Supporting Information

High Mixing Entropy of MnFeCoNiCu-S to Drive High Performance Sodium Storage

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Experimental section

Manganese nitrate tetrahydrate ($Mn(NO_3)_2 \cdot 4H_2O$), iron acetate tetrahydrate ($Fe(CO_2CH_3)_2 \cdot 4H_2O$), cobalt nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$), copper nitrate trihydrate ($Cu(NO_3)_2 \cdot 3H_2O$), nickel nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$), 2, 5-dihydroxyterephthalic acid ($C_8H_6O_6$) were purchased from Shanghai Aladdin Biochemical Technology Co., LTD. N, N-dimethyl formamide (DMF), methanol (MeOH) and ethyl alcohol (EtOH) were purchased from Tianjin Deen Chemical Reagent Co., LTD. These reagents are analytically pure grade and used without further purification.

Synthesis of MnFeCoNiCu-MOF

0.1030 g Mn(NO₃)₂·4H₂O, 0.1220 g Fe(CO₂CH₃)₂·4H₂O, 0.1600 g Co(NO₃)₂·6H₂O, 0.1330 g Ni(NO₃)₂·6H₂O, 0.0190 g Cu(NO₃)₂·3H₂O and 0.1980 g 2, 5dihydroxyterephthalic acid (H₄dobdc) were dissolved in a mixed solvent containing 2.7 mL deionized water, 45 mL DMF and 2.7 mL EtOH. Then the mixtures were ultrasounded for 30 min to form a evenly mixed solution, and the solution was transferred to a 100 mL high-pressure reactor and reacted in an oven at 120 °C for 24 h. The product was washed several times with deionized water, DMF and EtOH, respectively, and then dried overnight at 60 °C.

Synthesis of MnFeCoNi-MOF

0.1080 g Mn(NO₃)₂·4H₂O, 0.1280 g Fe(CO₂CH₃)₂·4H₂O, 0.1660 g Co(NO₃)₂·6H₂O, 0.1660 g Ni(NO₃)₂·6H₂O, and 0.1980 g 2, 5-dihydroxyterephthalic acid were dissolved in a mixed solvent containing 2.7 mL deionized water, 45 mL DMF and 2.7 mL EtOH. The remaining steps are consistent with the synthesis of MnFeCoNiCu-MOF.

Synthesis of MnFeCoNiCu-S

Equal weight of MnFeCoNiCu-MOF and sulfur powder were ground until evenly mixed, and then transferred to a porcelain boat, which was heated to 500 °C at a heating rate of 5 °C/min under argon atmosphere and kept for 2 h. The process of synthesis of MnFeCoNi-S is similar.

Characterization of materials

Powder X-ray diffraction (PXRD, Bruker D8 ADVANCE) the XRD patterns were measured in a 2 θ range of 10-80° at a scan rate 5°/min with a Cu K α radiation (λ =1.5406Å). X-ray photoelectron spectroscopy spectrometer (XPS, Thermo Scientific Escalab 220i-XL), Raman (LABRAM HR Evolution 532 nm), Inductively coupled plasma-mass spectrometry (ICP-MS), Field emission scanning electron microscope (FESEM, Hitachi, SU8010) and transmission electron microscope (TEM, Hitachi, JEOL-JEM2100F) were used to study the crystal structure, elemental presence and morphology of the electrode material. The specific surface area and pore size distribution data were obtained using ASAP 2460 with N₂ adsorption/desorption test at 77 K.

Electrochemical measurements

The preparation of anode is as follows: MnFeCoNiCu-S, Ketjen black (ECP-600) and binder Polyvinylidene fluoride (PVDF) were dissolved in N-methylpyrrolidone (NMP)) are with a weight ratio of 7:2:1; the mixtures were ground into evenly slurry; the slurry was evenly coated on a copper foil with a diameter of 12 mm, and dried under vacuum at 110 °C for 12 h. The loading of the active substance was about $0.8\sim1.2$ mg/cm². The coin cell (CR2032) was assembled in an inert gas glove box (H₂O and O₂ concentrations <0.5 ppm). Whatman GF/F was used as seperator and 1.0 M NaCF₃SO₃ DLGLYME=100vol% solution was used as electrolyte. The voltage window of the half battery is set to $0.3\sim2.8$ V to analyze the electrochemical performance. Discharge/charge curves, specific capacity and rate performance were obtained using the LAND battery test system. CV and EIS tests were performed on an electrochemical workstation (CHI 660E) with CV scan rates of 0.1 to 1 mV/s and EIS measurements in the frequency range of 10^5 to 10^{-2} Hz.

Assembly and electrochemical test of the full battery: $Na_3V_2(PO_4)_3$ coated on aluminum foil with a diameter of 12 mm was cathode. The mass ratio of cathode and anode active materials is about 4:1. 1.0 M NaPF₆ was used as the electrolyte in the DLGLYME=100% solution, and Whatman GF/F was used as the seperator. The voltage test window for full battery is 0 to 3 V.

Theoretical calculation

We have employed the VASP^{1,2} to perform all the spin-polarized density functional theory (DFT) calculations within the generalized gradient approximation (GGA) using the Perdew-Burke-Ernzerhof (PBE)³ formulation. We have chosen the projected augmented wave (PAW) potentials^{4,5} to describe the ionic cores and take valence electrons into account using a plane wave basis set with a kinetic energy cutoff of 400 eV. Partial occupancies of the Kohn–Sham orbitals were allowed using the Gaussian smearing method and a width of 0.05 eV. The electronic energy was considered self-consistent when the energy change was smaller than 10^{-6} eV. A geometry optimization was considered convergent when the force change was smaller than $-0.05 \text{ eV}/Å^2$. Grimme's DFT-D3 methodology⁶ was used to describe the dispersion interactions among all the atoms. During structural optimizations of the surface models, the 1×2×1 gamma-point centered k-point grid for Brillouin zone was used.



Fig. S1 The synthetic scheme of the MnFeCoNiCu-S.



Fig. S2 XRD patterns of MnFeCoNiCu-MOF.

MnFeCoNiCu-MOF	Weight percent	Molar ratios in metal
Fe	4.12 %	27%
Со	5.01 %	32%
Ni	4.03 %	25%
Mn	1.93 %	13%
Cu	0.51%	3%



Fig. S3 The ICP-MS analysis of MnFeCoNiCu-S.



Fig. S4 XRD patterns of MnFeCoNi-S.



Fig. S5 XRD patterns of MnFeCoNiCu-S.



Fig. S6 (a, b) FESEM images of the MnFeCoNi-MOF and (c, d) the MnFeCoNi-S.



Fig. S7 XPS survey spectra of the MnFeCoNiCu-S.



Fig. S8 XPS survey spectra of the MnFeCoNi-S.



Fig. S9 High-resolution XPS spectra of MnFeCoNi-S (a) Mn 2p, (b) Fe 2p, (c) Co 2p and (d) Ni 2p.



Fig. S10 (a, c) Nitrogen adsorption and desorption isotherms of the MnFeCoNi-S sample and MnFeCoNiCu-S sample. (b, d) Plots of pore-size distribution for the MnFeCoNi-S sample and MnFeCoNiCu-S sample.



Fig. S11 Cycling performance of the MnFeCoNiCu-S anode at 2.0 A g^{-1} .



Fig. S12 Discharge-charge profiles of (a) CoS_2 , (b) NiS_2 , (c) Fe_7S_8 , (d) $Cu_{1.96}S$, (e) MnS_2 , electrodes at 5 A g⁻¹.



Fig. S13 Cycling performance of (a) CoS_2 , (b) NiS_2 , (c) $Cu_{1.96}S$, (d) MnS_2 and (e) Fe_7S_8 anode at 5.0 A g⁻¹.

Table S2 Comparison of electrochemical properties between the MnFeCoNiCu-S,MnFeCoNi-S and mono-metallic sulfide.

electrode	Current density	Cycle number	Specific	specific capacity
material	(A g ⁻¹)		capacity $(mA h g^{-1})$	retention rate
MnFeCoNiCu-S	5.0	7000	326.4	91.2%
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MnFeCoNi-S	5.0	3580	212	48.2%
CoS ₂	5.0	2500	99.8	49.9%
2				
NiS ₂	5.0	2500	83.6	42.6%
Cu _{1.96} S	5.0	2500	258.7	90.5%
MnS_2	5.0	2500	74.5	149%
Fe_7S_8	5.0	2500	257.9	67.6%



Fig. S14 Comparison of rate capability of MnFeCoNiCu-S with other reported different metal sulfides.

Electrode material	Current density (A g ⁻¹)	Cycle number	Specific capacity (mA h g ⁻¹)	References
NiS-HNP@CFs-900	5.0	600	251.4	[7]
Sn ₂ S ₃ @CHS	0.5	150	338	[8]
$Co_{0.5}Fe_{0.5}S_2$	2.0	5000	220	[9]
FeS ₂ /NG	2.0	10000	251	[10]
CuS	5.0	/	246	[11]
$FeS_2 @SnS_2$	5.0	1400	262.5	[12]
MnFeCoNiCu-S	5.0	7000	326.4	The work

Table S3 Comparison between this work and other reported different metal sulfides.



Fig. S15 Kinetic analysis of the MnFeCoNi-S anode, (a) CV curves in the scan rate range of $0.1 \sim 1 \text{ mV/s.}$ (b) Log (*i*) versus log (*v*) plots based on specific peak currents and scan rates. (c) Capacitance contribution ratio at a scan rate of 0.8 mV/s. (d) Capacitance contribution ratio and diffusion-limited ratio at different scan rates.



Fig. S16 EIS spectra of the CoS_2 , NiS_2 , Fe_7S_8 , $Cu_{1.96}S$, MnS_2 and an equivalent circuit model for EIS fitting.



Fig. S17 (a) XRD, and (b, c) FESEM of the MnFeCoNi-S anode after cycle at the current density of 5 A g^{-1} .



Fig. S18 FESEM images of the MnFeCoNiCu-S anode after (a) 100, (b) 500 and (c) 1000 cycles at the current density of 5 A g^{-1} .



Fig. S19 The optimized structure of Cu_7S_4 .



Fig. S20 The optimized structure of (MnFeCoNiCu)₇S₄.



Fig. S21 Na⁺ ion diffusion paths and energy barriers in $(MnFeCoNi)S_2$.



Fig. S22 The performance of MnFeCoNi-S//Na₃V₂(PO₄)₃ full battery. (a) Dischargecharge curves of the full battery at 0.5 A g^{-1} . (b) Cycling performance at 0.5 A g^{-1} . (c) Rate performance of the full battery.

Table S4 Comparison of performance of full batteries of MnFeCoNiCu- $S//Na_3V_2(PO_4)_3$ and MnFeCoNi-S//Na $_3V_2(PO_4)_3$ at different rates.

Current	MnFeCoNiCu-S	MnFeCoNi-S	
densities (A g ⁻¹)	Specific capacity (mA h g ')	Specific capacity (mA h g ')	
0.1	389.8	202.4	
0.2	319.9	104.3	
0.5	275.7	67.7	
1	224.5	39.3	
2	172.7	19.6	

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