Entropy engineering strategy boosting high-entropy spinel oxide

electrode with impressive capacitance and energy density

Feng Zhang^a, Xinpeng Huang^a, Xuehua Yan^{a,b,*}, Chu Chu^a, Lanyun Di^a, Jili Wu^a,

Jianmei Pan^a

^aSchool of Materials Science and Engineering, Jiangsu University, Zhenjiang 212013, Jiangsu, China ^bInstitute for Advanced Materials, Jiangsu University, Zhenjiang 212013, Jiangsu, China

*Corresponding author: Prof.Dr. Xuehua Yan, xhyan@ujs.edu.cn

1. Experimental Section

1.1 Characterization.

XRD patterns were obtained on a D8ADVANCE diffractometer to investigate the crystal structures and lattice parameters of various spinel oxides. SEM using a field emission scanning electron microscope (FE-SEM, JEOL JSM-7800F, Japan) was employed to investigate the morphologies and surface characteristics of all spinel oxide samples. TEM images were taken using a JEM-2100 F transmission electron microscope operated at 40 kV. HRTEM, HAADF-STEM, and EDS analyses were performed by using a JEOL JEM-ARF200F probe-corrected transmission electron microscope with aberration correction. The chemical states of various elements were determined by XPS using a Thermo VG ESCALAB250 X-ray photoelectron spectrometer. Micromeritics ASAP 2460 instruments were used to conduct the Low-temperature nitrogen gas adsorption/desorption experiments. The compositions of all samples were determined by ICP-MS (iCAP PRO, Agilent, USA).

1.2 Electrochemical Measurements.

The electrode material was tested using a three-electrode system (CHI 760e, CH Instruments Inc). The working electrode was nickel foam coated with active material. To prepare the HEO/NF electrode, the mass m_0 of the NF was first weighed, then the active material, acetylene black, and PVDF were mixed evenly in a mass ratio of 7:2:1. An appropriate amount of NMP was then added dropwise, and the suspension was uniformly coated on the NF. It was dried in a vacuum oven, and the mass m of the coated NF was weighed, note that the mass at this point is m. The working electrode was then immersed in a 1 M KOH solution for 12 h. The reference electrode, counter

electrode, and electrolyte were Ag/AgCl (saturated in 1 M KOH), platinum foil, and 1 M KOH, respectively. Cyclic voltammetry tests were conducted at scan rates from 1 to 5 mV s⁻¹, and galvanostatic charge-discharge tests were performed at current densities of 1, 2, 3, 5, and 10 A g⁻¹. Impedance spectroscopy tests were conducted over a frequency range from 0.1 Hz to 10^5 Hz.

2. Experimental Formulas

Starting from Boltzmann's fundamental entropy formula $S = K_b \ln \Omega$, we can enumerate the relationship between the number of microstates Ω related to the configurational entropy of multiple elements that occupy the same crystallographic positions (S_{conf}):

$$S_{conf} = -R \sum_{i} x_{i} \ln x_{i} \qquad |*MERGEFORMAT(1)|$$

Where x_i represents the mole fraction of the i-th component, and R is the universal gas constant. It is generally considered that $S_{conf} \ge 1.5$ R for high entropy materials. The calculation formula of mass-specific capacitance (Cm, F g⁻¹) used in this paper is:

$$C_m = \frac{I\Delta t}{m\Delta V} \qquad |*MERGEFORMAT(2)$$

Where I (A), t (s), V (V), and m (g) are respectively the discharge current, discharge time, voltage range, and active load mass.

The charge balance equation is used to calculate the optimal mass ratio of positive and negative electrode active materials, which can be obtained.

$$\frac{m^{+}}{m^{-}} = \frac{C_{-}\Delta V_{-}}{C_{+}\Delta V_{+}} \qquad |*MERGEFORMAT(3)$$

Where, m^+ , ΔV^+ , and C^+ are the weight of the active material, the voltage window, and the specific capacitance of the electrode material. Again, m^- , ΔV^- , and $C^$ corresponds to the negative pole.

When the supercapacitor is tested with two electrodes, the calculation of the massspecific capacitance (Cs, F g^{-1}) is similar to that of the three electrodes:

$$C_{s} = \frac{I\Delta t}{m\Delta V} \qquad |*MERGEFORMAT(4)$$

The energy density (E) and power density (P) of the supercapacitor are calculated as shown in (Formula 5 and 6):

$$E = \frac{I \int V dt}{3.6 * m} \qquad |*MERGEFORMAT(5)|$$

Where I (A), V (V), t (s), m (g), and E (Wh Kg⁻¹) are the discharge current, discharge time, voltage, active load mass, and energy density, respectively.

$$P = \frac{3600 * E}{\Delta t} \qquad |*MERGEFORMAT(6)|$$

Where E (Wh Kg⁻¹), t (s), and P (W Kg⁻¹) are the energy density, discharge time, and power density, respectively.

3. Supplementary Figures



Fig.S1 Electrochemical properties. (a) CV curves of (Co, Fe)O; (b) GCD curves of (Co, Fe)O.



Fig.S2 Electrochemical properties. (a) CV curves of (Ni, Fe)O; (b) GCD curves of (Ni, Fe)O



Fig.S3 Electrochemical properties. (a) CV curves of (Cr, Fe)O; (b) GCD curves of (Cr, Fe)O



Fig.S4 Electrochemical properties. (a) CV curves of (Mn, Fe)O; (b) GCD curves of (Mn, Fe)O



Fig.S5 Electrochemical properties. (a) CV curves of (Cu, Fe)O; (b) GCD curves of (Cu, Fe)O.



Fig. S6 Cycling performance of the S-HEO electrode in a three-electrode system.

4. Supplementary tables

Metal Ion	Oxidation States (XPS)	Active Fraction (XPS)	Estimated e⁻/mol	Molar Mass (g/mol)	Estimated Theoretical Capacitance $(F \cdot g^{-1})$
Со	Co ³⁺ /Co ²⁺	52% / 48%	0.52	58.93	~850
Ni	Ni ³⁺ /Ni ²⁺	50% / 50%	0.50	58.69	~821
Cr	Cr^{3+}/Cr^{2+}	60% / 40%	0.60	51.99	~1112
Mn	Mn ³⁺ only	100%	1.00	54.94	~1756
Cu	Cu ²⁺ only	100%	~0.30 (e st.)	63.55	~455
Fe	Fe^{3+}/Fe^{2+}	66% / 34%	0.66	55.85	~1140

Table S1 Estimated Capacitance Contributions of A/B site Metals.

References

- [1] Q. Zhang; W. Zhang; P. Hei et al., Appl. Surf. Sci., 2020, 527, 146682.
- [2] S. Yu; N. Yang; M. Vogel et al., Adv. Energy Mater., 2018, 8, 1702947.
- [3] Q. Zhang; W. Zhang; X. Ma et al., J. Alloys Compd., 2021, 864, 158106.