

Electronic Supplementary Information

Versatile design of metal-organic framework cathode for Li–O₂ and Li–O₂/CO₂ batteries

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Synthesis of materials

ZIF67 nanoparticles were grown on CNTs by a hydrothermal method. First, cobalt (II) acetate tetrahydrate (1.331 g) and 2-methylimidazole (2.596 g) were separately dissolved in methanol (60 mL). Next, MWCNTs (58.8 mg) with diameters of 15–30 nm were dispersed into the as-prepared 2-MIM solution. Next, the cobalt acetate solution was mixed with the CNT-containing solution and the mixture was stirred for 30 min. The mixture was then transferred into a Teflon-lined autoclave (200 mL) and heated at 90 °C for 6 h. After cooling, the ZIF67/CNT powder was collected by vacuum filtration. The resulting powder was carbonised at 900 °C for 6 h under an Ar atmosphere, and then chemically etched with 1 M H₂SO₄. Finally, the as-prepared ZIF67-C/CNT powder was mildly oxidised in air at various temperatures of 150 °C, 250 °C, and 350 °C for 1 h with a ramping rate of 2 °C min⁻¹.

Material characterisation

The morphologies and microstructures of the synthesised materials were characterised by field-emission scanning electron microscopy (FESEM, JEOL, JSM-7000F) and high-resolution transmission electron microscopy (HRTEM, JEOL, JEM-2100F). The crystal structures of the materials were investigated using power X-ray diffraction (XRD, PANalytical, Empyrean) and Raman spectroscopy (inVia, Raman microscopes). The surface chemistry was investigated using X-ray photoelectron spectroscopy (XPS, Thermo Scientific, Sigma Probe), whereas the surface area and porosity of the materials were measured with a porosity analyser (Micromeritics, Tristar II 3020). The electrical conductivities were determined using a four-point probe method (MCP-PD51).

Electrochemical experiments

Coin-type LOB and LOCB cells comprised a Li anode, an electrolyte, and a carbon cathode (ZIF67-C/CNT). 1 M LiTFSI in TEGDME was impregnated into a glass-fibre separator. To prepare the cathodes, ZIF67-C/CNT was dispersed in deionised water, followed by sonication for 1 h and filtration through a glass-fibre separator under vacuum. The cathode did not contain a binder or an additional conductive agent. The area and mass loading of the cathode were 0.785 cm² and 1.0 mg cm⁻², respectively. High-purity O₂ or O₂/CO₂ (1:2 in volume) gas was supplied to

the cell chamber. Discharge–charge experiments were performed using a battery tester (WonATech, WBCS3000S). For the PITT experiments, the cell was first discharged to 500 mAh g⁻¹ at 50 mA g⁻¹, followed by charging using a PITT procedure (voltage step = 12 mV). The cut-off current value was 12.5 mA g⁻¹. For cycling experiments, the cell was discharged to 500 mAh g⁻¹ at 200 mA g⁻¹, followed by CC charging at 200 mA g⁻¹ to 4.3 V vs. Li/Li⁺ (LOB) or 4.5 V vs. Li/Li⁺ (LOCB) and CV charging with a 20 mA g⁻¹ cut-off current and 500 mAh g⁻¹ cut-off capacity. AC impedance spectra were measured at frequency values of 10⁻²–10⁶ Hz (amplitude = 5 mV) using a Bio-Logic SP-200.

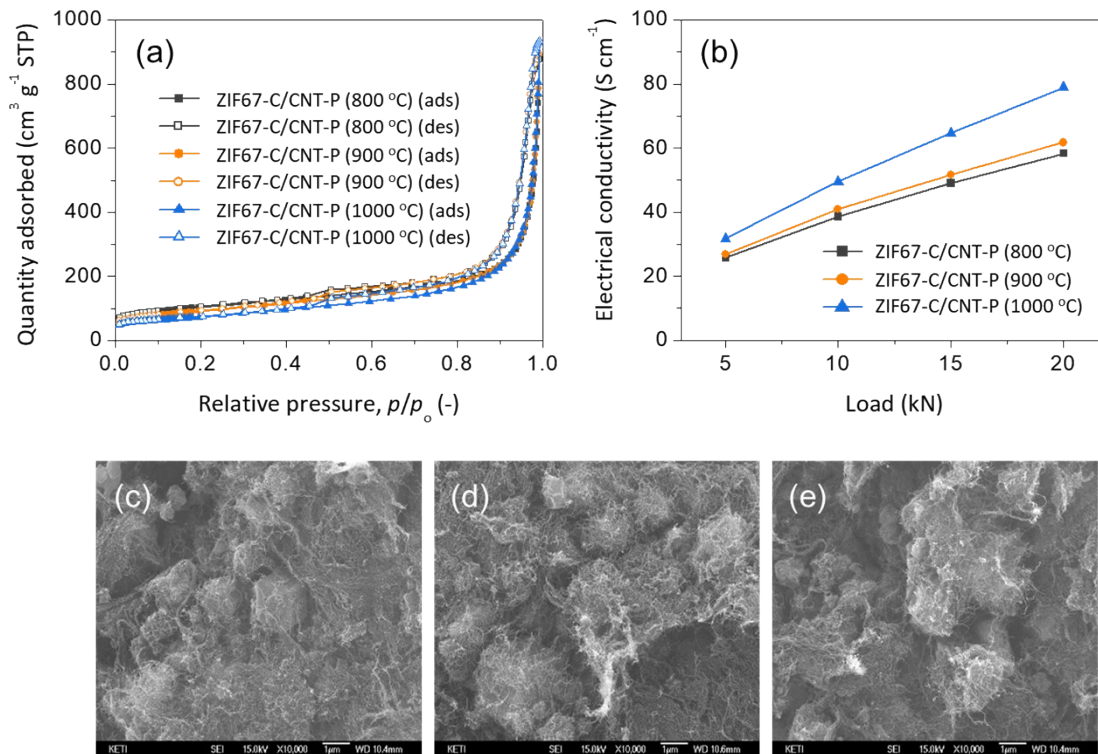


Fig. S1 Comparisons of (a) N_2 isotherms and (b) electrical conductivities of the ZIF67-C/CNT-P composites synthesised at various temperatures. SEM images of the ZIF67-C/CNT-P composites prepared at (c) 800 °C, (d) 900 °C, and (e) 1000 °C.

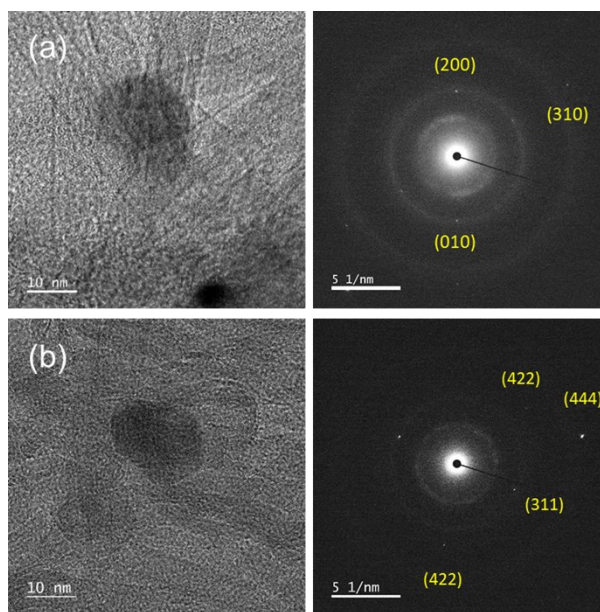


Fig. S2 TEM images combined with selected area electron diffraction (SAED) patterns of (a) ZIF67-C/CNT-P and (b) ZIF67-C/CNT-250 composites.

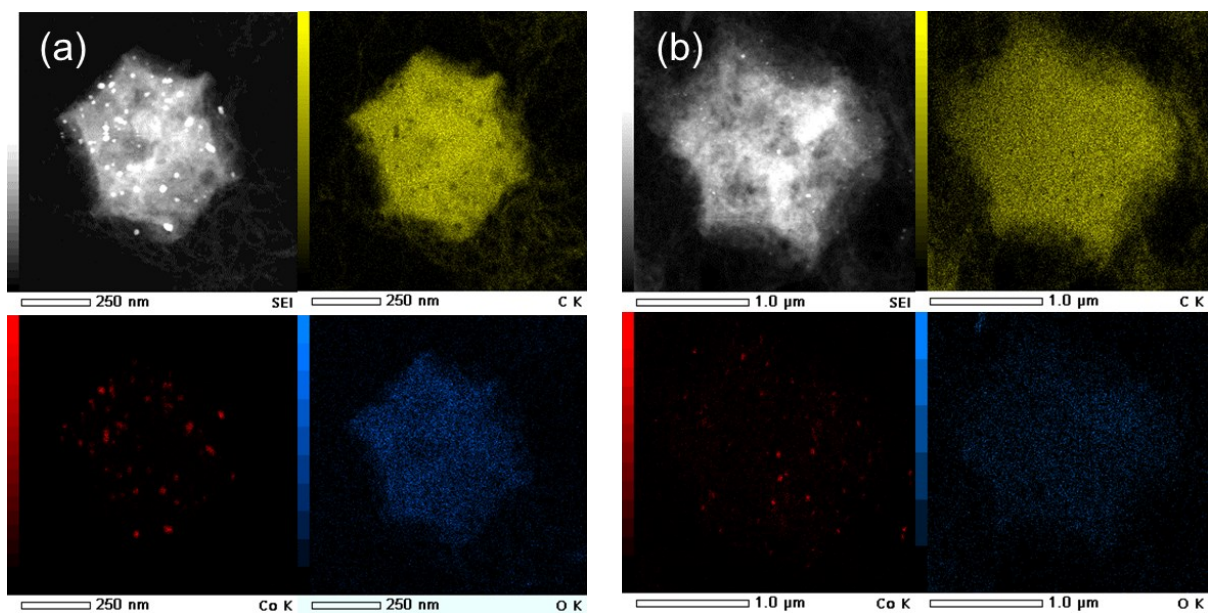


Fig. S3 EDS elemental mapping results of (a) ZIF67-C/CNT-P and (b) ZIF67-C/CNT-250 composites for C (yellow), Co (red), and O (blue).

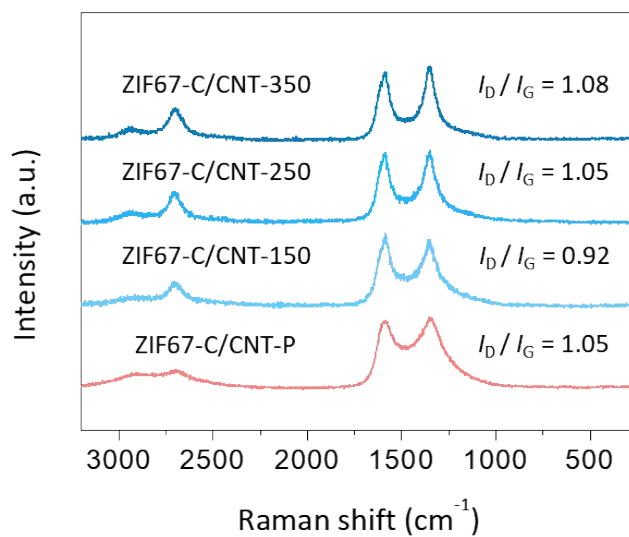


Fig. S4 Raman spectra of ZIF67-C/CNT-P and ZIF67-C/CNT-HT.

Table S1 BET surface areas and pore volumes of ZIF67-C/CNT-P and ZIF67-C/CNT-HT.

	BET surface area (m ² g ⁻¹)	Micropore volume (cm ³ g ⁻¹)	Mesopore volume (cm ³ g ⁻¹)	Macropore volume (cm ³ g ⁻¹)
ZIF67-C/CNT-P	309	0.07	0.95	0.05
ZIF67-C/CNT-150	291	0.05	1.05	0.04
ZIF67-C/CNT-250	316	0.05	1.06	0.04
ZIF67-C/CNT-350	301	0.04	1.25	0.04

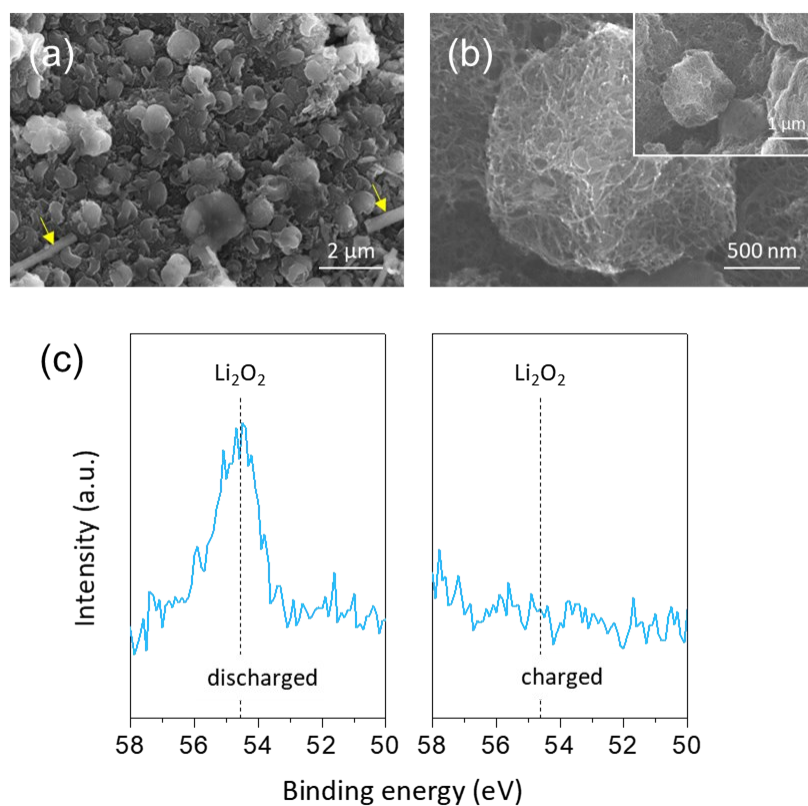


Fig. S5 SEM micrographs of the ZIF67-C/CNT-250 cathode in the LOB mode after (a) discharge and (b) recharge. The arrows in (a) show the residues from the glass fibre separator. (c) Li 1s XPS spectra of the discharged and recharged ZIF67-C/CNT-250 electrodes in O₂.

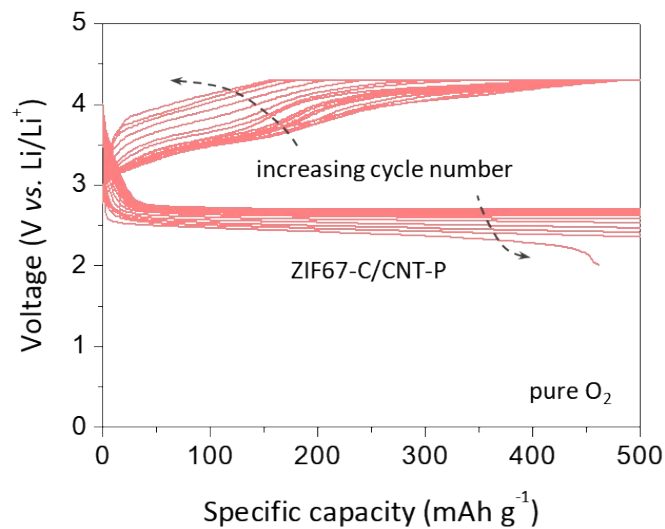


Fig. S6 Discharge–charge profiles of the LOB with ZIF67-C/CNT-P during cycling at 200 mA g⁻¹.

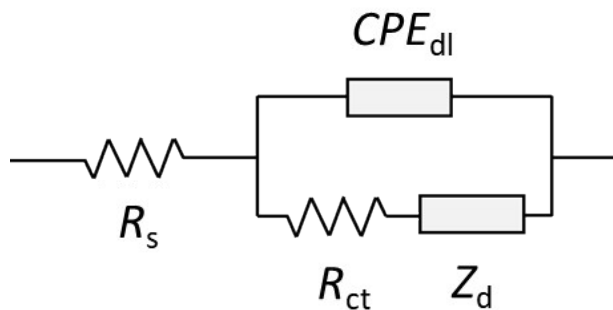


Fig. S7 Equivalent circuit employed for fitting of the measured impedance data in Fig. 4(a). R_s , R_{ct} , CPE_{dl} , and Z_d represent the uncompensated solution resistance, charge-transfer resistance, constant phase element for double-layer charging, and diffusion impedance, respectively.

Table S2 Electrical parameters of the LOB (O₂) and LOCB (O₂/CO₂) with ZIF67-C/CNT-250 determined from the CNLS fitting of the impedance spectra to the equivalent circuit (Fig. S7).

	R_s (Ω)	CPE_{dl}		R_{ct} (Ω)	Z_d		
		C	η		R_d	T	ϕ
		(mF s $^{\eta-1}$)	(-)		(Ω)	(ms)	(-)
Pure O ₂	9.6	30.3	0.84	226.3	1.4	5.9	0.48
O ₂ /CO ₂	13.7	10.1	0.82	466.2	1.8	7.7	0.48

$$CPE = C(j\omega)^\eta \text{ and } Z_d = R_d \coth([jT\omega]^\phi) / ([jT\omega]^\phi)$$

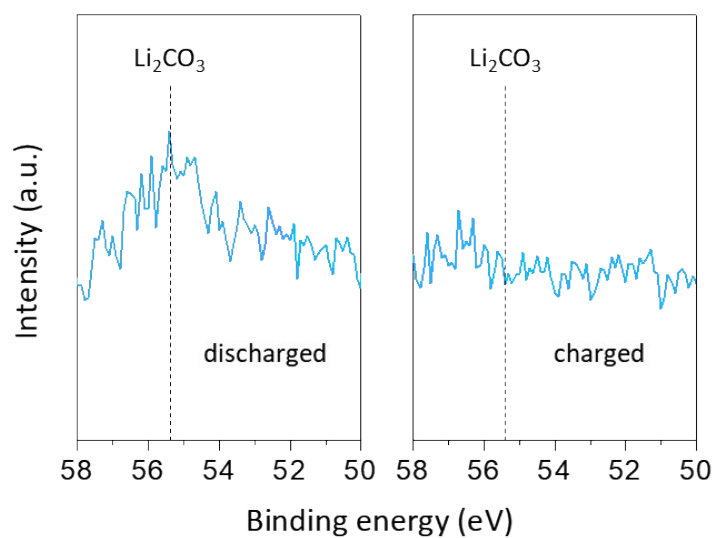


Fig. S8 Li 1s XPS spectra of the discharged and recharged ZIF67-C/CNT-250 electrodes in O₂/CO₂.

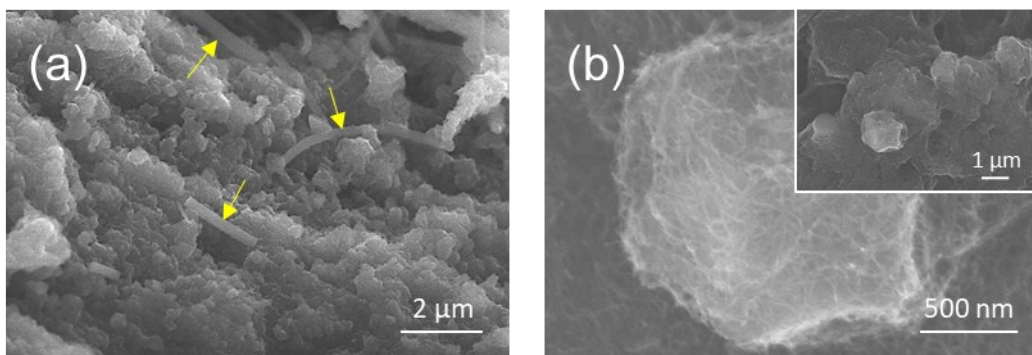


Fig. S9 SEM micrographs of the ZIF67-C/CNT-250 cathode in the LOCB mode after (a) discharge and (b) recharge. The arrows in (a) show the residues from the glass fibre separator.

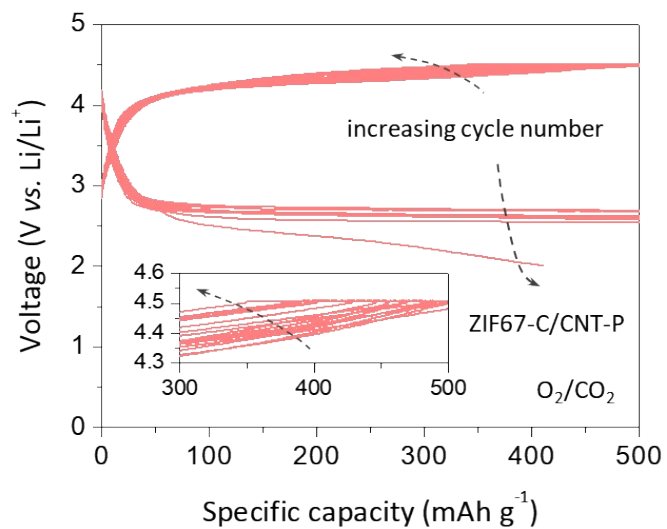


Fig. S10 Discharge-charge profiles of the LOCB with ZIF67-C/CNT-P during cycling at 200 mA g⁻¹.

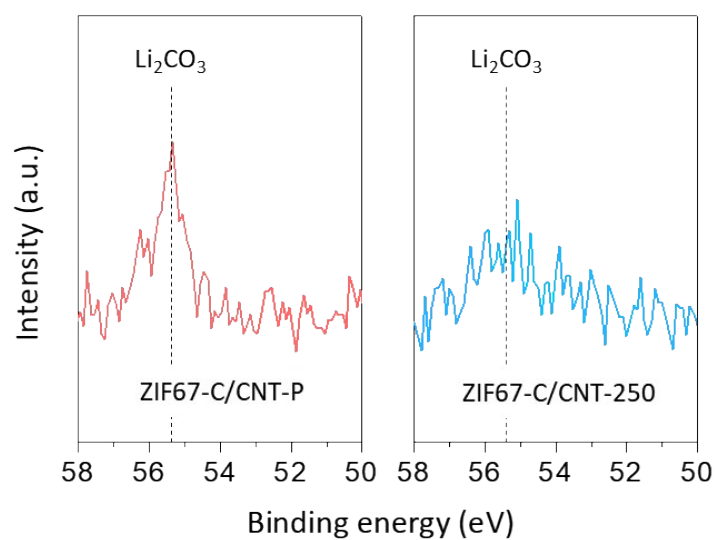


Fig. S11 Li 1s XPS spectra of the discharged ZIF67-C/CNT-P and ZIF67-C/CNT-250 electrodes after cycling test in O₂/CO₂.

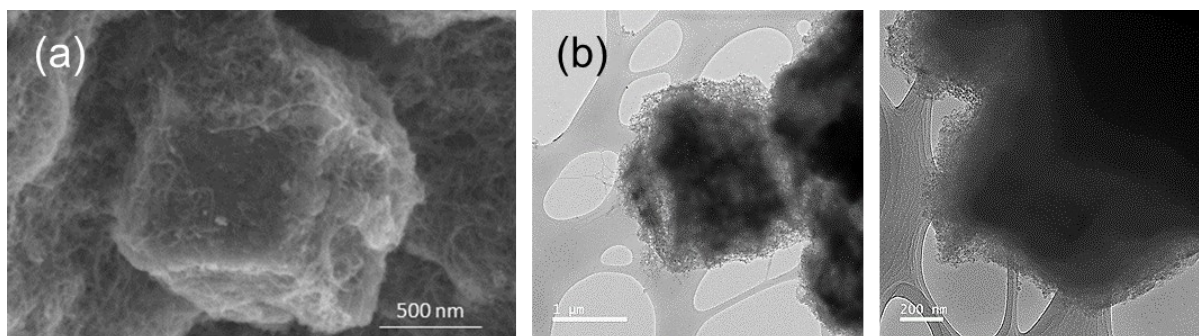


Fig. S12 (a) SEM and (b) TEM images of ZIF67-C/CNT-250 after 130 cycles.