Electronic Supporting Information

Significantly enhance the lithium-ion conductivity of solid-state electrolytes via strategy of fabricating hollow metal-organic frameworks

Zixin Liu, Pengyu Liu, Li Tian, Jiannan Xiao, Ruixue Cui, and Zhiliang Liu*

Inner Mongolia Key Laboratory of Chemistry and Physics of Rare Earth Materials, School of Chemistry and Chemical Engineering, Inner Mongolia University, Hohhot 010021, China.

E-mail: cezlliu@imu.edu.cn.

Fax/Tel: +86-471-4992261.

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Experimental Section

Synthesis of ZIF-67: In a typical procedure, $Co(NO_3)_2 \cdot 6H_2O$ (2.5 mmol) and 2-methylimidazole (0.2 mol) were dissolved in 50 mL of methanol (MeOH), and allowed the solution to stay for 24 h at room temperature to obtain purple ZIF-67 precipitate. The precipitate was collected by centrifugation and washed several times with methanol. Then, the product was dried for 12 h to obtain a purple powder.

Synthesis of Hollow ZIF-67@ZIF-8: $Zn(NO_3)_2 \cdot 6H_2O$ (0.25 mmol), 2-methylimidazole (0.25 mmol), and dried ZIF-67 powder (20 mg) were dissolved in 12 mL of methanol (MeOH), then sealed in Teflon-lined autoclave and kept at 100 °C for 24 h prepared by a homoepitaxial growth method. The precipitate was collected by centrifugation and washed several times with methanol. Afterward, the pale pink precipitate was dried for 12 h to obtain a dry powder.

Synthesis of Co-doped ZIF-8: $Zn(NO_3)_2 \cdot 6H_2O$ (1.75 mmol), $Co(NO_3)_2 \cdot 6H_2O$ (0.75 mmol) and 2-methylimidazole (0.2 mol) were dissolved in 50 mL of methanol (MeOH), and allowed the solution to stay for 24 h at room temperature to obtain purple Co-doped ZIF-8 precipitate. The precipitate was collected by centrifugation and washed several times with methanol. Then, the product was dried for 12 h to obtain a purple powder.

Preparation of Hollow ZIF-67@ZIF-8 Electrolyte Membranes: Hollow ZIF-67@ZIF-8 powders were uniformly dispersed in isopropanol, and 10 wt % PTFE aqueous solution was added to the mixture. After continuous grind and evaporation of the solvent, the mixture was rolled into membrane. The membrane was cut into the required size and dried overnight to remove water. Hereafter, the membranes were immersed in $LiPF_6$

electrolyte (1 M $LiPF_6$ EC/DMC/EMC = 1:1:1) for 24 h, activated and adsorbed to a certain amount of Li^+, and then pressed to extrude excess liquid electrolyte, wiped with filter paper and dried them in argon atmosphere.

Preparation of ZIF-8, ZIF-67 and Co-doped ZIF-8 Electrolyte Membranes: The same procedure as that for hollow ZIF-67@ZIF-8 electrolyte membranes was used.

Electrochemical Studies

Ionic conductivity of the electrolyte membranes was measured by electrochemical impedance spectroscopy (EIS) with frequency ranging from 1 Hz to 1 MHz. The solid electrolyte membranes were sandwiched between two stainless steel electrodes. The ionic conductivity was calculated according to the following formula $\sigma = L / (R \times S)$, which L (cm), R (ohm) and S (cm^2) are the thickness, bulk resistance and the area of the membrane, respectively.

The Li^+ transference number ($t_{Li}{}^+$) was measured by combining an A.C. impedance measurement and an amperometric i-t curve measurement using Li|electrolyte|Li cells. The $t_{Li}{}^+$ can be calculated according to the following formula $t_{Li}{}^+ = I_{SS} (\Delta V - I_0R_0) / I_0 (\Delta V - I_{SS}R_{SS})$, which ΔV is the DC polarization voltage, and I_0 and I_{SS} are the initial stable currents before and after polarization, respectively. R_0 and R_{SS} are the initial stable resistance before and after polarization.

The electrochemical window was determined by cyclic voltammetry (CV) and linear sweep voltammetry (LSV) using SS|electrolyte|Li cells with the voltage range of 0 to 7 V and the scanning rate of 10 mV s^{-1}.

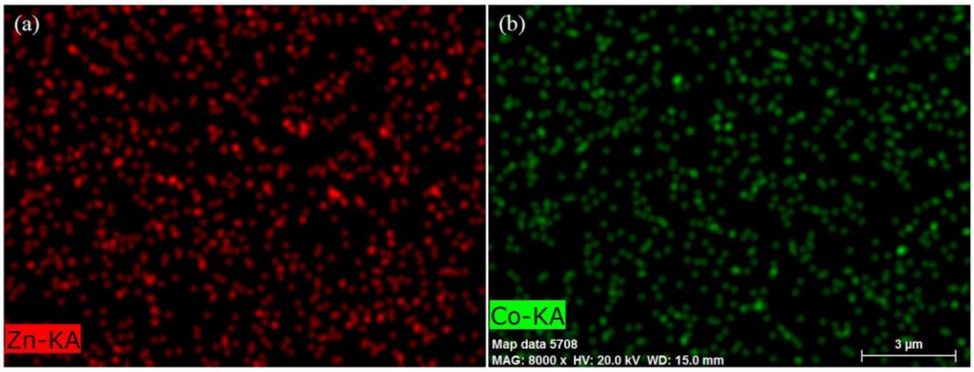

Fig. S1 SEM-EDX of the as-synthesized hollow ZIF-67@ZIF-8.

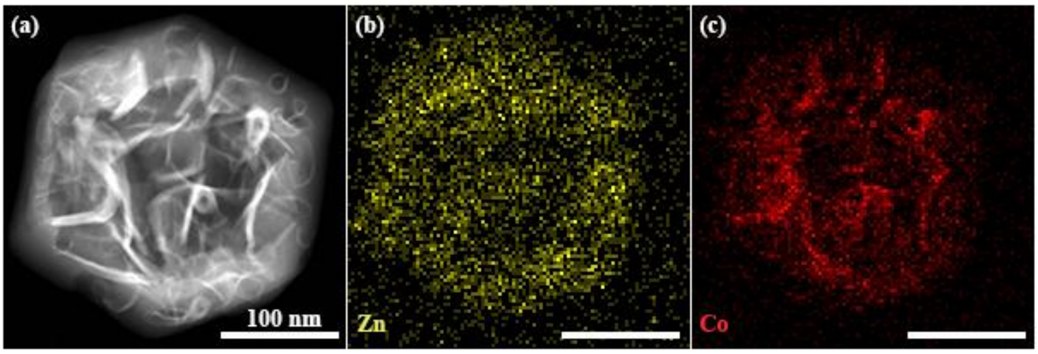

Fig. S2 (a) HAADF-STEM images of hollow ZIF-67@ZIF-8 with (b), (c) corresponding EDX elements mappings.

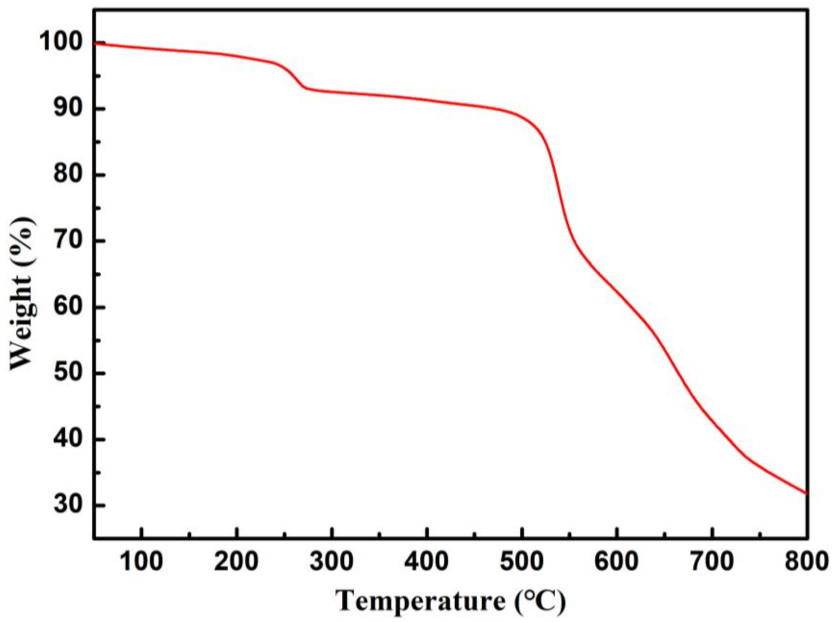

Fig. S3 TGA of the as-synthesized hollow ZIF-67@ZIF-8.

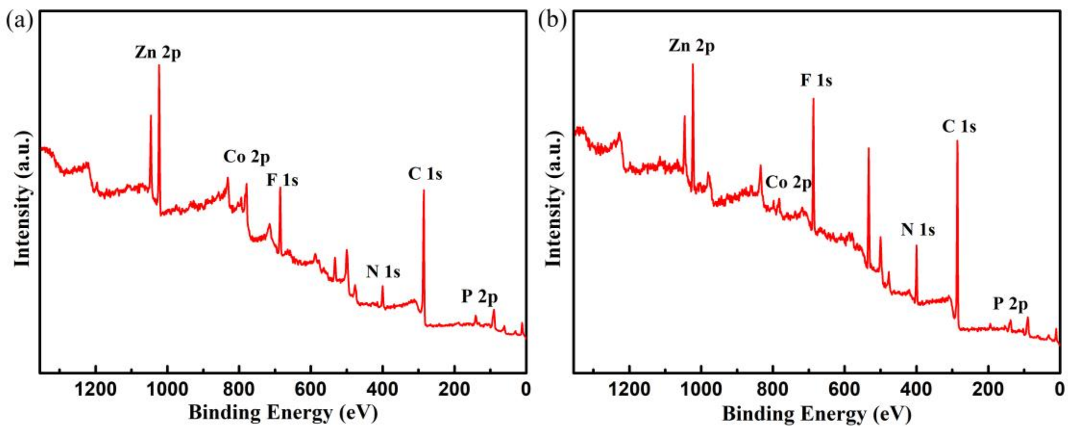

Fig. S4 Wide-scan X-ray photoelectron spectroscopy (XPS) spectrum of (a) the surface of the hollow ZIF-67@ZIF-8 which activation by $LiPF_6$. (b) After Ar ion etching for 20 minutes.

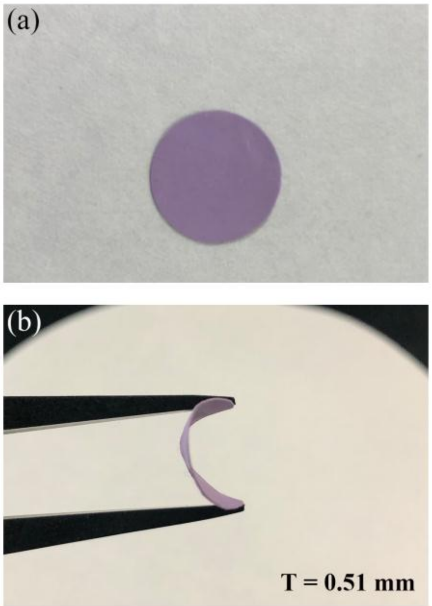

Fig. S5 Photograph of the (a) freestanding electrolyte membrane. (b) Flexible electrolyte membrane in bend state.

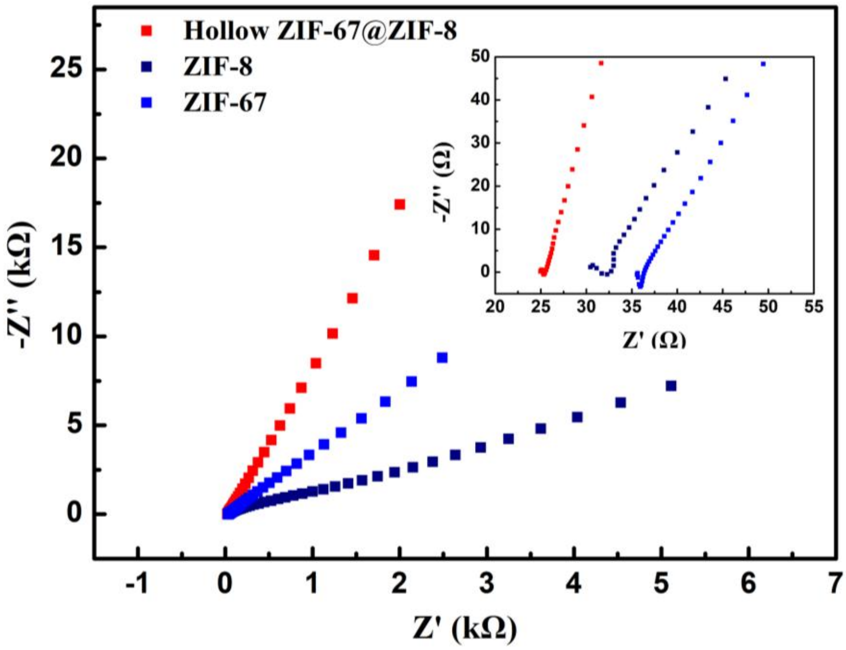

Fig. S6 EIS of hollow ZIF-67@ZIF-8 electrolyte (25 °C), ZIF-8 electrolyte (25 °C) and ZIF-67 electrolyte (25 °C).

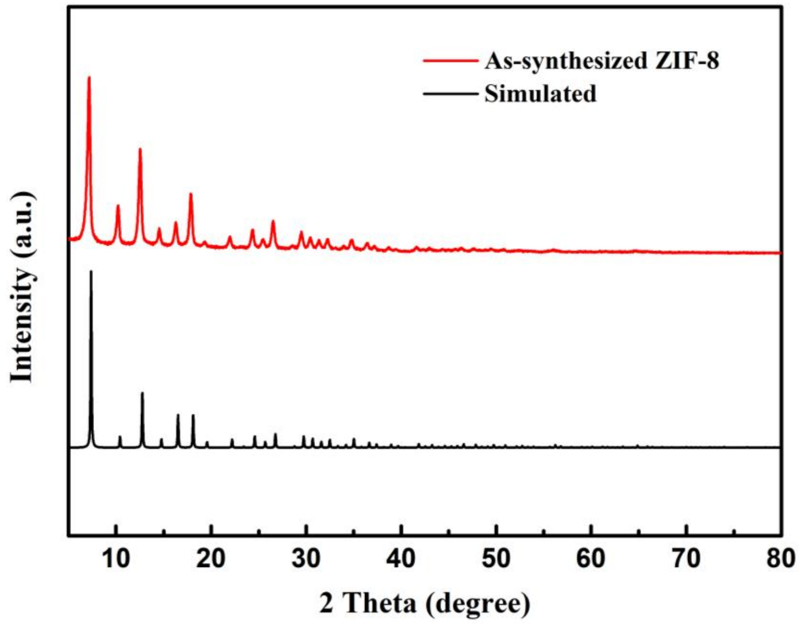

Fig. S7 XRD of the as-synthesized ZIF-8.

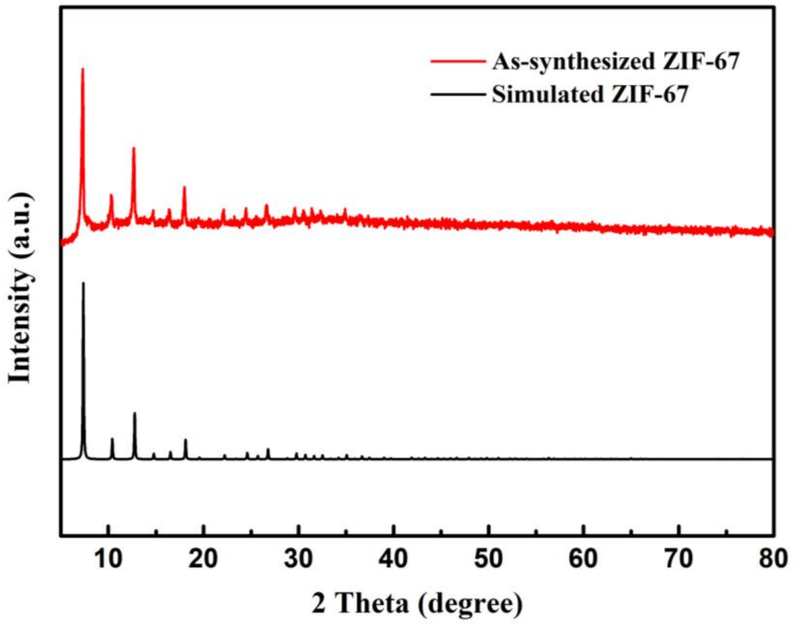

Fig. S8 XRD of the as-synthesized ZIF-67.

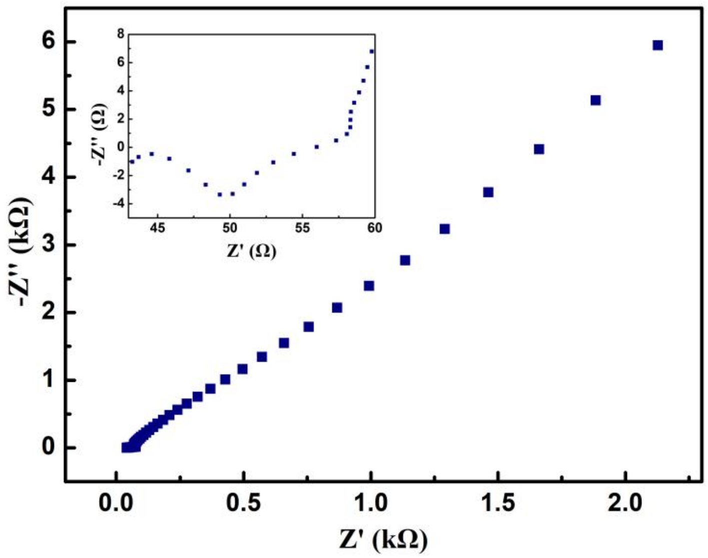

Fig. S9 EIS of Co-doped ZIF-8 electrolyte (25 °C).

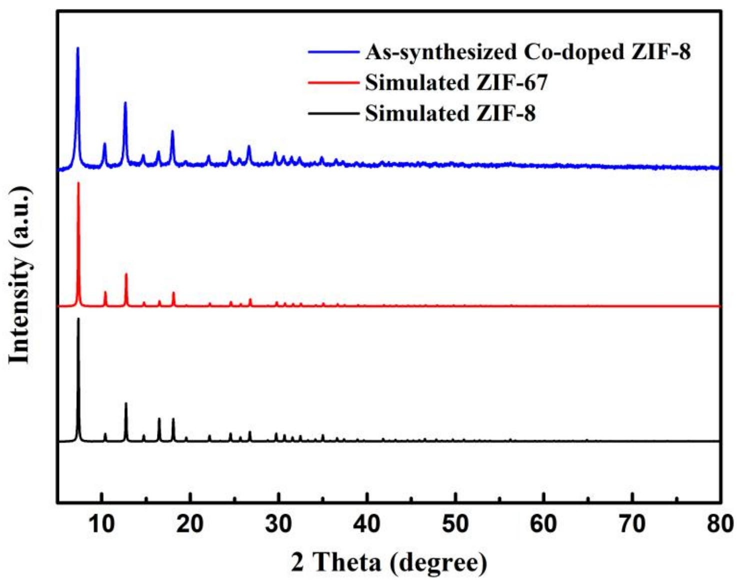

Fig. S10 XRD of the as-synthesized Co-doped ZIF-8.

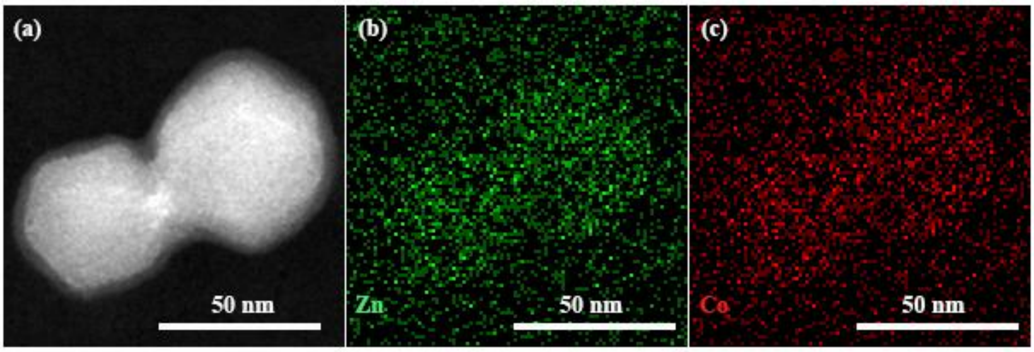

Fig. S11 (a) HAADF-STEM images of Co-doped ZIF-8 with (b), (c) corresponding EDX elements mappings.

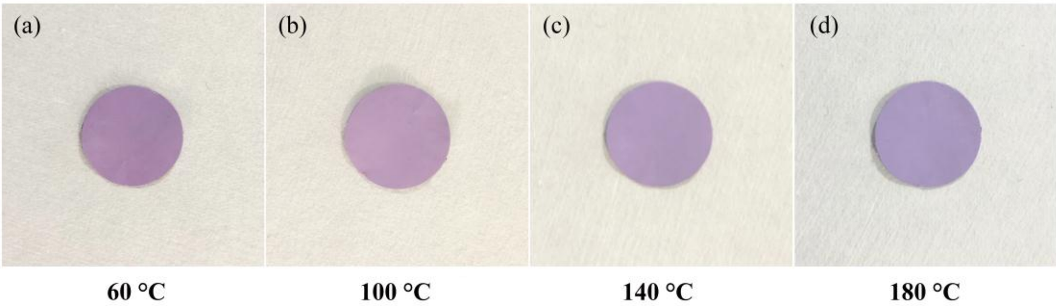

Fig. S12 Photograph of the electrolyte membrane after being stored in an electric blast drying oven for 1 h.

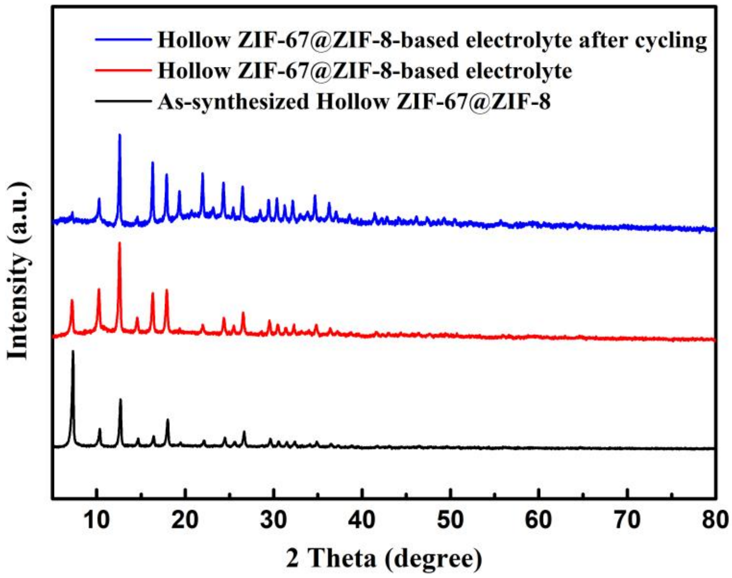

Fig. S13 XRD of hollow ZIF-67@ZIF-8-based solid-state electrolyte before and after cycling in a $LiFePO_4$-Li asymmetric cell.

Table S1. Summary of MOF-based lithium ion solid state electrolytes.

No.	Materials	σ (S cm^{-1})	t_{Li}^{+}	Ref
1	Mg_2(dobdc)	3.1×10^{-4} S cm^{-1}	-	S1
2	MOF-5	3.16×10^{-5} S cm^{-1}	-	S2
3	Mg-BTC	10^{-4} S cm^{-1}	-	S3
4	MOF-525	3.0×10^{-4} S cm^{-1}	0.36	S4
5	MIT-20	4.8×10^{-4} S cm^{-1}	-	S5
6	UIO-66	LP 2.9×10^{-3} S cm^{-1}	LP 0.59	S6
		LC 1.9×10^{-3} S cm^{-1}	LC 0.79	
7	UIO-67	1.0×10^{-4} S cm^{-1}	0.13	S7
8	UIO-66-NH_2	2.07×10^{-4} S cm^{-1}	0.84	S8
9	Cu-azolate MOF	MOF-LiCl 2.4×10^{-5} S cm^{-1}	MOF-LiCl 0.69	S9
		MOF-LiBr 3.2×10^{-5} S cm^{-1}	MOF-LiBr 0.42	
		MOF-LiI 1.1×10^{-4} S cm^{-1}	MOF-LiI 0.34	

10	ZIF-8	1.05×10^{-4} S cm^{-1}	0.52	S10
11	MOF-688	3.4×10^{-4} S cm^{-1}	0.87	S11
12	**Hollow ZIF-67@ZIF-8**	**1.35×10^{-3} S cm^{-1}**	**0.82**	**This work**

Table S2. Summary of variable temperature conductivity of MOF-based lithium ion solid electrolytes at different temperature ranges.

No.	Materials	Temperature Range	σ (S cm^{-1})	Ref
1	MOF-525	-20-100 °C	-20 °C 2.2×10^{-5} S cm^{-1} 100 °C 4.9×10^{-3} S cm^{-1}	S4
2	UIO-66-LiSS	25-90 °C	25 °C 6.0×10^{-5} S cm^{-1} 60 °C 7.9×10^{-5} S cm^{-1} 90 °C 1.1×10^{-4} S cm^{-1}	S5
3	UIO-66-NH_2	25-70 °C	25 °C 2.07×10^{-4} S cm^{-1} 70 °C 1.39×10^{-3} S cm^{-1}	S8
4	ZIF-8	25-70 °C	25 °C 10^{-4} S cm^{-1} 70 °C 10^{-3} S cm^{-1}	S10
5	UIO-66	30-90 °C	-	S12
6	PCN-777	-25-130 °C	>10^{-2} S cm^{-1} above 70 °C	S13
7	**Hollow ZIF-67@ZIF-8**	**-20-100 °C**	**-20 °C 3.44×10^{-4} S cm^{-1}** **25 °C 1.35×10^{-3} S cm^{-1}** **100 °C 4.98×10^{-3} S cm^{-1}**	**This work**

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