Supporting information

Hierarchical mesoporous octahedral K₂Mn_{1-x}Co_xFe(CN)₆ as a superior cathode

material for sodium-ion batteries

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Fig. S1 XPS spectra of (A) Fe2p and (B) Mn2p of KMCHFC (*x*=0); (C) Fe2p, (D) Mn2p and (E) Co2p of KMCHFC (*x*=0.1).



Fig. S2 TG curve of KMCHFC (x=0, 0.05, 0.1, 0.2). TG measurement was carried out at a heating rate of 10 °C min⁻¹ in air.



Fig.S3 HRTEM images of (A) KMHFC and (B) KMCHFC (x=0.1).



Fig. S4 The pore-size-distribution curves of (A) KMHFC and (B) KMCHFC (x=0.1) using DFT method. The model is N₂-cylindrical pores in an Oxide surface at 77K.



Fig. S5 XRD patterns of KMCHFC (*x*=0, 0.05, 0.1, 0.2) after 1 cycle.



Fig. S6 (A) Charge/discharge profiles of the KMCHFC (x=0.1) electrode tested at 1st charge-discharge process, the numbers 1-12 stand for the depths of charge/discharge; (B) XRD patterns of the electrode at various states (the number 13 was taken for the electrode when the voltage goes down to 2 V); (C-D) The corresponding magnified

XRD patterns.



Fig. S7 TEM images of the electrodes made of KMCHFC (x=0.1) after 150 cycles.

Samples	a ()	b ()	c ()
KMHFC	15.12	15.12	18.20
KMCHFC (<i>x</i> =0.05)	15.09	15.09	18.09
KMCHFC (<i>x</i> =0.1)	15.07	15.07	17.98
KMCHFC (<i>x</i> =0.2)	15.04	15.04	17.89

Table S2 Unit cell parameters of $K_2Mn_{1-x}Co_xFe(CN)_6$ (x=0, 0.05, 0.1, 0.2) after 1 cycle

Samples	a ()	b ()	c ()
NMHFC	15.10	15.10	18.14
NMCHFC (<i>x</i> =0.05)	15.06	15.06	18.07
NMCHFC (<i>x</i> =0.1)	15.02	15.02	17.95
NMCHFC (<i>x</i> =0.2)	14.98	14.98	17.84

Samples	$R_s(\Omega)$	$R_{\rm f}(\Omega)$	$R_{ct}(\Omega)$	$\sigma(\Omega~{ m cm}^2{ m s}^{-0.5})$	D (cm ² s ⁻¹)
<i>x</i> =0	5.0	358.9	2120	83.0	5.27E-14
<i>x</i> =0.05	3.9	264.8	1910	63.5	9.01E-14
<i>x</i> =0.1	3.5	220.0	992	3.0	4.04E-11
<i>x</i> =0.2	3.2	194.5	1640	50.0	1.45E-13

 Table S3 EIS parameters and diffusion coefficient of sodium ion for KMCHFC (x=0,

0.05, 0.1, 0.2)