Supporting Information

Active Site-Engineered Bifunctional Electrocatalysts of Ternary Spinel Oxides, $M_{0.1}Ni_{0.9}Co_2O_4$ (M: Mn, Fe, Cu, Zn) for the Air Electrode of Rechargeable Zinc-Air Batteries

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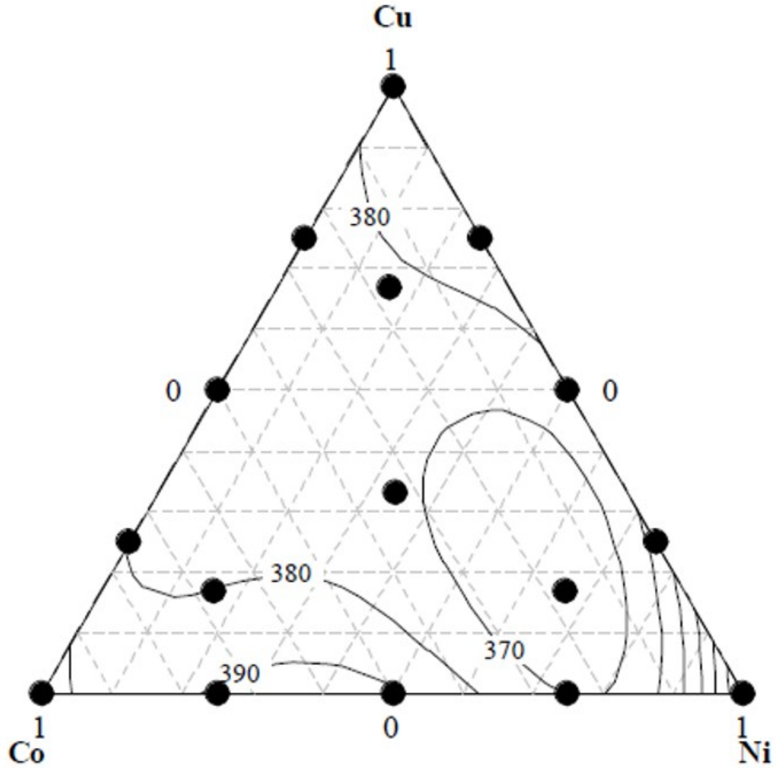

$$\eta=\underset{[5.6]}{385.2X_1}+\underset{[5.7]}{396.3X_2}+\underset{[5.9]}{433.3X_3}-\underset{[23.8]}{74.6X_1X_2}-\underset{[23.5]}{127.1X_1X_3}-\underset{[27.0]}{93.9X_2X_3}+$$

$$\underset{[45.8]}{142.X_1X_3(X_1-X_3)}+\underset{[45.7]}{212.5X_2X_3(X_2-X_3)}-\underset{[122.6]}{353.7X_2X_3(X_2-X_3)^2}$$

Fig. S1. Mixture design of ternary $(Cu_xNi_y)Co_{3-x-y}O_4$ ($x+y \leq 1$) for evaluating the OER overpotential; where η stands for the overpotential of the OER at a fixed current density; X_1 X_2, X_3 stand for pseudo-components.

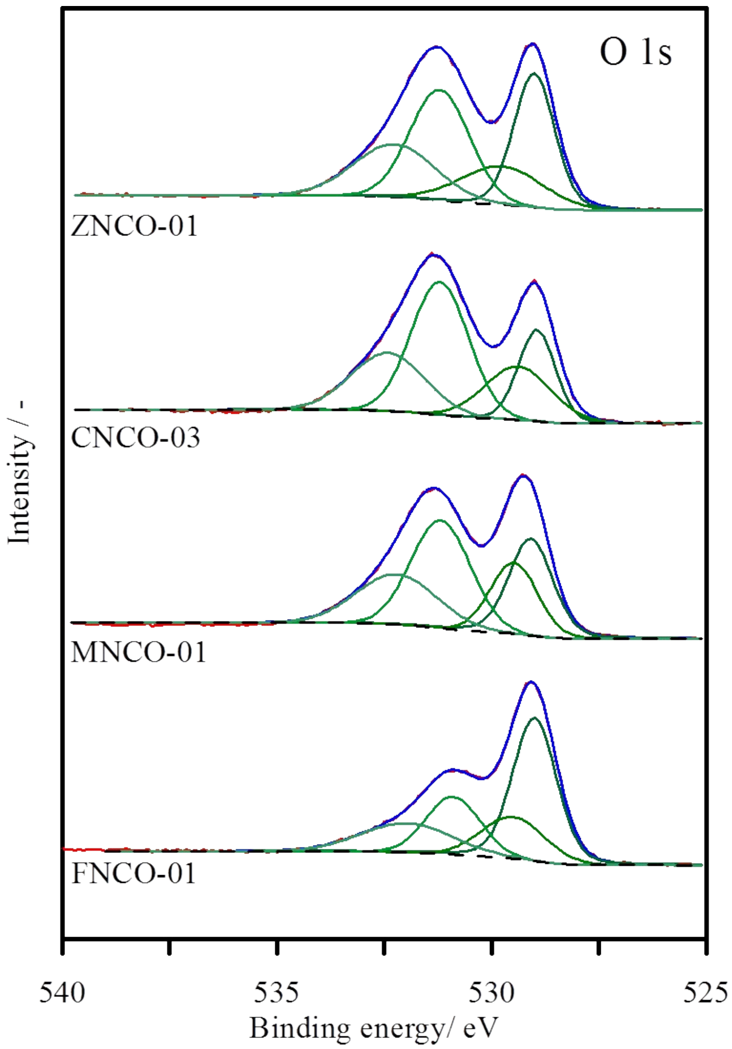

Fig. S2. High-resolution XPS spectra O 1s of FNCO-01, MNCO-01, CNCO-01, ZNCO-01.

Table S1 The specific surface area of the MNCO-01, FNCO-01, CNCO-01, and ZNCO-01

Catalysts	**BET surface area (m^2 g^{-1})**
MNCO-01	35
FNCO-01	32
CNCO-01	18
ZNCO-01	38

Table S2 ICP-MS analysis of FNCO-01, MNCO-01, CNCO-01, ZNCO-01.

$M_xNi_{1-x}Co_2O_4$ M=Mn, Fe, Cu, Zn	atom / conc.	M	Ni	Co	M	Ni	Co
		wt%			atom		
MNCO-01	x=0.1	2.007	21.83	43.87	0.09	0.97	1.94
FNCO-01	x=0.1	1.726	21.28	49.32	0.07	0.89	2.04
CNCO-01	x=0.1	2.485	16.85	48.57	0.12	0.75	2.13
ZNCO-01	x=0.1	2.472	13.51	55.76	0.12	0.57	2.31

With the exception of ZNCO-01, ternary oxides can be considered to be $M_xNi_{1-x}Co_2O_4$ and ZNCO-01 should be $(Zn_{0.1}Ni_{0.6}Co_{0.3})Co_2O_4$.

Table S3 The electron configuration, CFSE at octahedral and tetrahedral site and OSPE for Mn, Fe, Cu, and Zn ions at different oxidation states

Ion	Electron configuration	CFSE[a] Oct.	CFSE[a] Tet.[b]		OSPE[c]
Mn^{2+}	$3d^5$	0	0	0	0
Mn^{3+}	$3d^4$	$-3/5\Delta_o$	$-2/5\Delta_t$	$-8/45\Delta_o$	$-19/45\Delta_o$
Mn^{4+}	$3d^3$	$-6/5\Delta_o$	$-4/5\Delta_t$	$-16/45\Delta_o$	$-38/45\Delta_o$
Mn^{6+}	$3d^1$	$-2/5\Delta_o$	$-3/5\Delta_t$	$-12/45\Delta_o$	$-6/45\Delta_o$
Mn^{7+}	$3d^0$	0	0	0	0
Fe^{2+}	$3d^6$	$-2/5\Delta_o$	$-2/5\Delta_t$	$-12/45\Delta_o$	$-6/45\Delta_o$
Fe^{3+}	$3d^5$	0	0	0	0
Cu^{+}	$3d^{10}$	0	0	0	0
Cu^{2+}	$3d^9$	$-3/5\Delta_o$	$-3/5\Delta_t$	$-8/45\Delta_o$	$-19/45\Delta_o$
Zn^{2+}	$3d^{10}$	0	0	0	0

[a] $CFSE = \Delta E = E_{isotropic\,field} - E_{ligand\,field}$; where $E_{isotropic\ field}$ is the energy of isotropic field and $E_{ligand\ field}$ is the energy of octahedral ligand field

[b] Conversion of Δ_t, $\Delta_t = 4/9\Delta_o$

[c] $OSPE = CFSE_{oct} - CFSE_{tet}$; where the $CFSE_{oct}$ is the octahedral fields; $CFSE_{tet}$ is the tetrahedral fields.

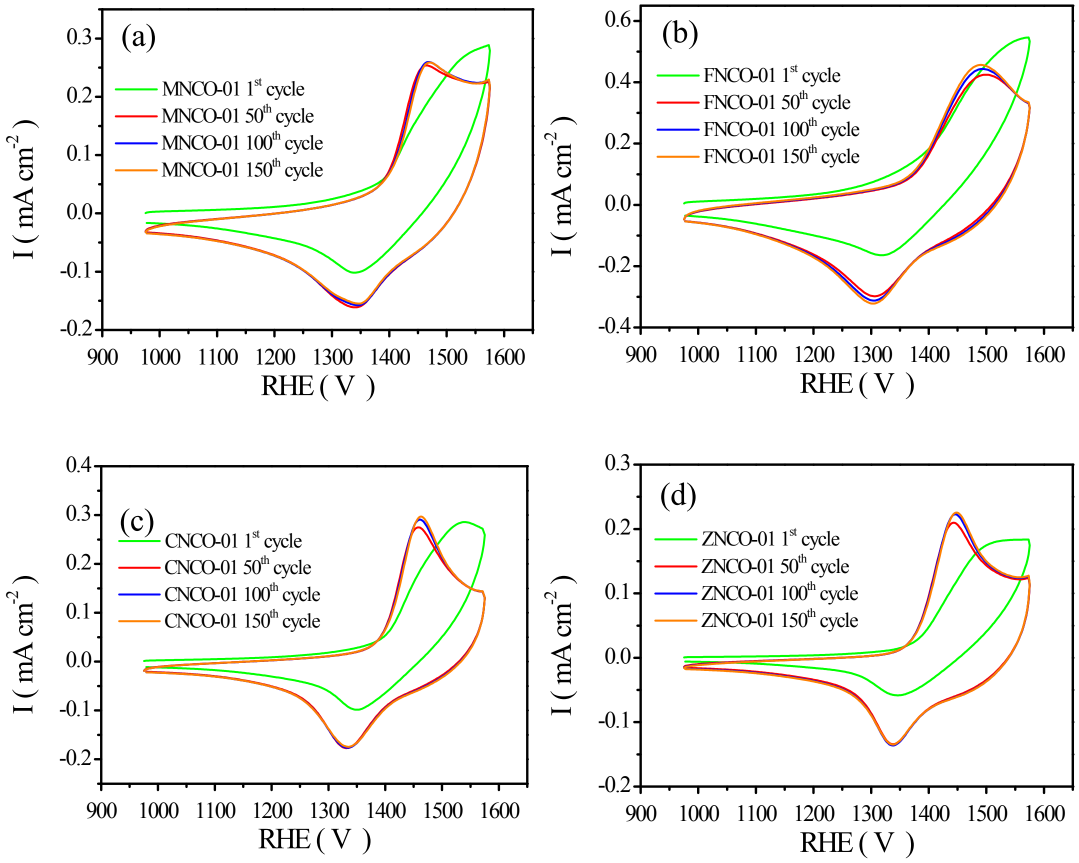

Fig. S3 Cyclic Voltammograms of the (a) MNCO-01, (b) FNCO-01, (c) CNCO-01, and (d) ZNCO-01 electrodes with 1st, 50th, 100th, and 150th cycle in 0.1 M KOH at 25 mV s^{-1}.