Dual-carbon coupling modulated bimetallic sulfides as high-efficiency bifunctional oxygen electrocatalysts in rechargeable Zn-air battery

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According to the disk current (I_d) and ring current (I_r) obtained from the RRDE measurements, H_2O_2% (the H_2O_2 yield rate) and n (electron transfer number) cab be calculated with the following equation:

$$H_2O_2\% = 100 \times \frac{2I_r / N}{I_d + I_r / N} \quad (1)$$

$$n = \frac{4I_d}{I_d + I_r / N} \quad (2)$$

Where N = 0.37 means the current collection efficiency of Pt ring, calibrated in 0.1M KOH with 10mM $K_3Fe(CN)_6$ electrolyte.

The kinetic parameters can be analyzed on the basis of the Koutecky-Levich equations:

$$\frac{1}{J} = \frac{1}{J_L} + \frac{1}{J_K} = \frac{1}{B\omega^{\frac{1}{2}}} + \frac{1}{J_K} \quad (1)$$

$$B = 0.62nFC_0D_0^{\frac{2}{3}}V^{-\frac{1}{6}} \quad (2)$$

$$J_K = nFkC_0 \quad (3)$$

In which J is the measured current density, J_K and J_L are the kinetic and diffusion-limiting current densities, x is the rotation rate in rad s^{-1}, n is the overall number of electrons transferred in oxygen reduction, F is the Faraday constant (F = 96485 C mol^{-1}), C_0 is the bulk concentration of O_2 (C_0 = 1.3 × 10^{-6} mol cm^{-3}), D_0 is diffusion coefficient of O_2 in the bulk solution (D_0 = 1.7 × 10^{-5} cm^2 s^{-1}), m is the kinematic viscosity of the solution (0.01 cm^2 s^{-1}), k is the electron-transfer rate constant. The number of electron transfer (n) can be obtained from the slope of the Koutecky-Levich plots (J^{-1} vs $\omega^{-1/2}$).

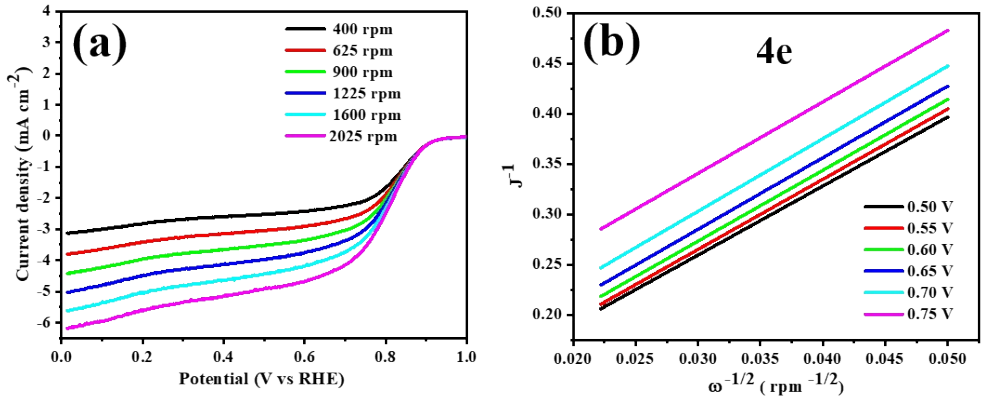

Fig. S1 (a) The LSV curves for ORR of $Co_{0.2}Fe_{0.6}S_x$-Gra/CNT at different rotating rates from 400 rpm to 2025 rpm; (b) Koutecky–Levich plots for oxygen reduction of $Co_{0.2}Fe_{0.6}S_x$-Gra/CNT at varied potentials.

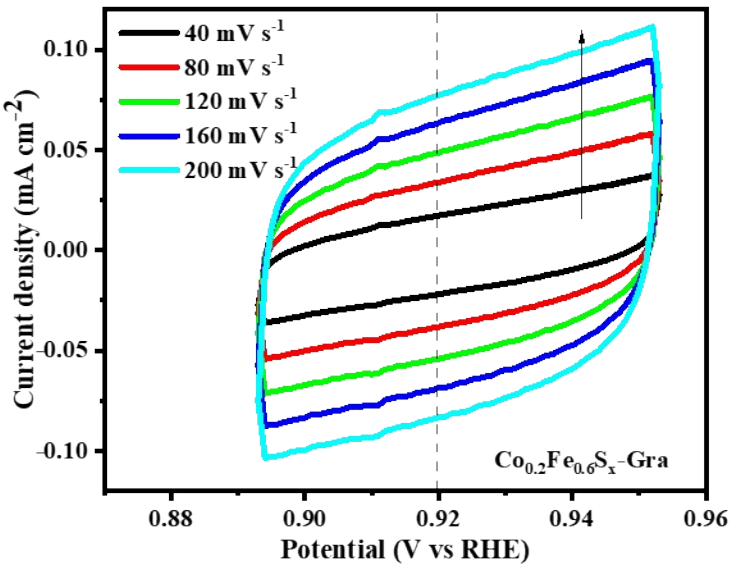

Fig. S2 The CV curves of $Co_{0.2}Fe_{0.6}S_x$-Gra for ORR scanning at different scanning rate range from 40 to 200 mV s^{-1}.

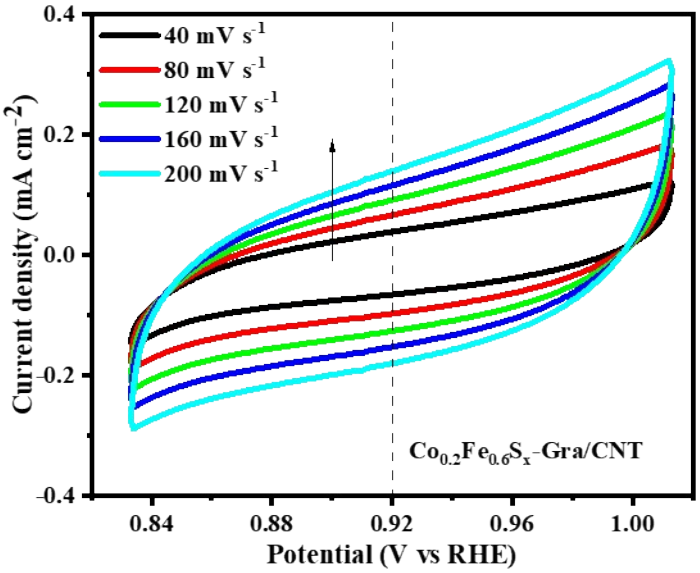

Fig. S3 The CV curves of $Co_{0.2}Fe_{0.6}S_x$-Gra/CNT for ORR scanning at different scanning rate range from 40 to 200 mV s^{-1}.

Table S1 Comparison of reported metallic sulfide based catalysts for ORR and OER

Catalyst	Electrolyte	ORR $E_{1/2}$ (V)	OER $E_{j=10}$ (V)	Ref.
Ni_1Co_4S@C-1000	0.1M KOH	0.6	1.51	[1]
Co_9S_8/C NSs	0.1M KOH	0.778	1.667	[2]
NiFeVS	0.1M KOH	0.789	1.557	[3]
$Co_{0.5}Fe_{0.5}S$@N-MC	0.1M KOH	0.808	1.64	[4]
CoNiFe-S MNs	0.1M KOH	0.78	1.49	[5]
N-$Co_{0.8}Fe_{0.1}Ni_{0.1}S_x$	0.1M KOH	0.80	1.60	[6]
Co-NC@$CoFeS_2$	0.1M KOH	0.805	1.451	[7]
$(Ni,Co)S_2$	0.1M KOH	0.71	1.50	[8]

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