

A New Zeolitic Lithium Aluminum Imidazolate Framework

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1 Experimental

1.1 DUT-174 synthesis

LiAlH₄ (1 mL 2M THF solution) and 2-methylimidazole (660 mg) was diluted and dissolved in 20 mL and 30 mL tetrahydrofuran (THF), respectively. The LiAlH₄ solution was syringed into of 2-methylimidazole solution in 2 hours at 0 °C. The white precipitate was generated with H₂ released and then was stirred for another 18 h at 25 °C. The whole operations were carried out at Schlenk line under Ar atmosphere. The product was filtered under Ar atmosphere and the obtained filter cake is heated at 120 °C for 16 h under dynamic vacuum conditions.

1.2 Characterization

X-ray diffraction (XRD) patterns were collected by capillary tube on STOE STADI MP diffractometer (Cu K α radiation, 0.15406 nm). The porosity was determined using N₂ and CO₂ adsorption/desorption at 77 K and 195K, respectively, test using ASiQwin (Quantachrome) instrument. Brunauer-Emmett-Teller (BET) theory was employed to calculate specific surface area. The pore distribution was analyzed based on NLDFT model. Fourier-transform infrared spectroscopy (FTIR) data was collected on a Bruker VERTEX 70. All solid-state NMR spectra were measured on a BRUKER Ascend 300 MHz spectrometer using a commercial 2.5 mm MAS NMR probe and a MAS frequency of 15 kHz. Following resonance frequencies were used: 75.5 MHz for ¹³C CP NMR spectrum, 78.2 MHz for ²⁷Al NMR spectrum, 116.6 MHz for ⁷Li NMR spectrum, and 300.1 MHz for ¹H NMR spectrum. Inductively coupled plasma optical emission spectrometer (ICP-OES) was conducted on ICP OES Optima 7000DV from Perkin Elmer with S10 Autosampler. Thermogravimetric analysis (TGA) was conducted on NETZSCH STA 409PC/PG from room temperature to 800 °C with Ar flow rate of 100 ml min⁻¹ at 10 °C min⁻¹. Element analysis was carried out on the EURO EA Elemental

Analyzer from EuroVector. The geometrical surface area, accessible pore volume and pore size distribution were calculated using Zeo++ software using the default settings¹.

1.3 Rietveld refinement of DUT-174 structure

The crystal structure of DUT-174 was refined using Rietveld method². The structural model was built in visualization module of Materials Studio 5.0 software using ZIF-8 structure as initial model. The symmetry of the original structure was reduced to P23 in order to get two independent atoms in the structure. The Thompson-Cox-Hastings function with axial divergence was used in the Pawley fit of PXRD patterns. The Rietveld refinement with energy contribution of 1% (based on integrated UFF module) was performed using rigid-body refinement with metal ions, imidazole rings and methyl groups, refined as the separate units. This results in the refinement of 6 motion groups with 26 degrees of freedom. The Rietveld plot is given in Figure S1.

Structural data for DUT-174: $C_{16}H_{20}N_8AlLi$, $M = 358.32 \text{ g mol}^{-1}$, cubic, $P23$ (No 195), $a = 16.83041(3) \text{ \AA}$, $V = 4767.42(5) \text{ \AA}^3$, $Z = 6$; Profile function: Thompson-Cox-Hastings, $U = 0.13036$, $V = 0.00211$, $W = 0.00251$, $X = 0.08921$, $Y = 0.18169$; Asymmetry correction function: Berar-Baldinozzi $P_1 = -0.08303$, $P_2 = -0.01204$, $P_3 = -0.00019$, $P_4 = 0.00000$; Global isotropic temperature factor $U = 0.07817$; Refined Motion Groups 6, refined degree of freedom 26; $R_w = 2.63\%$, $R_p = 1.86\%$.

1.4 Electrochemical test

100 mg DUT-174 were distributed homogeneously in the test cell and compressed into a pellet at 300 Mpa. The pellet was assembled in Swagelok-type symmetrical cell with lithium plates as electrodes. The test cell was closed with a torque screw at 3.5 Nm (corresponding to ~20 MPa). The solvent mixture ethylene carbonate/dimethyl carbonate (50:50 EC/DMC, 1.05×pore volume of DUT-174) was added into DUT-174 solid-state electrolyte and mixed thoroughly in a mortar before assembling the test cells. The current response was recorded under constant voltage at different 0.1, 1.0, 9.0 or 10 V using a VMP-300 (Bio-logic, France).

2. Supporting figures

Table S1 Synthesis conditions and sample name of DUT-174

Synthesis conditions		DUT-174 sample name
Effect of LiAlH ₄ Addition time (Fig. S1a)	5 min	5min
	2 h	2 h
Effect of solvent (Fig. S1b)	DOL	DOL
	DME	DME
	THF+DME	THF+DME
	THF	THF
Effects of Reaction at low temperature and solvothermal (Fig. S1c)	Reaction at -196 °C	-196 °C
	Reaction at -196 °C+ solvothermal at 150°C	-196 °C Solvothermal
Effect of reaction temperature (Fig. S1d)	25 °C	25 °C
	50 °C	50 °C
	75 °C	75 °C
Effects of Triethylamine (TEA) additive + solvothermal temperature (Fig. S1e)	No TEA+120 °C (Solvothermal temperature)	120 °C
	TEA+120 °C(Solvothermal temperature)	TEA+120 °C
	TEA+150 °C (Solvothermal temperature)	TEA+150 °C

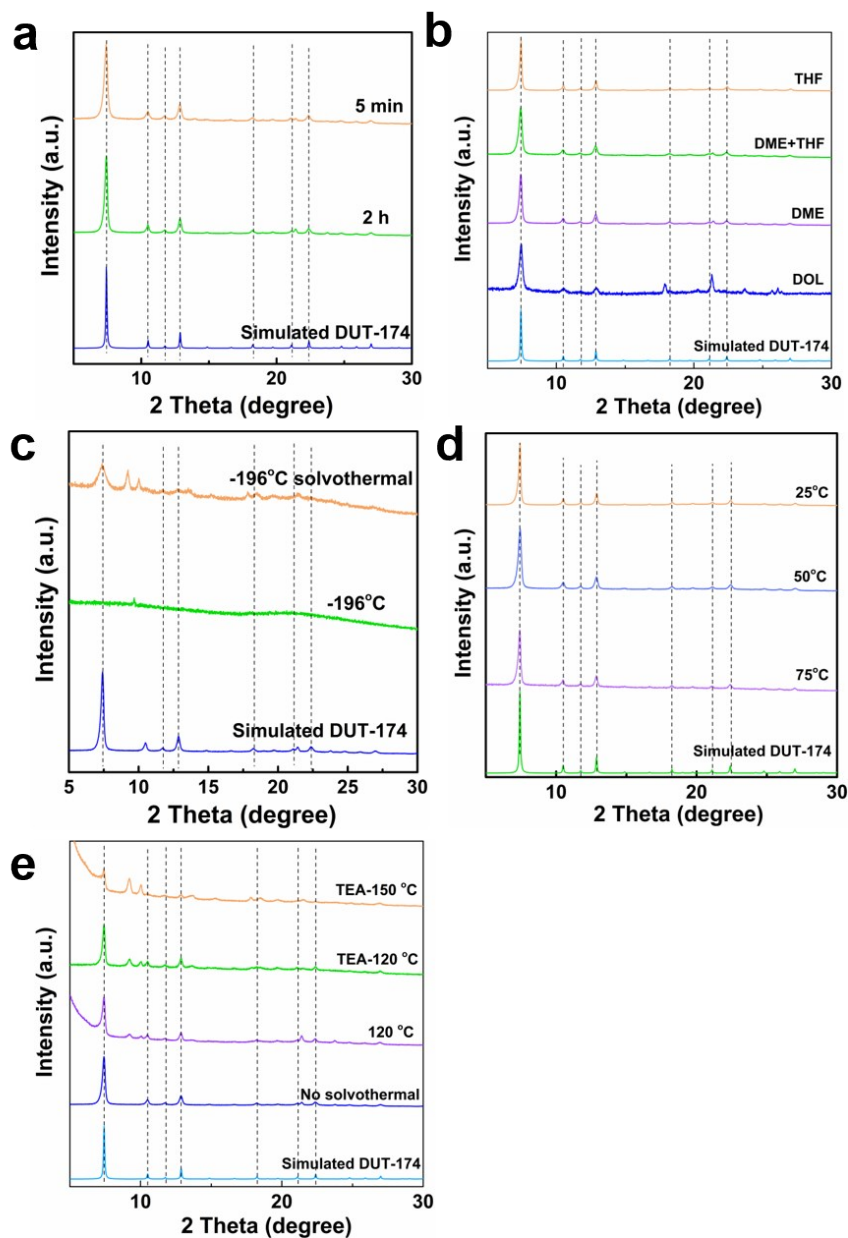


Fig. S1 a) Effect of addition time of LiAlH_4 solution into 2-methylimidazole, b) solvent effect, c) and d) effect of reaction temperature on the formation of DUT-174, e) effects of TEA additive and solvothermal on the formation of DUT-174 (THF: Tetrahydrofuran, DME: 1,2-Dimethoxyethane, DOL: 1,3-Dioxolane, TEA: triethylamine).

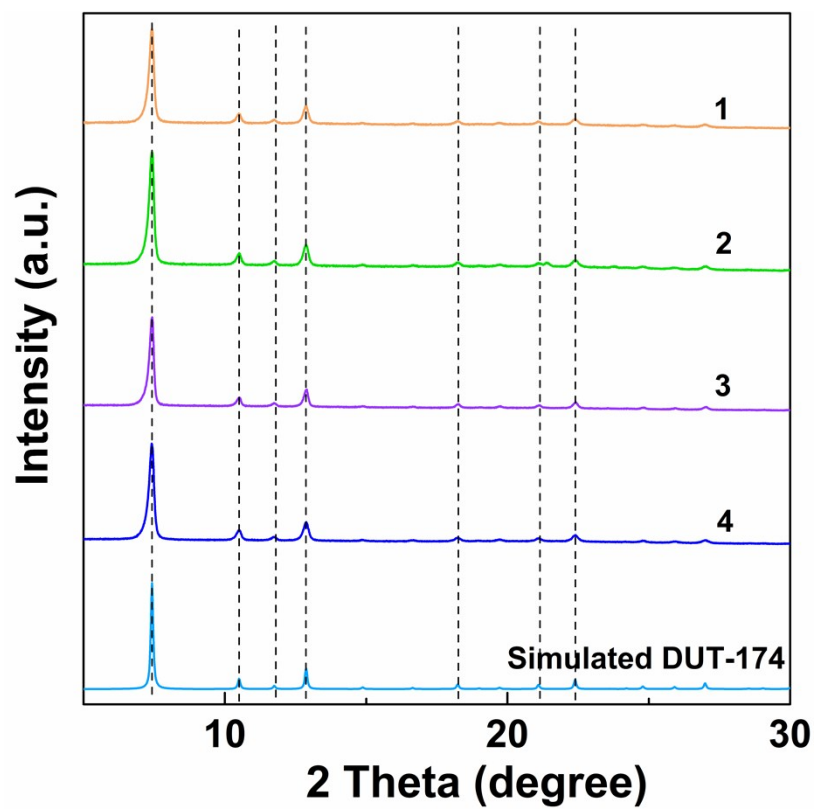


Fig. S2 XRD patterns of four DUT-174 samples all synthesized at 25 °C and activated 120 °C.

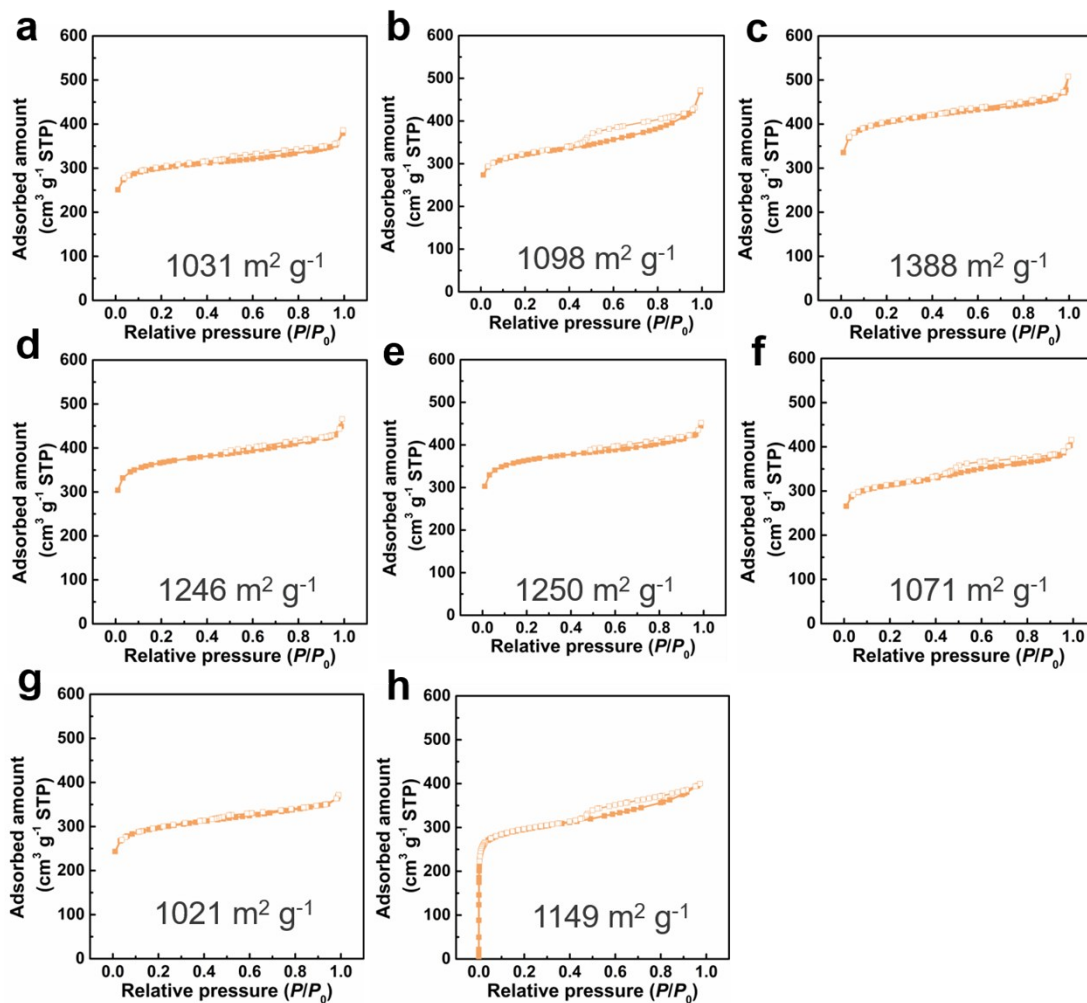


Fig. S3 N₂ adsorption/desorption isotherms of DUT-174 samples all synthesized at 25 °C and activated 120 °C. Note: a)-g) p/p₀ tested from 10⁻²~1; g) p/p₀ tested from 10⁻⁶~1

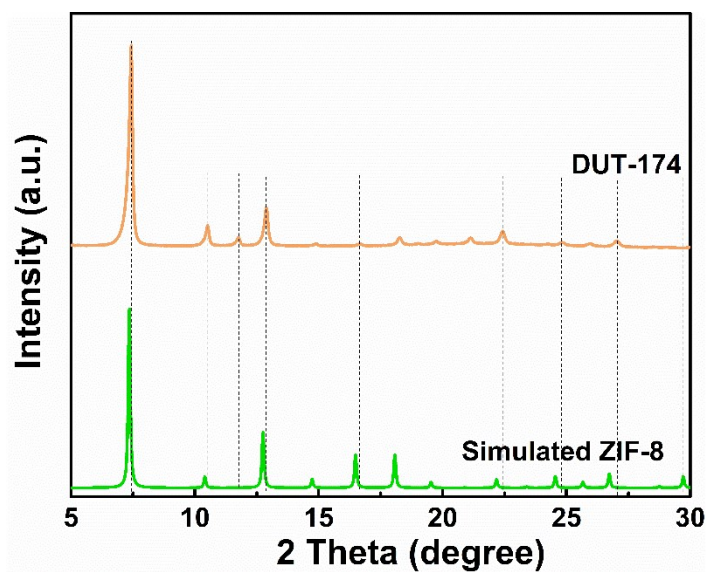


Fig. S4 Comparison of XRD patterns between DUT-174 with simulated ZIF-8.

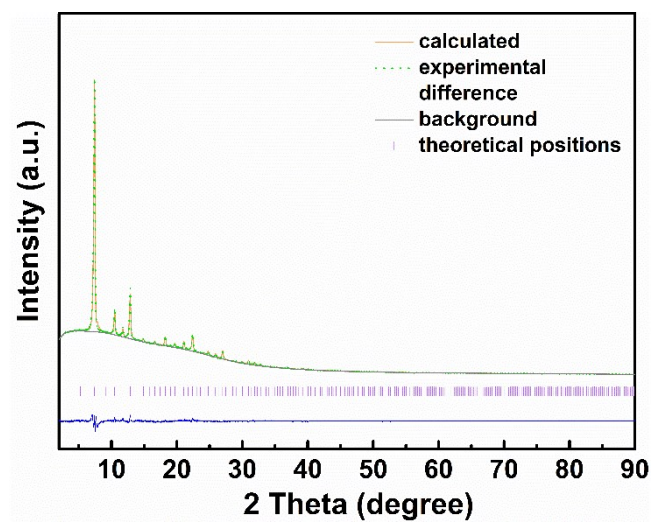


Fig. S5 Rietveld plot for DUT-174.

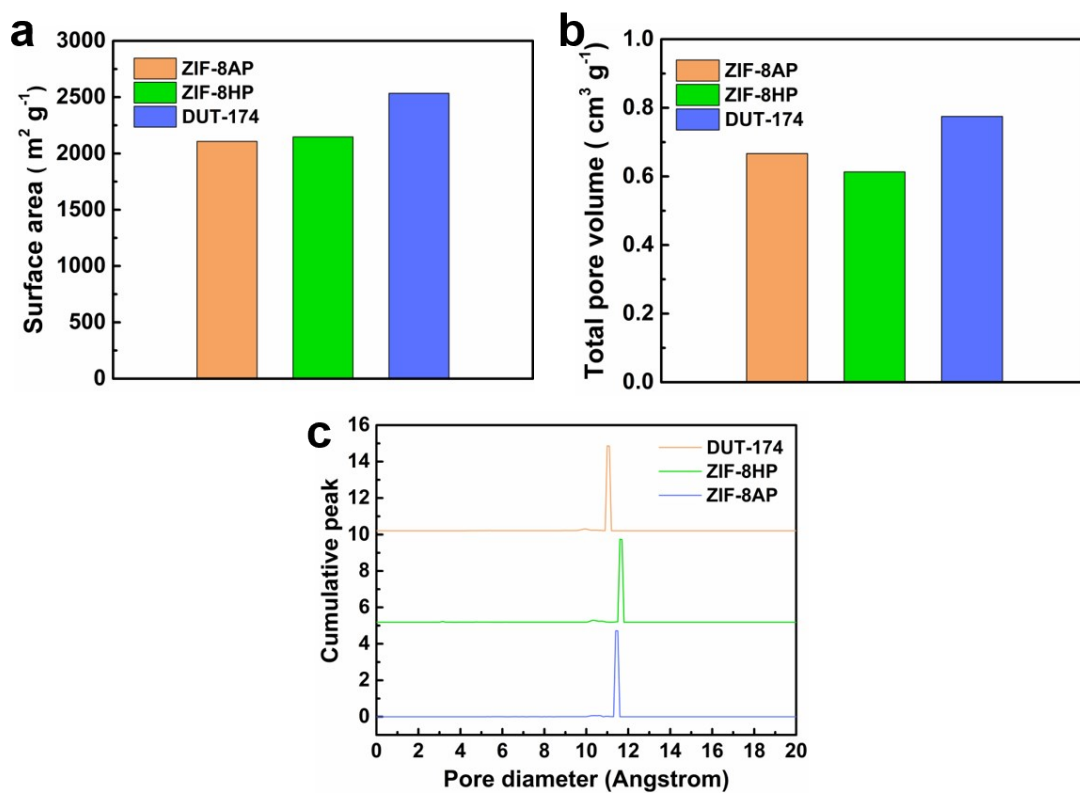


Fig. S6 a) Geometric surface area, b) total pore volume and c) pore size distribution for DUT-174, ZIF-8AP and ZIF-8HP.

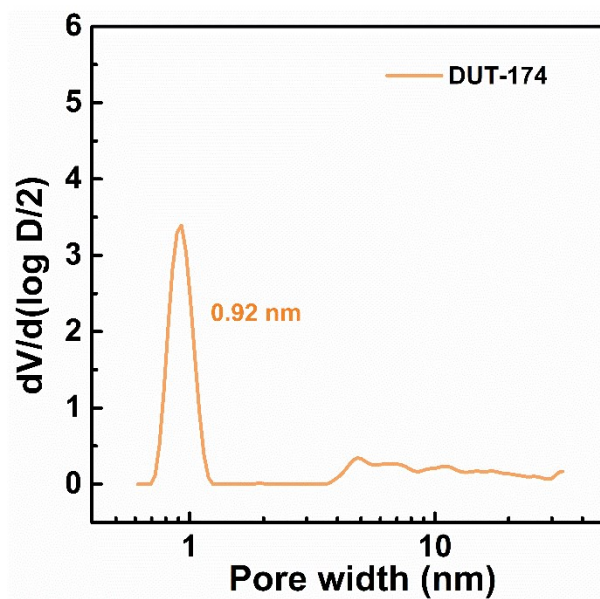


Fig. S7 Pore distribution of DUT-174 calculated by N₂ adsorption/desorption test.

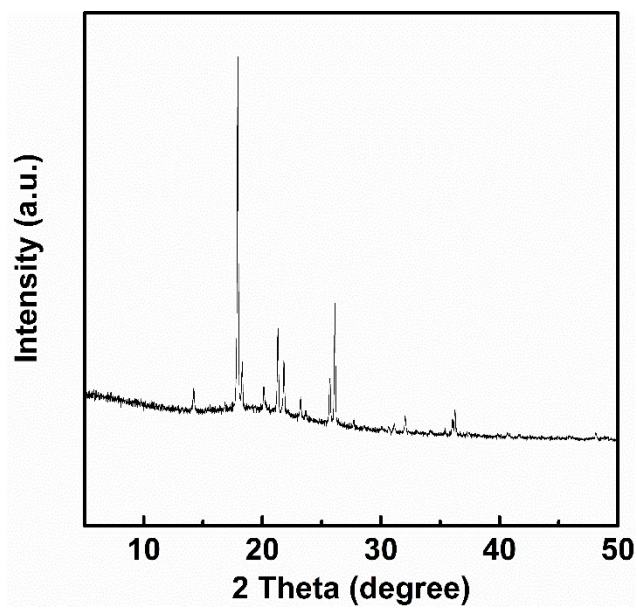


Fig. S8 XRD pattern of DUT-174 upon exposure to moisture.

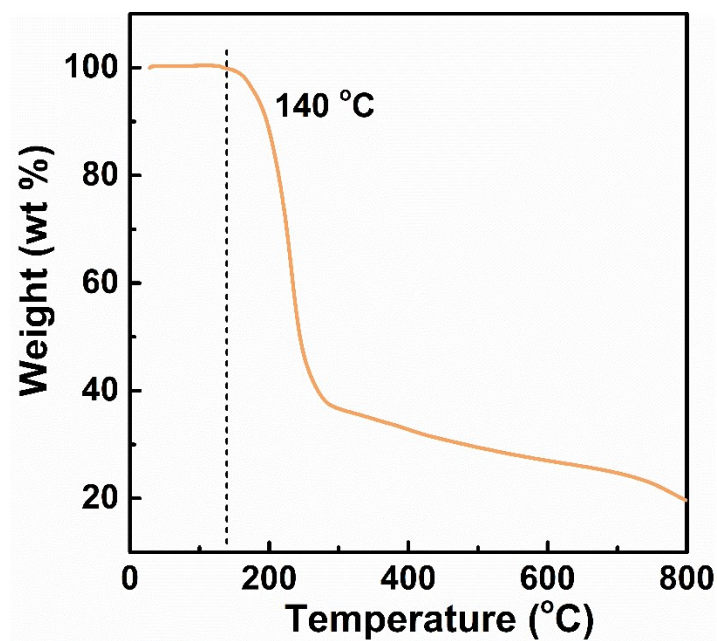


Fig. S9 TG curve of DUT-174 at 10 °C min⁻¹ in Ar atmosphere.

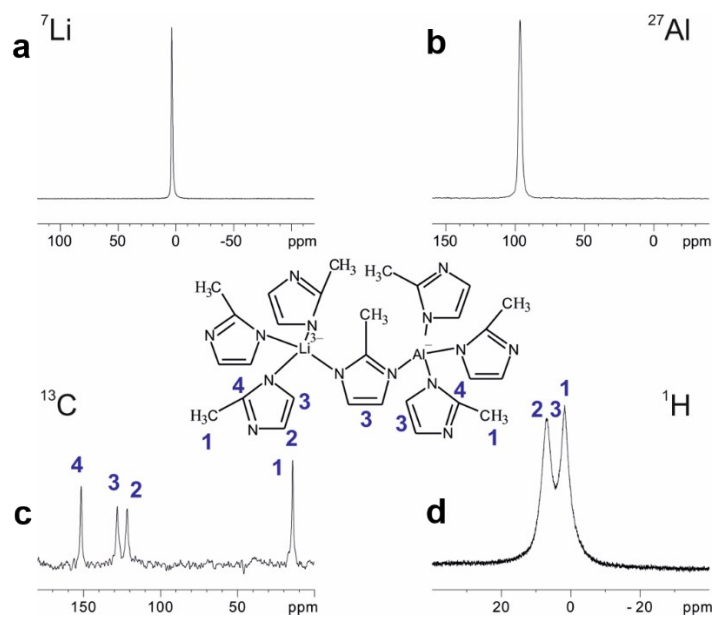


Fig. S10 ssNMR spectra of a) ⁷Li, b) ²⁷Al, c) ¹³C and d) ¹H in DUT-174.

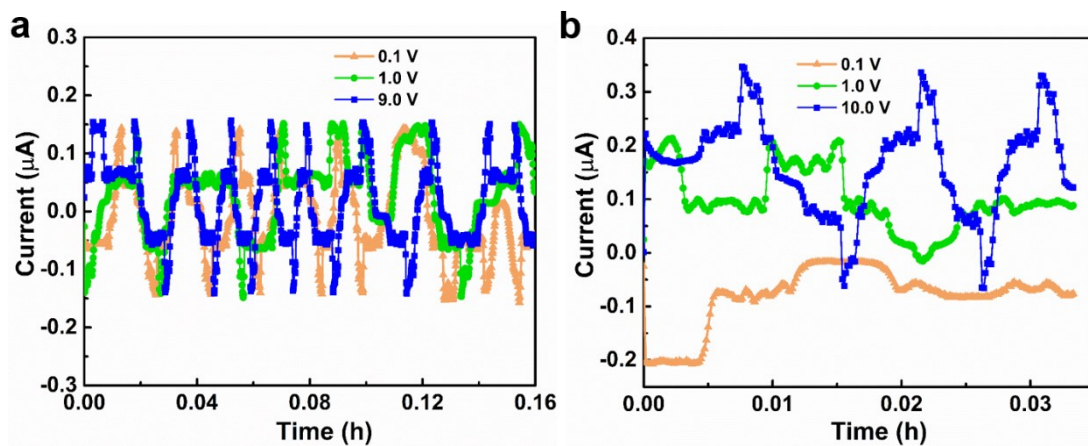


Fig. S11 Current response of DUT-174 as solid-state electrolyte a) without and b) with the addition of EC/DMC.

3. Supporting references

1. M. Pinheiro, R. L. Martin, C. H. Rycroft and M. Haranczyk, *Cryst. Eng. Comm.*, 2013, **15**, 7531-7538.
2. H. M. Rietveld, *J. Appl. Crystallogr.*, 1969, **2**, 65-71.