a glove box prior to use.

Material characterization

The X-ray powder diffraction patterns were characterized using a diffractometer (D8 Advance, Bruker) with Cu Kα radiation. The morphology investigation was performed using a scanning electron microscope (SEM, MAIA3, TESCAN Brno, s.r.o.). Thermogravimetric analysis (TGA) was tested from 30 to 800 °C at 10 °C min^{-1} under Ar atmosphere.

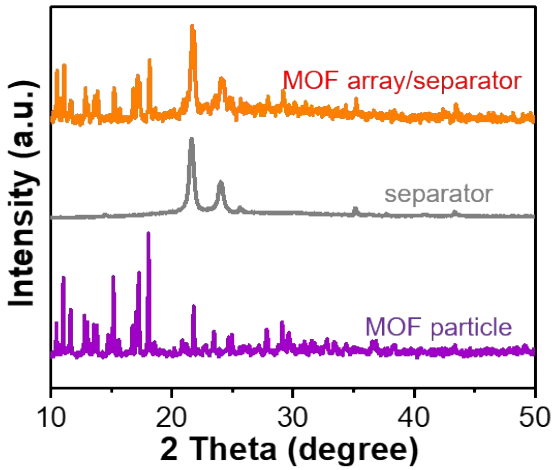

Fig. S1. XRD pattern of MOF particle, separator, and MOF array/separator.

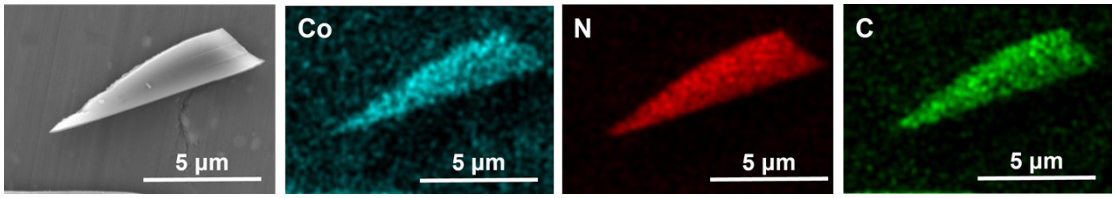

Fig. S2. SEM image and corresponding EDS element mapping images of the MOF particle.

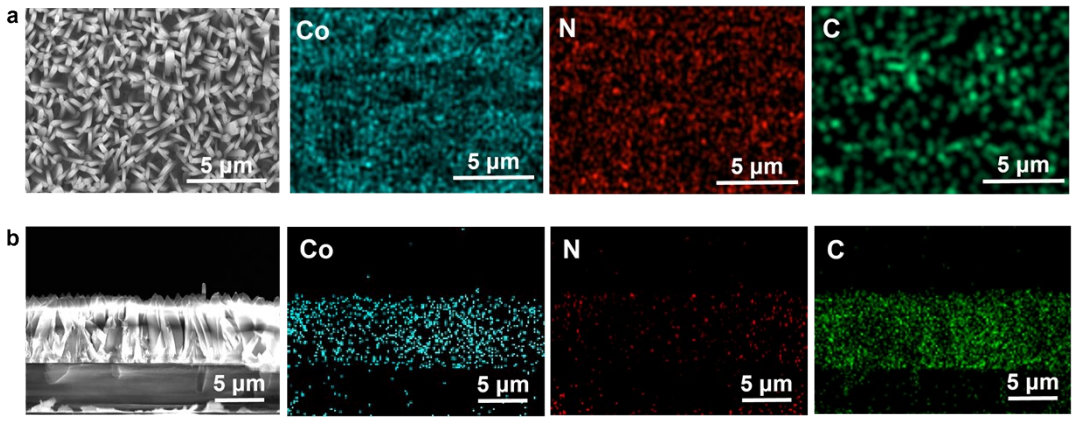

Fig. S3. (a) Top view and (b) cross-sectional view of SEM images and corresponding EDS element mapping images of MOF array.

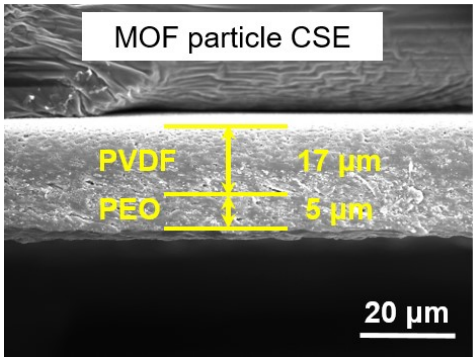

Fig. S4. Cross-sectional SEM image of MOF particle CSE.

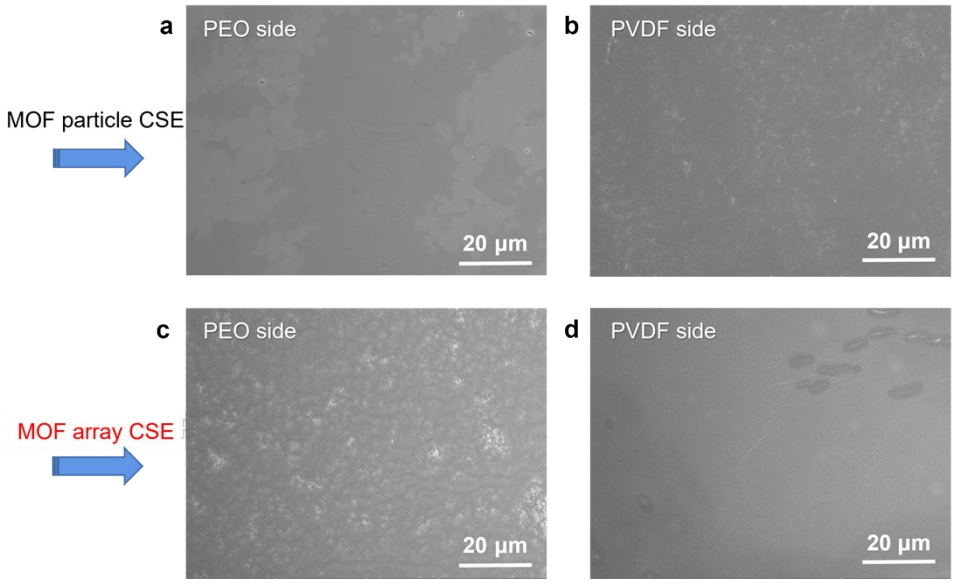

Fig. S5. The top view SEM images of (a, b) MOF particle CSE and (c, d) MOF array CSE.

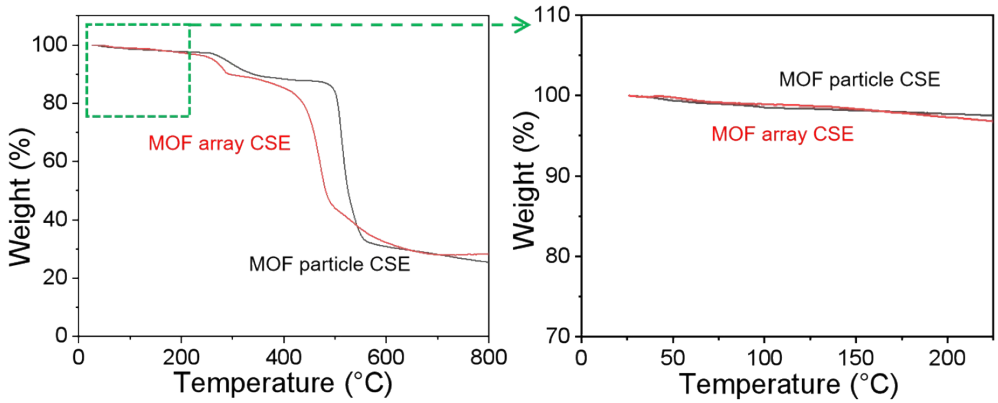

Fig. S6. TGA curves of the MOF array CSE and MOF particle CSE.

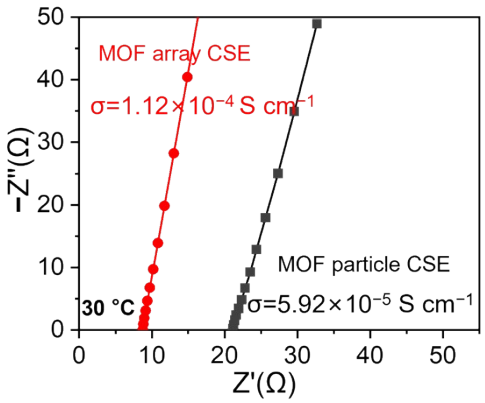

Fig. S7. Ionic conductivities of MOF array CSE and MOF particle CSE at 30 °C.

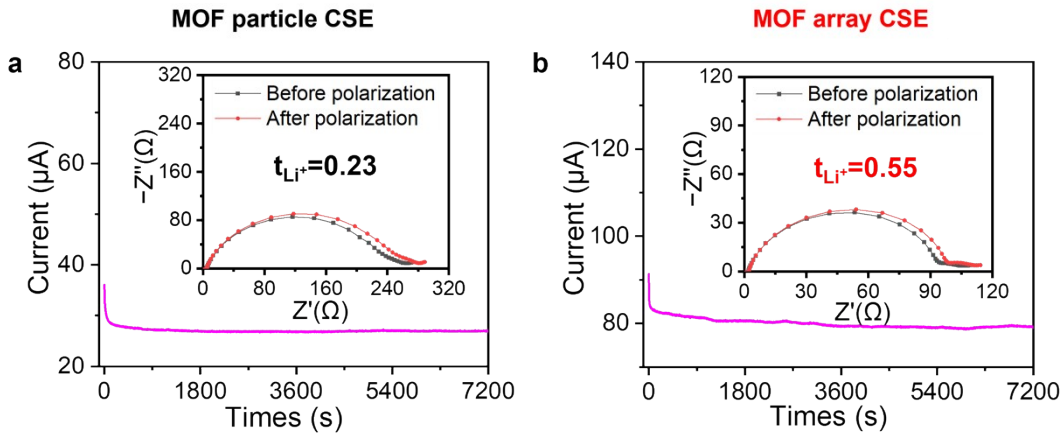

Fig. S8. Li^+ transference number of (a) MOF particle CSE and (b) MOF array CSE at 30 °C.

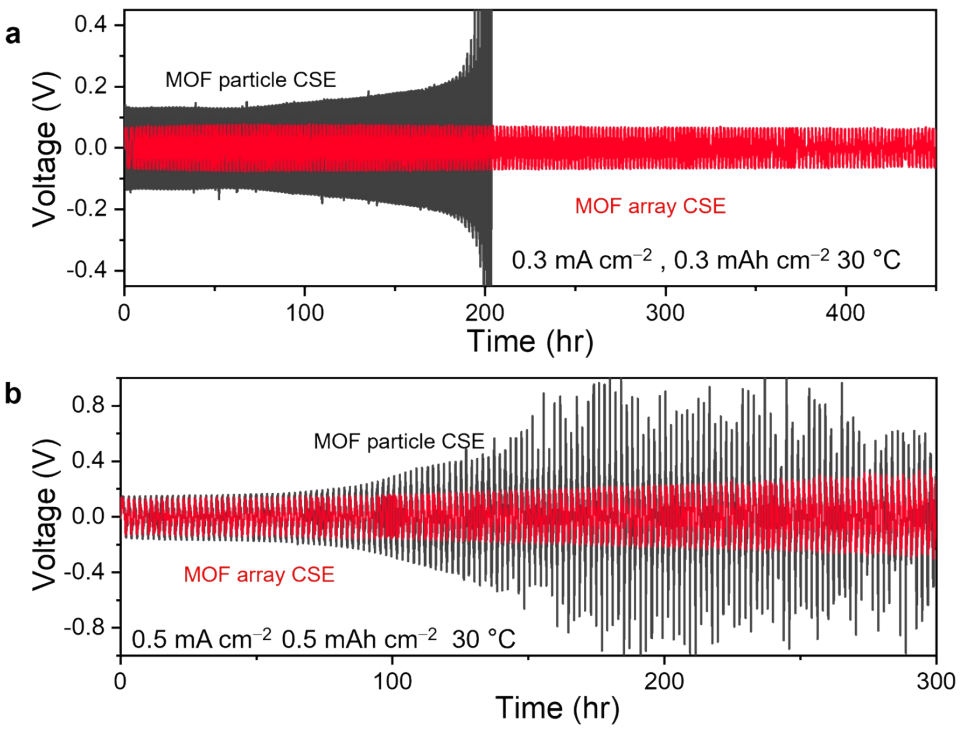

Fig. S9. Long-term cycling stability of symmetric Li||Li cells using MOF particle CSE and MOF array CSE at current density of (a) 0.3 mA cm^{-2} for 0.3 mA h cm^{-2} and (b) 0.5 mA cm^{-2} for 0.5 mA h cm^{-2} at 30 °C.

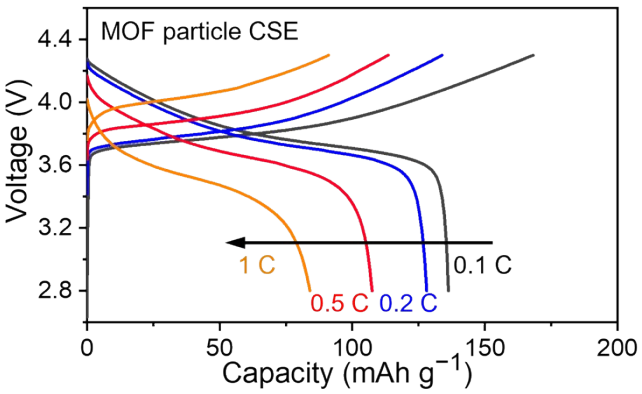

Fig. S10. Selected charge-discharge curves of Li||NCM cell using MOF particle CSE at different current densities.

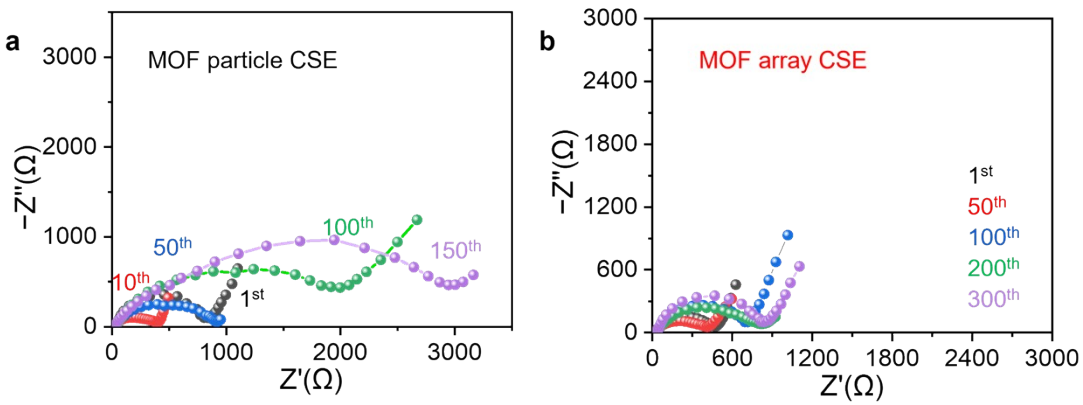

Fig. S11. Electrochemical impedance spectra of Li||NCM cells using (a) MOF particle CSE and (b) MOF array CSE after different cycles at 30 ℃.

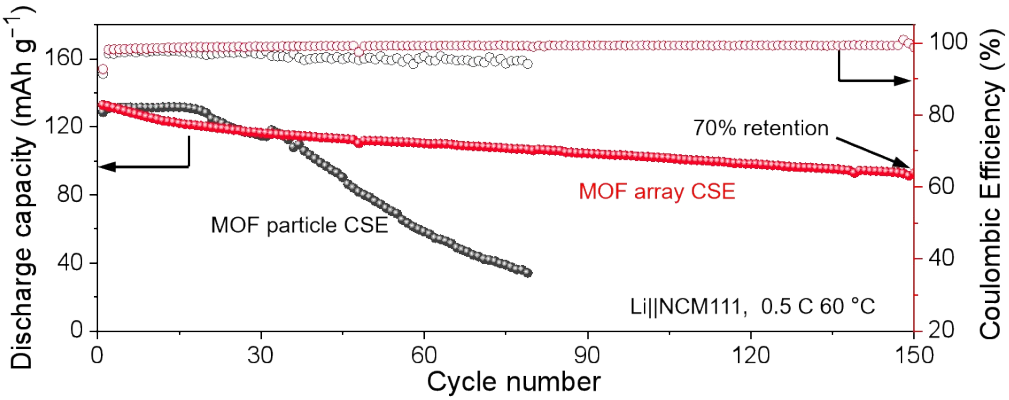

Fig. S12. Cycling performance of Li||NCM cells using MOF particle CSE and MOF array CSE at 0.5 C at 60 °C.

Table S1. Comparison of this work with state-of-the-art reported MOF-based CSEs without any liquid.

CSE	σ (S cm^{-1})	Thickness (μm)	t_{Li^+}	Cathode material	Cycling condition	Cut-off voltage (V)	Capacity retention (%)	Ref.
PEO-LiTFSI/ZIF-8	2.20×10^{-5} (30 °C)	~100	0.36	$LiFePO_4$	350 cycles 0.5 C, 60 °C	3.80	85.0 %	[1]
UiO-66-LiSS	6.00×10^{-5} (25 °C)	~198	/	$LiFePO_4$	100 cycles 0.2 C, 25 °C	4.20	88.1 %	[2]
MGPL-12	1.51×10^{-3} (25 °C)	~80	0.64	$LiFePO_4$	50 cycles 0.2 C, 25 °C	4.30	96.4 %	[3]
NCPE	1.66×10^{-5} (25 °C)	~130	0.378	$LiFePO_4$	50 cycles, 0.1 C, 30 °C	4.00	100.0 %	[4]
NWF@Cu(BDC)-PVDF	2.40×10^{-4} (30 °C)	~40	0.61	NCM811	80 cycles, 0.1 C, 30 °C	-	95.0 %	[5]
HKUST@PI /PVDF	2.38×10^{-4} (30 °C)	~25	0.56	NCM111	500 cycles, 0.2 C, 30 °C	4.30	86.0 %	[6]
M-S-PEGDA	2.26×10^{-4} (30 °C)	-	0.44	NCM811	100 cycles, 0.5 C, 30 °C	4.25	92.7 %	[7]

The cross-linked MOF chains	7.78×10^{-4} (25 °C)	~88	0.88	$LiFePO_4$	600 cycles, 3 C, 30 °C	4.00	99.8 %	[8]
30 H-Z-CPE	1.41×10^{-4} (25 °C)	~42	0.41	NCM811	100 cycles, 0.1 C, 60 °C	4.30	73.0 %	[9]
MOF array CSE	**1.12×10^{-4} (30 °C)**	**~20**	**0.55**	**NCM111**	**300 cycles 0.2 C, 30 °C**	**4.30**	**75 %**	**This work**

Reference

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