Electronic supplementary information

Self-templated construction of peanut-like P3-type $K_{0.45}Mn_{0.5}Co_{0.5}O_2$ for highly reversible potassium storage

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Experimental Section

Synthesis of peanut-like P3-type $K_{0.45}Mn_{0.5}Co_{0.5}O_2$ (p-KMCO). Uniform peanut-shaped $Mn_{0.5}Co_{0.5}CO_3$ microparticles as the precursor were synthesized through a solvothermal method. First, 0.9 mmol Mn(CH₃COO)₂·4H₂O (Aladdin, 99.0%) and 0.9 mmol Co(CH₃COO)₂·4H₂O (Sigma, 98.0%) were added into a solution containing 10 mL of glycerol (Aladdin, 99.0%), 20 mL of H₂O, and 0.6 g of urea under (Aladdin, 99.5%) stirring. After stirring for 1 h, the pink solution was transferred to a 40 mL Teflon-lined autoclave and heated at 180 °C for 12 h. After cooling down naturally, the precursor (Mn_{0.5}Co_{0.5}CO₃) was collected by centrifugation and washed with water and ethanol several times and dried at 60 °C overnight. The as-obtained precursor was calcinated at 500 °C for 4 h in air to obtain peanut-like MnCoO₃ microparticles. Then 2 mmol MnCoO₃ and 2 mmol of KOH pellets (Aladdin, 95.0%) were dispersed and dissolved in 0.2 mL H₂O, respectively. After being homogeneously mixed, the suspension was dried at 80 °C overnight. Finally, the solid mixture was calcined at 800 °C for 10 h in air to obtain the peanut-like P3-type $K_{0.45}Mn_{0.5}Co_{0.5}O_2$. In order to prevent contamination in the air, the sample was transferred in an argon-filled glovebox when the temperature drops to 200 °C.

Synthesis of irregular P3-type $K_{0.45}Mn_{0.5}Co_{0.5}O_2$ (i-KMCO). The irregular $K_{0.45}Co_{0.5}Mn_{0.5}O_2$ particles were synthesized using a typical sol-gel method. Stoichiometric amounts of K_2CO_3 (Aladdin, 99.0%), Mn (CH₃COO)₂·4H₂O, Co (CH₃COO)₂·4H₂O, and citric acid (Aladdin, 99.5%) were dissolved in 50 mL distilled water. Then the resultant solution was evaporated overnight at 100 °C to obtain a gel precursor. subsequently, the gel precursor was calcined at 500 °C for 4 h to decompose the acetates. Finally, the powder was recalcined at 800 °C for 10 h under an air atmosphere. Similarly, the product was transferred in an argon-filled glovebox when the temperature declines to 200 °C.

Materials Characterization. The morphology and microstructure of the materials were determined by using transmission electron microscope (TEM, JEOL JEM-2100F) and field-emission scanning electron microscope (FESEM, JEOL JSM-7600F). The crystal structures were examined by X-ray diffraction (XRD; Rigaku, SmartLab). X-ray photoelectron spectroscopy (XPS) spectra were recorded on an ESCALab250Xi electron spectrometer equipped with 300 W Al Kα radiation. The

elemental ratio of synthesized material was studied by inductively coupled plasma (ICP; Shimadzu, ICPS-8100).

Electrochemical Measurements. The electrochemical characterizations were carried out using CR2032 coin-type batteries. The working electrodes were fabricated by pasting the slurry containing 70 wt% active material, 20 wt% Super-P carbon black, and 10 wt% polyvinylidene fluoride binder onto an Al foil. The loading mass of active material is in the range of 0.8–1.2 mg cm⁻². The electrolyte was 1.5 M KFSI dissolved in a mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) (1:1 v/v). Potassium thin disks and glass fiber (Whatman) were employed as the counter and reference electrodes and the separators, respectively. All the cells were assembled in an argon-filled glovebox (MBRAUN) with water/oxygen content lower than 0.1 ppm. The galvanostatic discharge/charge tests were conducted within a voltage range of 1.2–3.9 V vs. K/K⁺ on a Land CT2001A battery testing system. Cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and galvanostatic intermittent titration technique (GITT) measurements were performed on a PARSTAT 4000 electrochemical workstation. The negative electrode was prepared by mixing 80 wt% pitch-derived soft carbon, 10 wt% super-P carbon black, and 10 wt% sodium carboxymethyl cellulose onto an Al foil. Before assembling full cells, the p-KMCO and soft carbon electrodes were pre-cycled for several cycles. The full batteries were assembled with p-KMCO as the cathode, soft carbon as the anode and 1.5 M KFSI in EC/DEC (1:1 in volume) as the electrolyte, and were examined from 0.5 to 3.6 V. The specific capacities were calculated on the basis of the mass of p-KMCO or i-KMCO.



Fig. S1 XRD patterns of p-KMCO and i-KMCO.



Fig. S2 (a) SEM image and (b) TEM image of i-KMCO.



Fig. S3 (a, b) SEM images, (c) XRD pattern and (d) energy-dispersive X-ray spectroscopy (EDX) spectrum of peanut-shaped $Mn_{0.5}Co_{0.5}CO_3$ microparticles.



Fig. S4 SEM images of the precursor prepared by the mixed solvent with 25 mL of glycerol and 5 mL of H_2O (a, d), 15 mL of glycerol and 15 mL of H_2O (b, e), and 5 mL of glycerol and 25 mL of H_2O (c, f).



Fig. S5 (a, b) SEM images, (c) XRD pattern and (d) EDX spectrum of peanut-like MnCoO₃ microparticles.



Fig. S6 (a, b) SEM images of p-KMCO.



Fig. S7 EDX spectra of (a) p-KMCO and (b) i-KMCO.



Fig. S8 Nitrogen adsorption-desorption isotherms of (a) p-KMCO and (b) i-KMCO.



Fig. S9 High-resolution O 1s XPS spectrum of p-KMCO.



Fig. S10 CV curves of p-KMCO in the voltage range of 1.2-3.9 V at a scanning rate of 0.1 mV s⁻¹.



Fig. S11 (a) Galvanostatic discharge/charge profiles and (b) cycling stability of p-KMCO at 20 mA g^{-1} in the voltage range of 1.5–3.9 V.



Fig. S12 Galvanostatic discharge/charge profiles of i-KMCO at 20 mA g⁻¹ in the voltage window of 1.2–3.9 V.



Fig. S13 (a) Galvanostatic discharge/charge profiles and (b) long-term cyclic performance of p-KMCO at 20 mA g^{-1} in different electrolytes.



Fig. S14 (a) SEM image of the fresh p-KMCO electrode. (b, c) SEM images of the p-KMCO electrode after 150 cycles. (d) SEM image of the fresh i-KMCO electrode. (e, f) SEM images of the i-KMCO electrode after 150 cycles.



Fig. S15 XRD patterns of the fresh electrode and the electrode after 150 cycles for (a) p-KMCO and (b) i-KMCO.



Fig. S16 Galvanostatic discharge/charge profiles of p-KMCO at 300 mA g^{-1} .



Fig. S17 Enlarged view of (003) and (006) diffraction peaks in ex-situ XRD.



Fig. S18 XPS spectra of (a) Mn 2p and (b) Co 2p at the initial, full charging, and full discharging states.

During the first charging process, according to the peak area ratio between Mn^{3+} and Mn^{4+} , it can be estimated that the valence state of Mn changes from +3.6 to +4. In the subsequent discharging process, the valence state of Mn changes from +4 to +3.45 (**Fig. S18a**). Similarly, based on the peak area ratio between Co^{3+} and Co^{4+} the valence state of Co changes from +3.29 to +3.43 during the first charging process, and the valence state of Co changes from +3.43 to +3.38 during the subsequent discharge process (**Fig. S18b**).



Fig. S19 (a) CV curves of i-KMCO at different sweep rates from 0.1 to 1.0 mV s⁻¹. (b) Linear fitting for the peak current densities (i_p) versus the square root of sweep rates $(v^{1/2})$ obtained from CV curves in (a).

The K⁺ diffusion coefficient (D_{K+}) can be calculated based on the following Randles–Sevcik equation:

$$i_{\rm p} = 2.69 \times 10^5 n^{3/2} A D_{\rm K^+}^{1/2} v^{1/2} C \tag{1}$$

where i_p indicates the peak current (A), *n* represents the number of electrons transferred during the redox reaction, *A* stands for the surface area of the electrode (cm²), D_{K^+} is the K⁺ diffusion coefficient (cm² s⁻¹), *v* means the scanning rate (V s⁻¹), and *C* is the concentration of K⁺ in the electrode (mol cm⁻³).



Fig. S20 (a) Nyquist plots toward K⁺ storage and (b) the coefficients of Warburg impedance (σ) obtained from the linear fitting of Z versus $\omega^{-1/2}$ plots for the p-KMCO and i-KMCO cathodes.

As shown as **Fig. S20a**, all the Nyquist plots consist of a depressed semicircle in the highmedium frequency region and a linear line in the low frequency region. The former is associated with the charge-transfer process (R_{ct}) at the electrolyte/electrode interphase, and the latter is related to the Warburg impedance (Z_w) corresponding to K⁺ diffusion in the p-KMCO and i-KMCO electrodes. R_e refers to the electrolyte resistance, and C_{dl} represents the constant phase element.



Fig. S21 (a) SEM and (b) TEM images of pitch-derived soft carbon.



Fig. S22 XRD pattern of pitch-derived soft carbon.



Fig. S23 (a) CV profiles of the initial three cycles at a scanning rate of 0.1 mV s⁻¹, (b) galvanostatic discharge/charge profiles at 50 mA g⁻¹, (c) rate property, and (d) cyclic performance at 50 mA g⁻¹ of pitch-derived soft carbon.



Fig. S24 A coin-type full battery that illuminates 31 light-emitting diode (LED) bulbs arranged in "PIB".

Formula	K _{0.45} Mn _{0.5} Co _{0.5} O ₂		
Space group	R3m		
<i>a</i> , Å	2.8670(1)		
b, Å	2.8670(1)		
<i>c</i> , Å	18.9282(6)		
V, Å ³	134.73(6)		
Z	3		
Radiation	X-rays, Cu Kα		
	$\lambda_1 = 1.54051$ Å, $\lambda_2 = 1.54433$ Å		
2θ range, step, deg.	5–90, 0.01		
χ^2	2.047		
R _{wp} , R _p	7.41%, 5.62%		

Table S1. Crystallographic data and parameters of the Rietveld refinement for p-KMCO.

Composition	Molar ratio		
	K	Mn	Со
p-KMCO	0.4537	0.5218	0.5071
i-KMCO	0.4487	0.5104	0.4977

Table S2. Chemical composition analysis of as-prepared samples.

Cathode materials	Initial reversible capacity (mAh g ⁻¹)	Cycling property (mAh g ⁻¹)	Rate capability (mAh g ⁻¹)	References
р-КМСО	123.2 (20 mA g ⁻¹)	73.8% (300 cycles)	66.8 (300 mA g ⁻¹)	This work
K _{0.32} MnO ₂	95.1 (10 mA g ⁻¹)	35.1% (50 cycles)	$35.5 (200 \text{ mA g}^{-1})$	1
K _{0.5} MnO ₂ hollow submicrosphere	104 (10 mA g ⁻¹)	89% (400 cycles)	34.2 (300 mA g ⁻¹)	2
$K_{5/9} Mn_{7/9} Ti_{2/9} O_2$	131.2 (20 mA g ⁻¹)	73% (100 cycles)	52.2 (500 mA g^{-1})	3
$\begin{array}{c} K_{0.7}Fe_{0.5}Mn_{0.5}O_2\\ nanowires \end{array}$	178 (20 mA g ⁻¹)	85% (200 cycles)	58 (1000 mA g ⁻¹)	4
P3-K _{0.45} Mn _{0.5} Co _{0.5} O ₂	$140 (10 \text{ mA g}^{-1})$	86% (100 cycles)	68 (100 mA g ⁻¹)	5
$K_{0.48}Ni_{0.2}Co_{0.2}Mn_{0.6}O_2$	57 (40 mA g ⁻¹)	71% (350 cycles)	29.8 (0.8 A g ⁻¹)	6
$K_{0.5}Mn_{0.72}Ni_{0.15}Co_{0.13}O_2$	83 (10 mA g ⁻¹)	75% (300 cycles)	58 (500 mA g ⁻¹)	7
$K_{0.6}Mn_{0.8}Ni_{0.1}Ti_{0.1}O_2$	118 (10 mA g ⁻¹)	88% (100 cycles)	48 (500 mA g ⁻¹)	8

Table S3. Comparison of potassium storage properties of Mn-based layered transition metal oxide cathodes.

Electrode	$R_{\rm e}\left(\Omega ight)$	$R_{ m ct}\left(\Omega ight)$	$\sigma_{ m w}~(\Omega~{ m s}^{-1/2})$	$D_{\rm K^+}({ m cm}^2~{ m s}^{-1})$
р-КМСО	22	3770	62	1.25×10^{-12}
i-KMCO	42	4751	126	2.93×10^{-13}

Table S4. the fitted impedance values (R_e and R_{ct}), Warburg factors (σ_w), and K⁺ diffusion coefficient of (D_{K^+}) of the electrodes.

 $D_{\rm K^+}$ can be calculated by EIS based on the following equation: ^{9,10}

$$D_{K^+} = \frac{R^2 T^2}{2A^2 n^4 F^4 C^2 {\sigma_w}^2}$$

where *R* is the gas constant, *T* means the temperature in Kelvin, *A* represents the surface area of electrode, *n* indicates the number of transferred electrons, *F* is the Faraday constant, *C* refers to the concentration of K⁺, and σ_w is the Warburg factor. σ_w correlates to $Z_{\rm re}$ (i.e., *Z'*) through the following equation and its value can be achieved from the slope of $Z_{\rm re} \sim \omega^{-1/2}$ plot as demonstrated in **Fig. S20b**.

$$Z_{\rm re} = R_{\rm e} + R_{\rm ct} + \sigma \omega^{-0.5}$$

In **Table S4**, the D_{K^+} value of the p-KMCO electrode (1.25 × 10⁻¹² cm² s⁻¹) is much higher than that of i-KMCO electrode (2.93 × 10⁻¹³ cm² s⁻¹), which reflects that peanut-like hierarchical architecture can accelerate the K⁺ diffusion kinetics.

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