Supporting information

In-situ Self-Segregation Construction of a Six-Metal LDH/Co-Mn-Oxide Heterostructure on Copper Foam for Alkaline Oxygen Evolution

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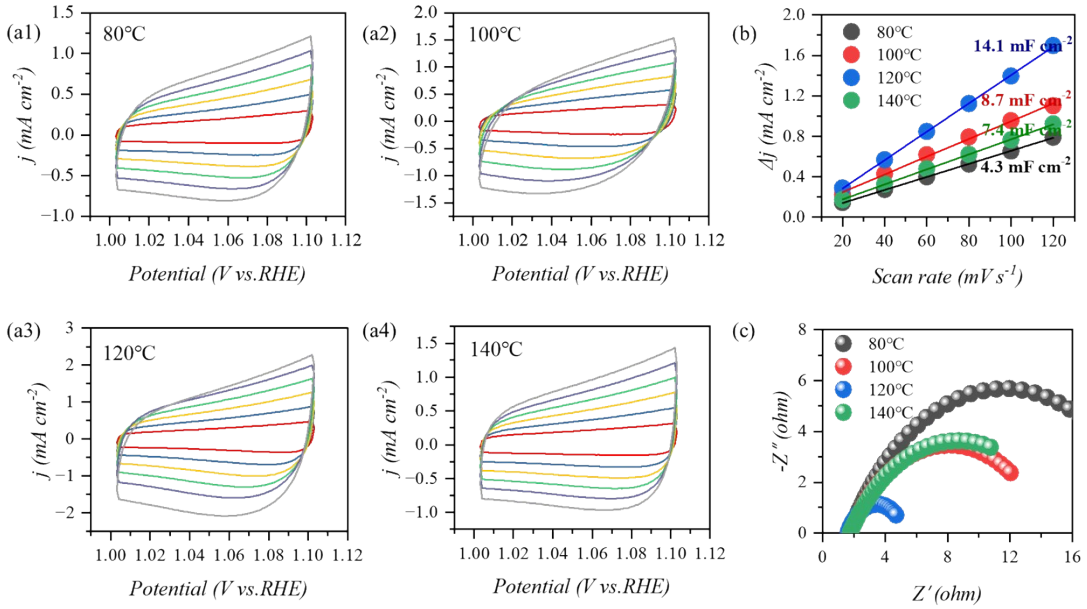

Fig.S1 Electrochemical performance testing of samples prepared at a series of hydrothermal temperatures: (a1-a4) CV at different scanning speeds of 20 mV s^{-1}, 40 mV s^{-1}, 60 mV s^{-1}, 80 mV s^{-1}, 100 mV s^{-1}, 120 mV s^{-1}, (b) C_{dl}, (c) EIS

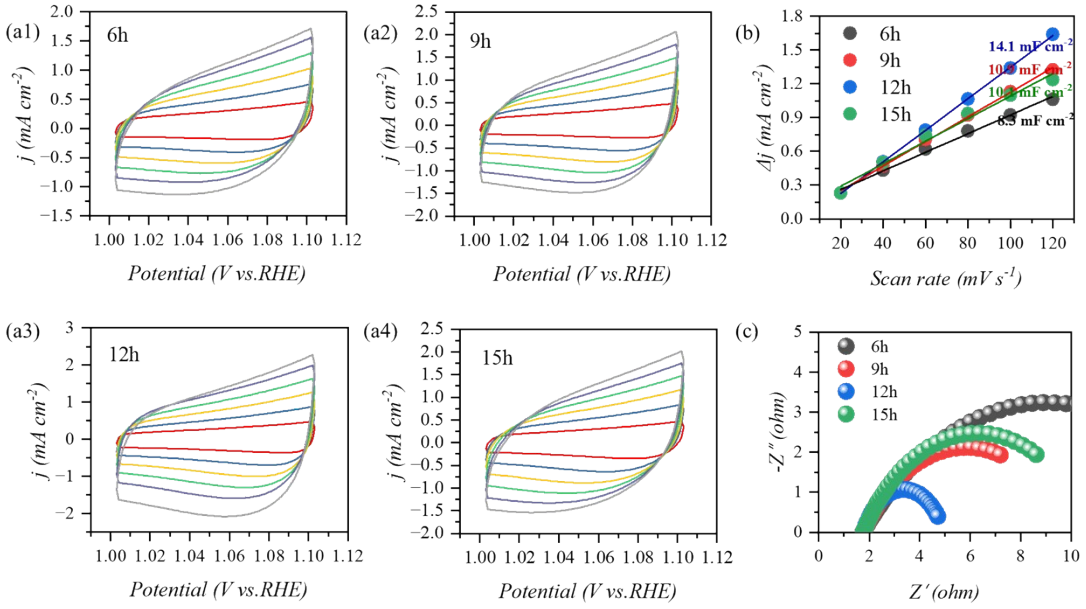

Fig.S2 Electrochemical performance testing of samples prepared at a series of hydrothermal time: (a1-a4) CV at different scanning speeds of 20 mV s^{-1}, 40 mV s^{-1}, 60 mV s^{-1}, 80 mV s^{-1}, 100 mV s^{-1}, 120 mV s^{-1}, (b) C_{dl}, (c) EIS

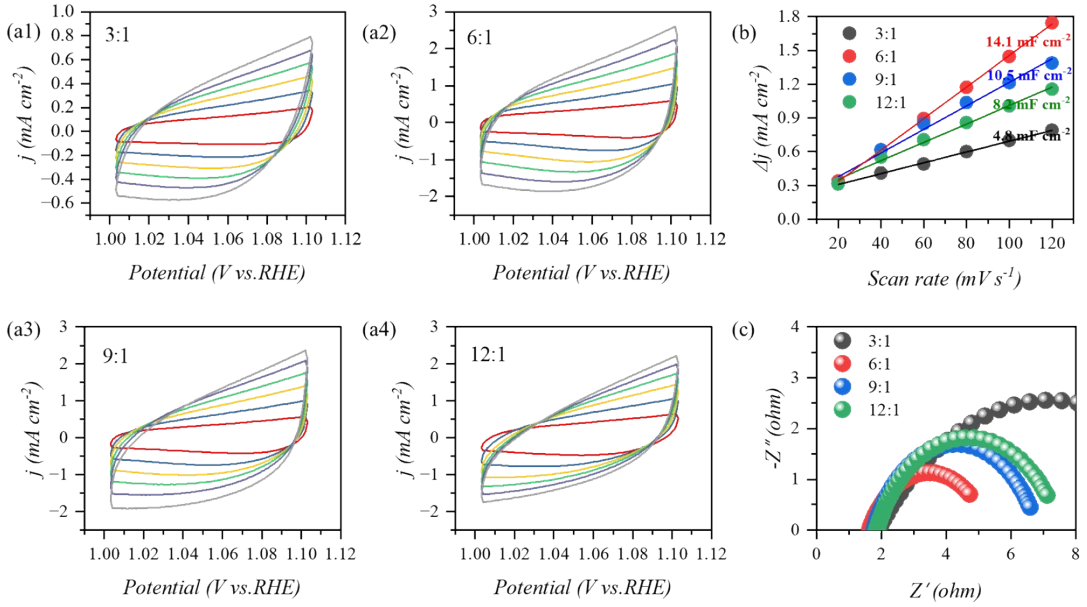

Fig.S3 Electrochemical performance testing of samples prepared at a series of Urea/M^{2+} ratios: (a1-a4) CV at different scanning speeds of 20 mV s^{-1}, 40 mV s^{-1}, 60 mV s^{-1}, 80 mV s^{-1}, 100 mV s^{-1}, 120 mV s^{-1}, (b) C_{dl}, (c) EIS

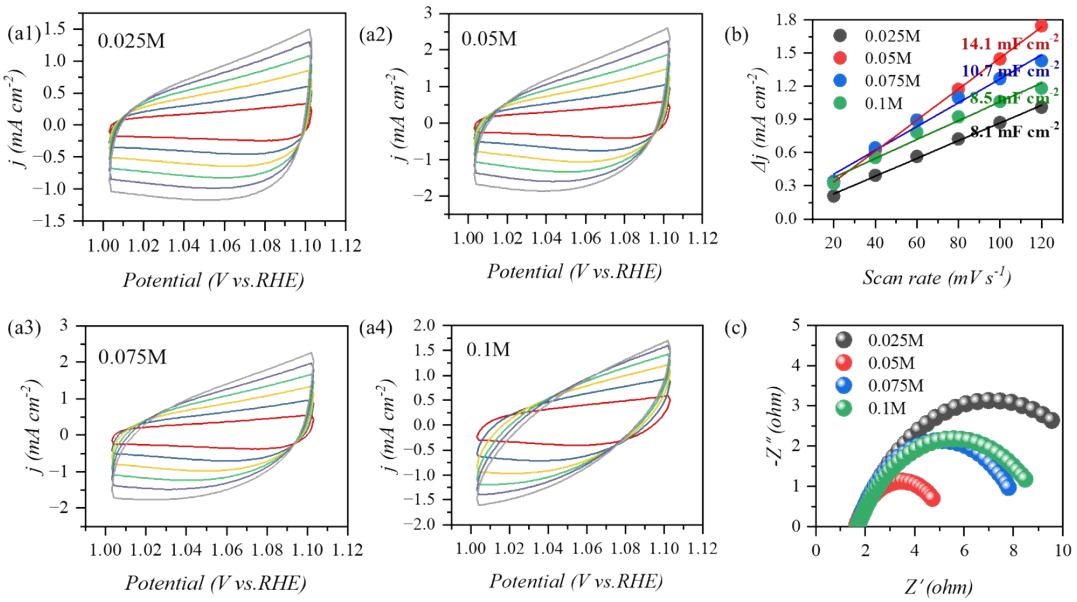

Fig.S4 Electrochemical performance testing of samples prepared at a series of M^{2+} concentrations: (a1-a4) CV at different scanning speeds of 20 mV s^{-1}, 40 mV s^{-1}, 60 mV s^{-1}, 80 mV s^{-1}, 100 mV s^{-1}, 120 mV s^{-1}, (b) C_{dl}, (c) EIS

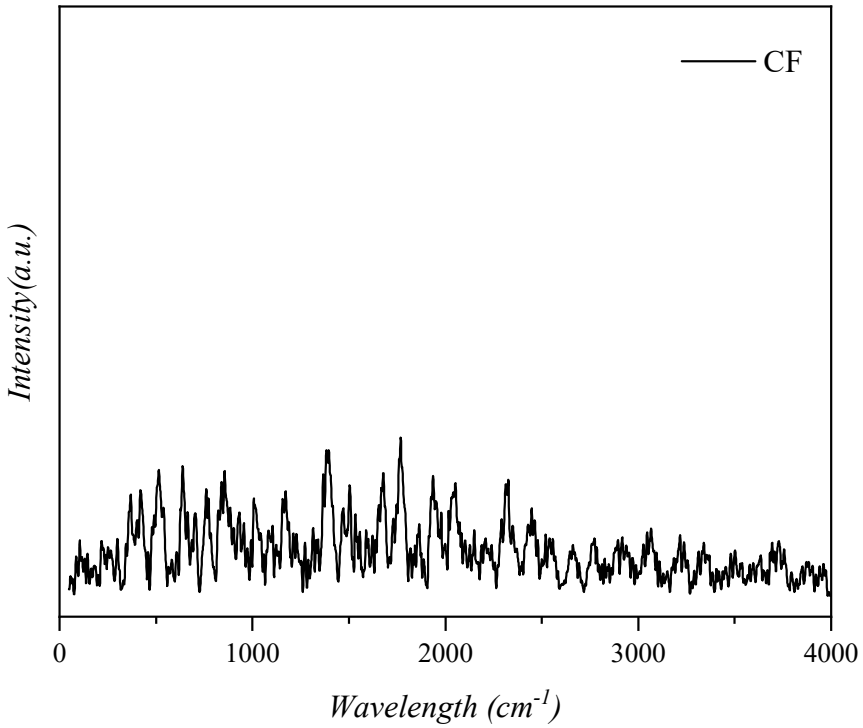

Fig.S5 Raman spectra of CF

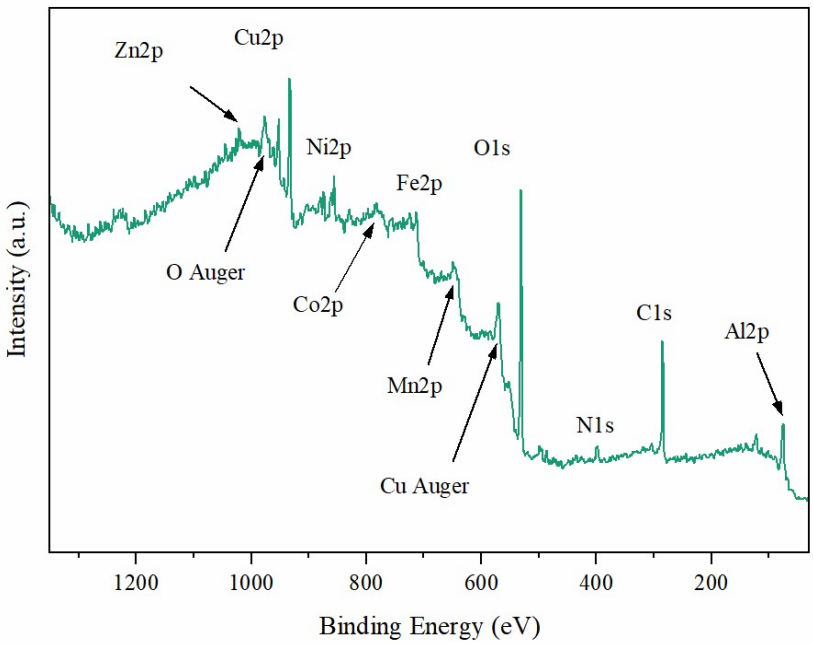

Fig.S6 the XPS survey spectrum of M6-LDH/CF

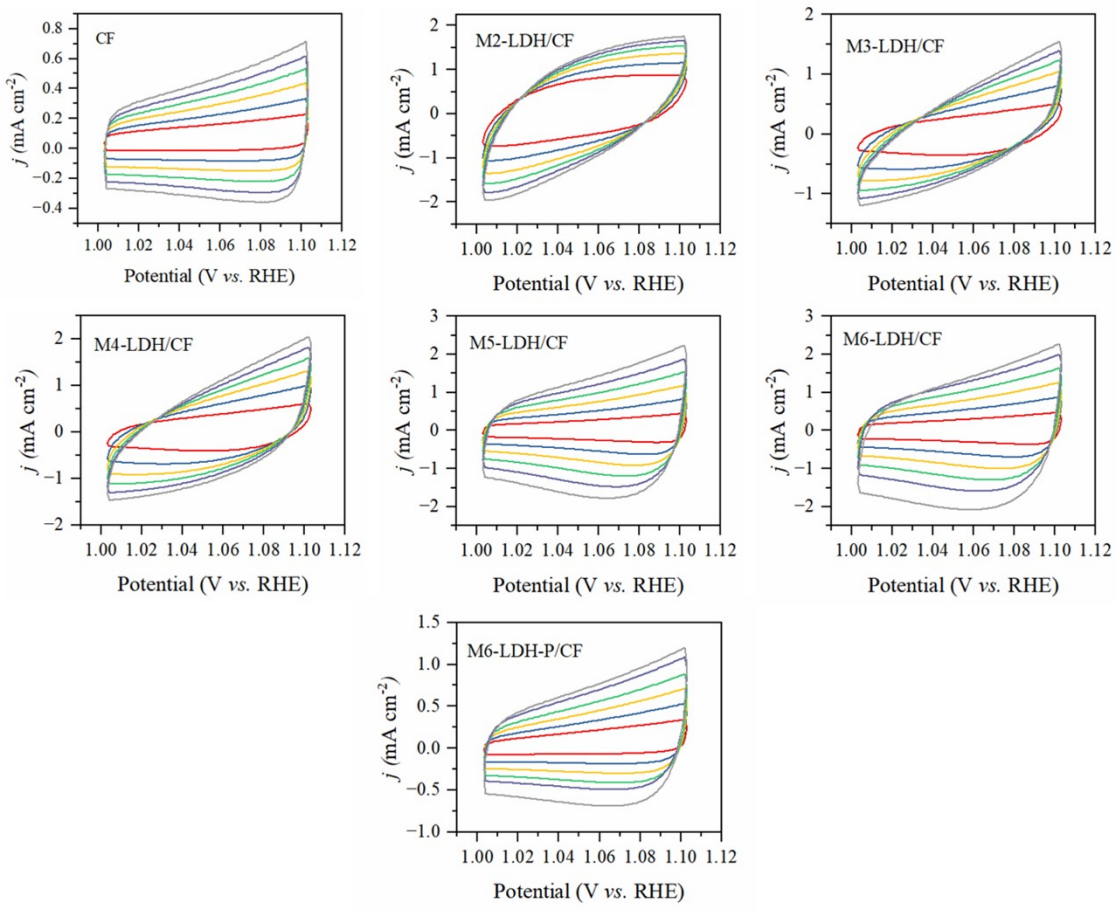

Fig.S7 CV testing of samples with different numbers of components at scanning speeds of 20 mV s^{-1}, 40 mV s^{-1}, 60 mV s^{-1}, 80 mV s^{-1}, 100 mV s^{-1}, 120 mV s^{-1}, respectively

Table S1 Overpotential of the samples at different current densities

Samples	10 (mA·cm^{-2})	50 (mA·cm^{-2})	100 (mA·cm^{-2})
CF	333	548	/
M6-LDH-P/CF	313	480	634
M2-LDH/CF	296	451	630
M3-LDH/CF	257	438	603
M4-LDH/CF	256	423	592
M5-LDH/CF	212	399	558
M6-LDH/CF	181	392	502

Note: Within the current measurement potential range (0.9~1.9 V *vs*. RHE), the current density of CF does not reach 100 mA·cm^{-2}.

Table S2 thermodynamic parameters under standard conditions (298.15 K)

Substance	State	ΔH_f^0 (kJ/mol)	S^0 (J/mol·K)	ΔG_f^0 (kJ/mol)
Cu	*s*	0	33.1	0
Cu_2O	*s*	-168.6	93.1	-146.0
CuO	*s*	-157.3	42.6	-129.7
H_2O	*l*	-285.8	69.9	-237.1
O_2	*g*	0	205.1	0
NO_3^-	*aq*	-205.0	146.4	-108.7
NO_2^-	*aq*	-104.6	145.6	-37.2
OH^-	*aq*	-230.0	-10.75	-157.2

Ionic state explanation: For ions in aqueous solution, the parameters are measured under standard conditions of infinite dilution. In our calculations, we add a concentration correction term of 0.175 M to match the actual experimental environment.

Thermodynamics of CF surface oxidation by nitrate ions s in alkaline hydrothermal conditions

In the synthesis of the M6-LDH/CF sample, the initial concentration of nitrate ions was 0.175 mol/L, and the initial concentration of urea was 0.3 mol/L. Under such conditions, nitrate ions were used as the oxidizing agent to perform a non-standard thermodynamic derivation of the oxidation process of copper foam at 120°C in the alkaline hydrothermal environment. The two-stage redox reaction equations are as follows:

Stage I ($Cu \rightarrow Cu_2O$)：

$$2Cu(s) + NO_3^-(aq) + H_2O(l) \rightarrow Cu_2O(s) + NO_2^-(aq) + 2OH^-(aq)$$

Stage II ($Cu_2O \rightarrow CuO$):

$$Cu_2O(s) + NO_3^-(aq) + H_2O(l) \rightarrow 2CuO(s) + NO_2^-(aq) + 2OH^-(aq)$$

The formation free energy of each species at 298.15 K was obtained from the thermodynamic database (see Table S1), and the standard free energy change at 298.15 K was calculated as follows:

$$\Delta G^0_{I,298.15} \approx -149.2\text{kJ/mol}$$

$$\Delta G^0_{II,298.15} \approx -116.6\text{kJ/mol}$$

At the actual hydrothermal temperature of 393.15 K, the free energy change under non-standard conditions was derived using the formula $\Delta G = \Delta G^0_T + RT\ln Q$. Since 0.3 mol/L urea in a closed system at 120°C typically stabilizes the pH around 10, the corresponding [OH^-] is approximately 0.01 mol/L. Additionally, assuming the generation of nitrite ions is minimal, [NO_2^-] is approximated as 10^{-4} mol/L. The reaction quotient, *Q*, is given by:

$$Q = \frac{[NO_2^-][OH^-]^2}{[NO_3^-]} = \frac{10^{-4}\times 0.01^2}{0.175} \approx 5.71\times 10^{-8}$$

Furthermore, the standard free energy change $\Delta G^0_{298.15}$ at 298 K was corrected to the free energy $\Delta G^0_{393.15}$ at 393.15 K (120°C) using the Gibbs-Hemholtz linear approximation method (where the standard reaction entropy $\Delta S^0_{298.15}$ can be obtained from the standard entropy of each substance in the reaction):

$$\Delta G^0_{I,393.15} \approx \Delta G^0_{I,298} - (393.15-298.15)\times \Delta S^0_{I,298.15} = -149.2 - 95\times(-149.5) = -135.0\text{kJ/mol}$$

$$\Delta G^0_{II,393.15} \approx \Delta G^0_{II,298} - (393.15-298.15)\times \Delta S^0_{II,298.15} = -116.6 - 95\times(-122.1) = -105.0\text{kJ/mol}$$

Finally, the free energy changes for the two stages at 120°C were obtained using the formula $\Delta G = \Delta G^0_T + RT\ln Q$:

$$\Delta G_I \approx -135000 + 8.314\times 393.15\times \ln(5.71\times 10^{-8}) = -192.4\text{kJ/mol}$$

$$\Delta G_{II} \approx -105000 + 8.314\times 393.15\times \ln(5.71\times 10^{-8}) = -162.4\text{kJ/mol}$$