Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Enhanced ethanol oxidation reaction of $CoSeO_3$ by Ni-doping for water electrolysis and innovative zinc-ethanol-air battery

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Experimental Section

Chemicals

Cobalt nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$), Nickel nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$), Dimethylimidazole ($C_4H_6N_2$) and Selenium (Se) were purchased from Aladdin. Diethylenetriamine ($C_4H_{13}N_3$) was purchased from Meryer. Deionized water is obtained using an ultrapure water manufacturing machine. All chemicals are used directly after purchase without any purification.

Synthesis of Ni-doped ZIF-67

0.9 mmol of $Co(NO_3)_2 \cdot 6H_2O$ and 0.1 mmol of $Ni(NO_3)_2 \cdot 6H_2O$ were dispersed in 25 mL methanol. Meanwhile, 4 mmol of dimethylimidazole was dispersed in 25 mmol methanol. After the two solutions were mixed, they were stirred at room temperature for 30 minutes, and then aged for 24 hours by standing still. Subsequently, the mixture was centrifuged and dried at 60 °C for 6 hours to obtain Ni-doped ZIF-67.

Synthesis of Ni-m-$CoSeO_3$

2 mmol of selenium powder, 2 mmol of the previously prepared Ni-doped ZIF-67 and 1 mmol of $Ni(NO_3)_2 \cdot 6H_2O$ were dispersed in a solution containing 26.6 mL of diethylenetriamine (DETA) and 13.3 mL of deionized water. The mixture was stirred at room temperature for 30 minutes and then transferred to a reaction vessel, which was heated at 160 °C for 10 hours in a constant temperature drying oven. After the reaction, the resulting solution and precipitate were filtered and dried at 60 °C for 3 hours to obtain Ni-doped m-$CoSeO_3$ (noted as Ni-m-$CoSeO_3$).

Electrochemical tests

The electrochemical performance of the prepared catalyst was measured on an electrochemical workstation (CHI660E and Bilogic-VSP-300). The catalyst was thoroughly ground and 5 mg was weighed and added to a centrifuge tube containing 500 μL of ethanol and 10 μL of 5% Nafion. The mixture was sonicated for 30 minutes to obtain a homogeneous black liquid. The material was then dropped onto a square carbon cloth (side length: 5 mm, area: 0.25 cm^2) as the working electrode. 100 μL of the mixture was dropped on both the front and back of the carbon cloth, resulting in a catalyst loading of 7.843 mg cm^{-2} on the carbon cloth. The working electrode, Hg/HgO reference electrode, and carbon rod counter electrode were combined to form a three-electrode testing system. CV tests for EOR were conducted in a solution containing 1 M EtOH + KOH, while tests for OER were conducted in a solution containing 1 M KOH. The reference electrode was calibrated with respect to a reversible hydrogen electrode (RHE) by referring to the following equation: $E_{RHE} = E_{Hg/HgO} + 0.059 \times pH + 0.098 - 0.317 \times 10^{-3}(T-298) - 5.664 \times 10^{-6}(T-298)$.[2, 3, 4] The Hg/HgO reference electrode was calibrated relative to the reversible hydrogen electrode before each use. After 96 h of chronopotentiometry test at a current of 20 mA, 300 uL of electrolyte was taken out and mixed with 200 uL of D_2O to obtain a test sample solution for ^1H NMR measurement. The Faradic efficiency (FE) of acetate is calculated using the following equation: $FE = (4 \times C \times V \times F)/Q \times 100\ \%$ (C is the concentration of acetic acid in the electrolyte after the CP test, V is the volume of the electrolyte after the CP test, F is Faraday's constant, Q is the total passed charge calculated by 20 mA × 96 h).

Preparation of Zinc (-Ethanol) -Air Battery

Rechargeable zinc (-ethanol) -air batteries were set up with a polished 0.4 mm Zn plate as the negative electrode, catalyst loaded carbon cloth as the positive electrode, and 6.0 M KOH (with 1.0 M EtOH) as electrolyte. The catalyst was Ni-m-$CoSeO_3$. 5 mg Ni-m-$CoSeO_3$ was dispersed in a centrifuge tube containing 1000 uL ethanol and 80 uL Nafion, and the catalyst ink was obtained after ultrasonication for 30 minutes. 300 uL of catalyst ink was dropped on the front and back of the carbon cloth with an area of 1 cm^2 (1 cm × 1 cm) to obtain a mass loading of 2.78 mg cm^{-2}. The electrolyte was changing every 12 hours to maintain the ethanol concentration of 1.0 M.

Characterizations

Scanning electron microscopy (SEM, Philips XL-30ESEM), transmission electron microscopy (TEM) images and high-resolution TEM (HRTEM) (JEM-2100F) were exploited to investigate the surface morphology of catalysts. XRD measurement was performed on a Miniflex600 diffractometer (Cu Kα, $\lambda = 1.54056$ Å radiation). X-ray photoelectron spectroscopy (XPS) spectra were tested using a Thermo-ESCA-Lab 250 instrument with Al Kα radiation. The Raman spectra were measured on an inVia Qontor Raman Spectrometer From RENISHAW. The analysis of experimental products was quantitatively detected by Nuclear Magnetic Resonance Spectroscopy (NMR, Bruker Ascend 600M).

Computational Methods

DFT calculations are performed using the open-source plane wave code Quantum Espresso. In all calculations, electron exchange and related effects are described by a generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) function. The atomic positions are relaxed until the force on each atom is below 0.03 eV Å^{-1}, and the convergence tolerance for the energy is set to 10^{-5} eV. To avoid interactions between crystal planes, the vacuum space is greater than 15 Å. The unit cell of $CoSeO_3 \cdot H_2O$ is in the P21/c group. All flat models are geometrically optimized and the top layer can be relaxed.

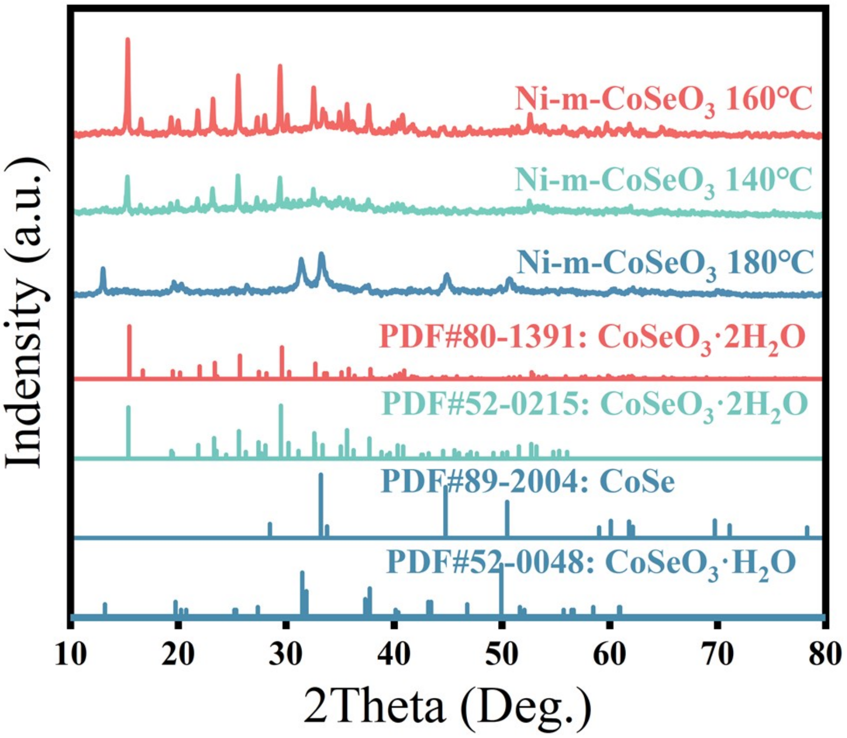

Figure. S1 X-ray diffraction (XRD) patterns of Ni-m-$CoSeO_3$ at various temperatures.

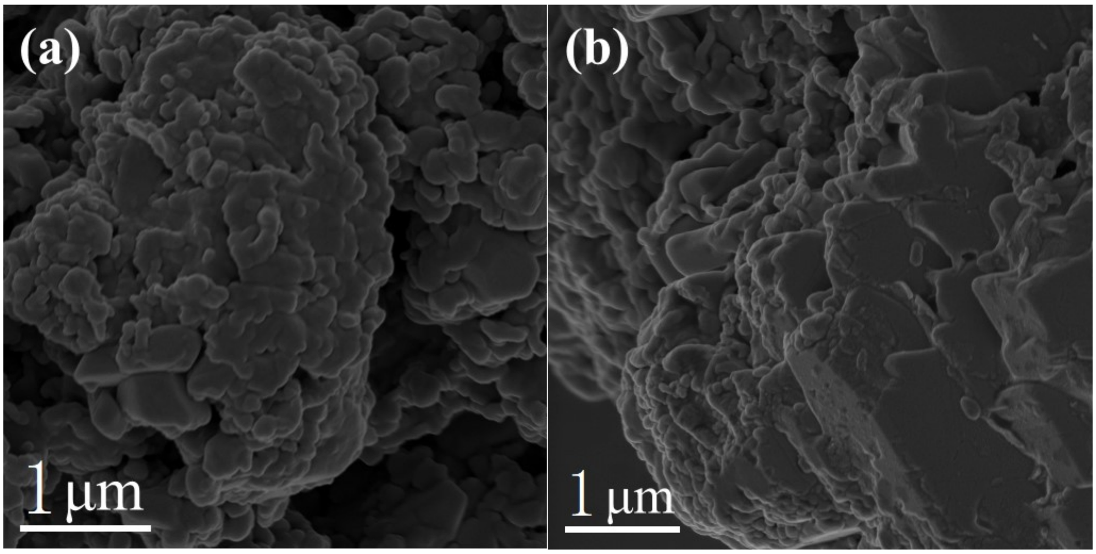

Figure. S2 SEM images for Ni-m-$CoSeO_3$ treated at 160 ℃.

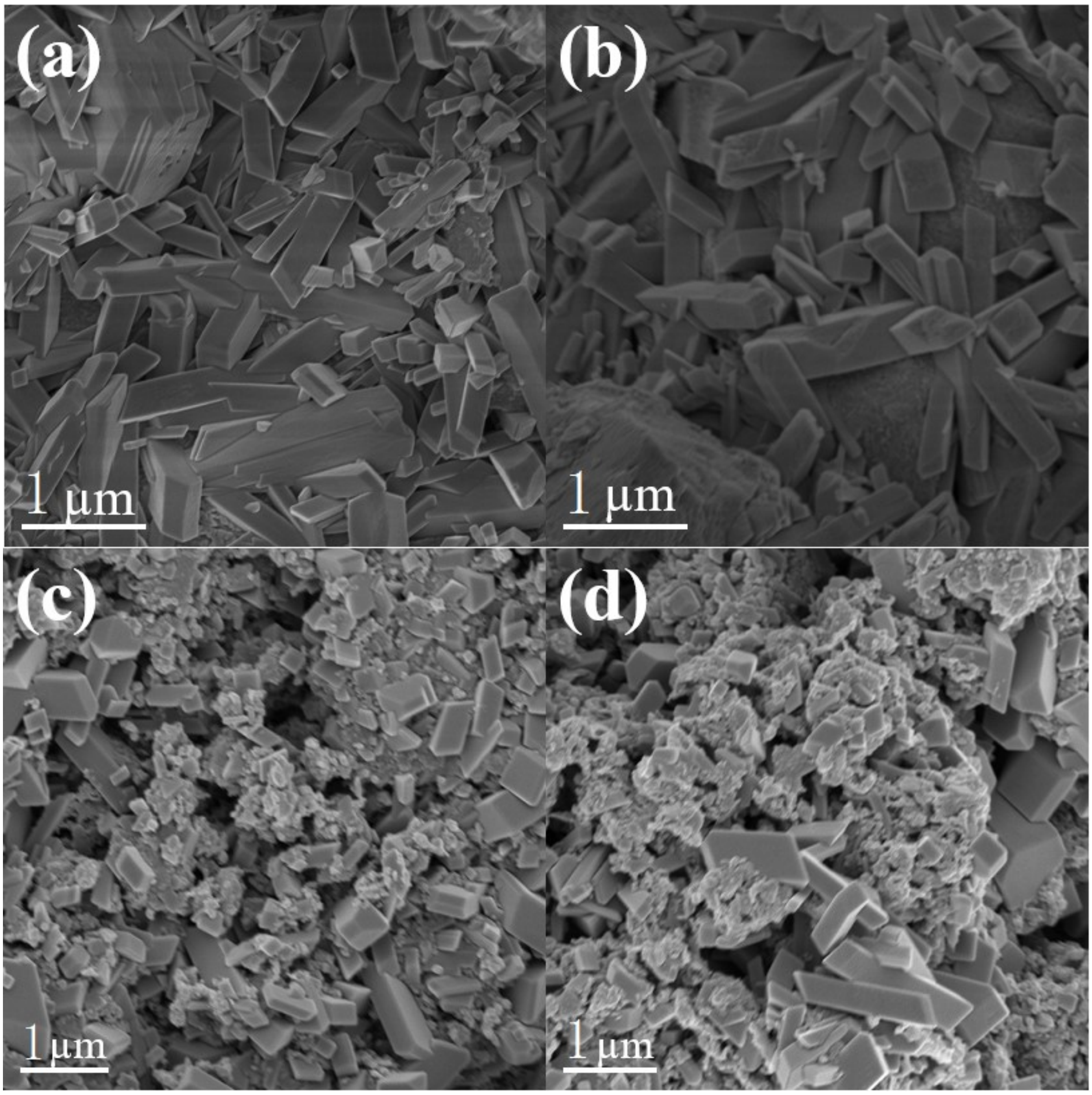

Figure. S3 SEM images for Ni-m-$CoSeO_3$ treated at **(a-b)** 140 °C and **(c-d)** 180 °C.

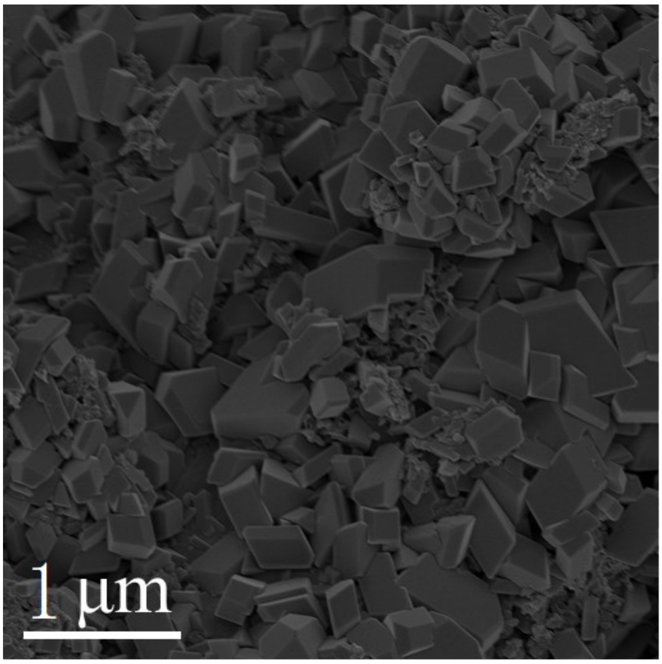

Figure. S4 SEM images for m-$CoSeO_3$ treated at 160 °C

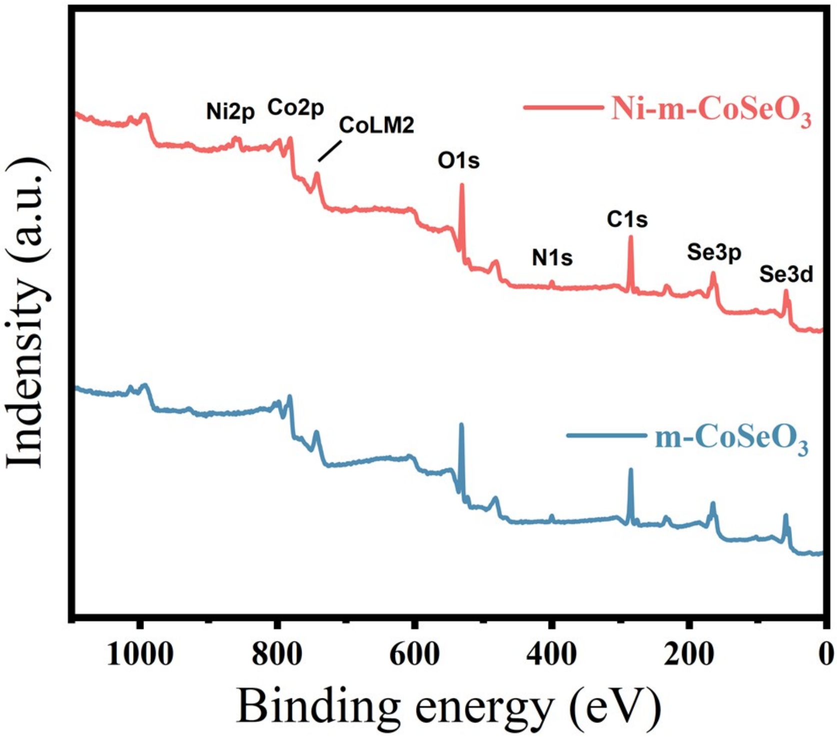

Figure. S5 XPS survey spectra of Ni-m-CoSeO$_3$ and m-CoSeO$_3$ treated at 160 ℃.

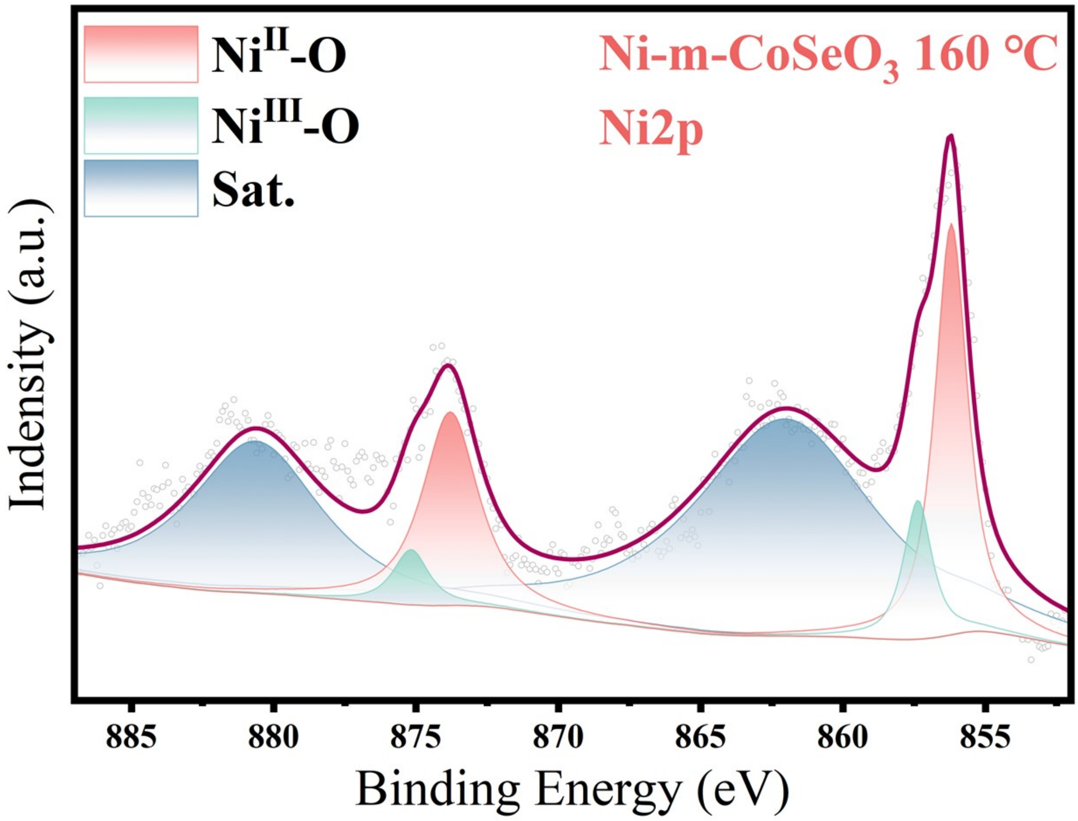

Figure. S6 High-resolution XPS of Ni 2p for Ni-m-$CoSeO_3$ treated at 160 °C.

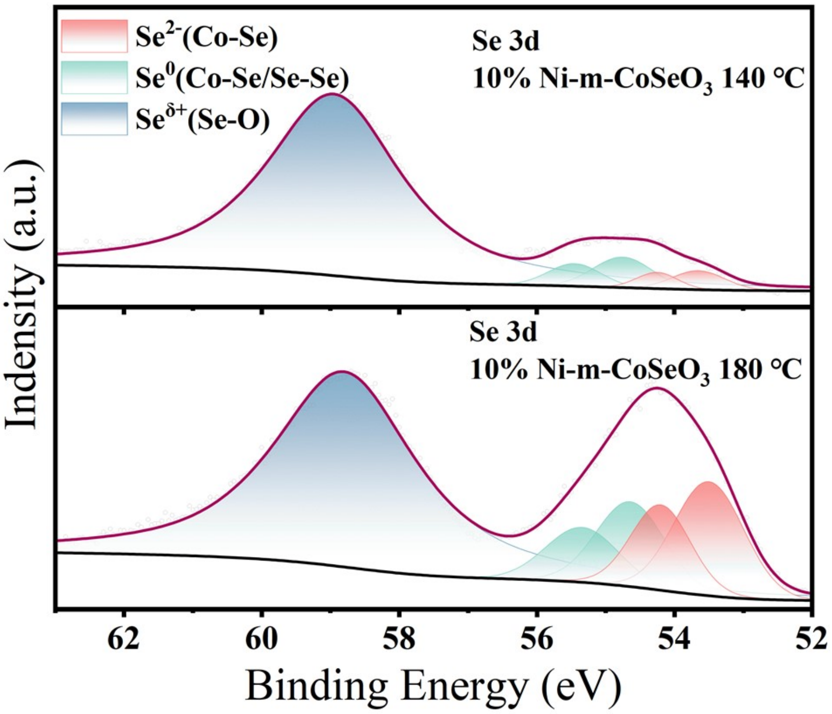

Figure. S7 High-resolution XPS of Se 3d for Ni-m-CoSeO$_3$ treated at 140 °C and 180 °C.

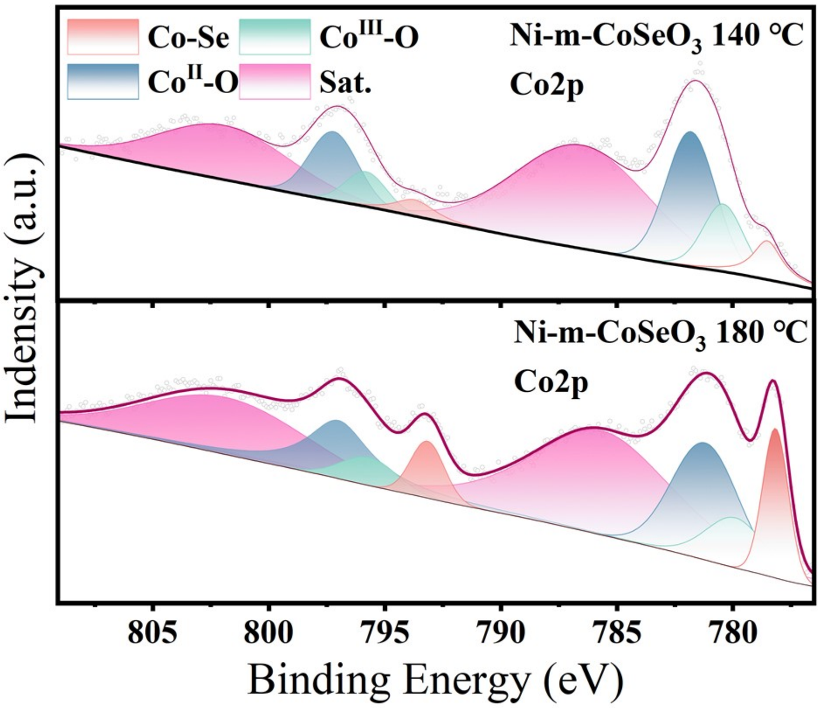

Figure. S8 High-resolution XPS of Co 2p for Ni-m-CoSeO$_3$ treated at 140 °C and 180 °C.

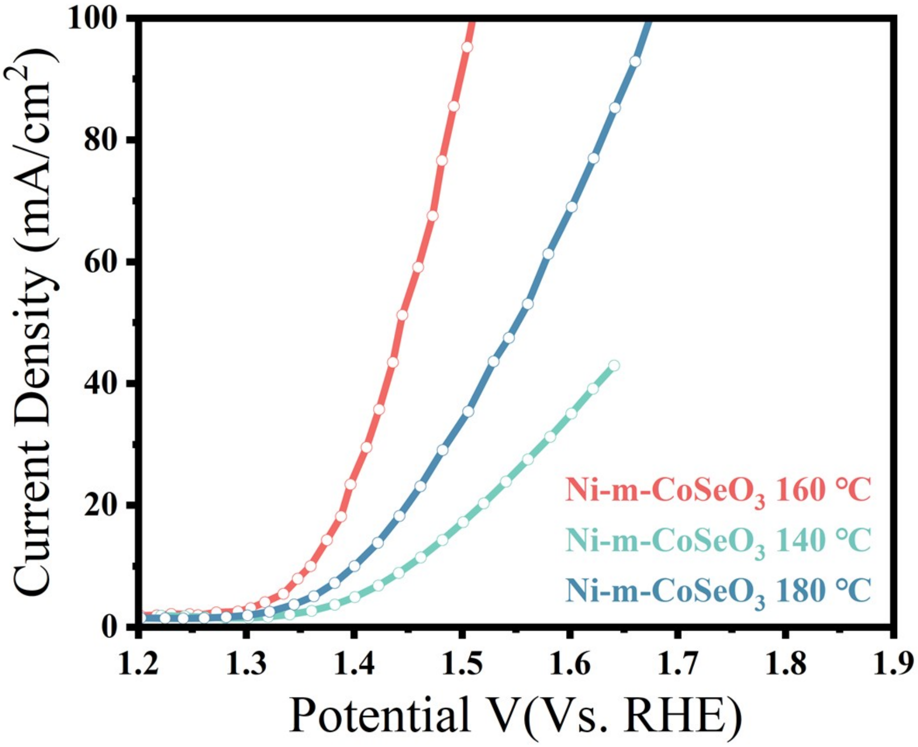

Figure. S9 IR-corrected CV curves for EOR conducted in a solution containing 1.0 M EtOH with KOH for Ni-m-CoSeO$_3$ (140 °C), (160 °C) and (180 °C).

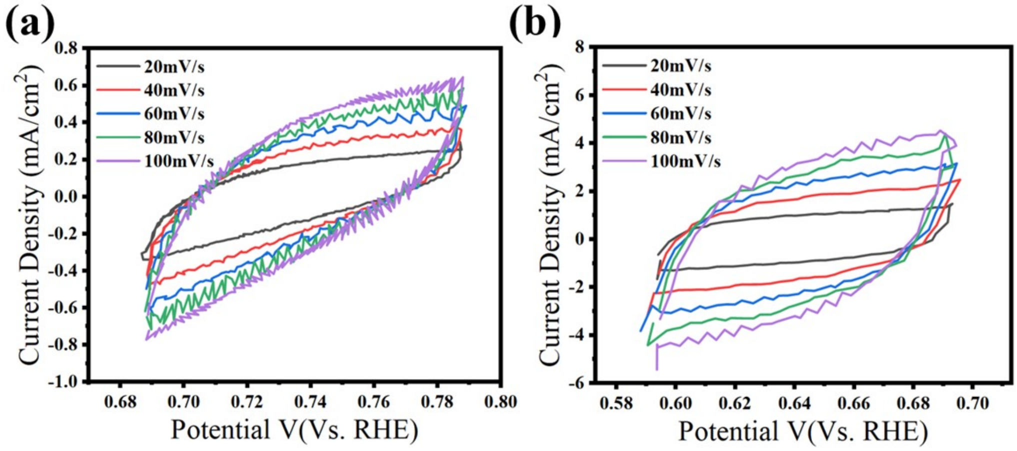

Figure. S10 CV results in the non-Faradaic region for **(a)** Ni-m-$CoSeO_3$ and **(b)** m-$CoSeO_3$.

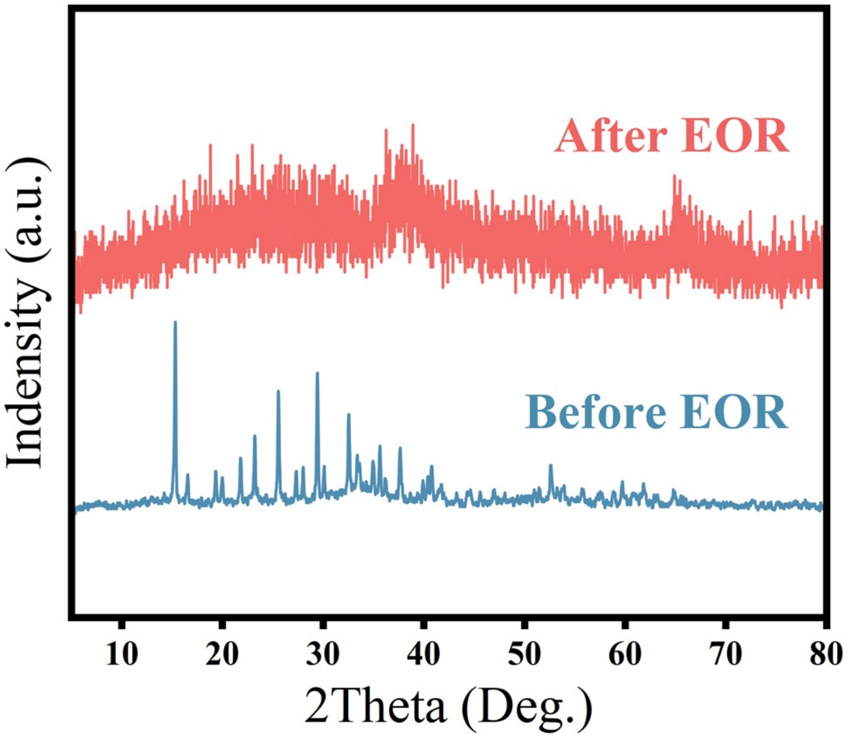

Figure. S11 XRD patterns for Ni-m-$CoSeO_3$ before and after chronopotentiometry test.

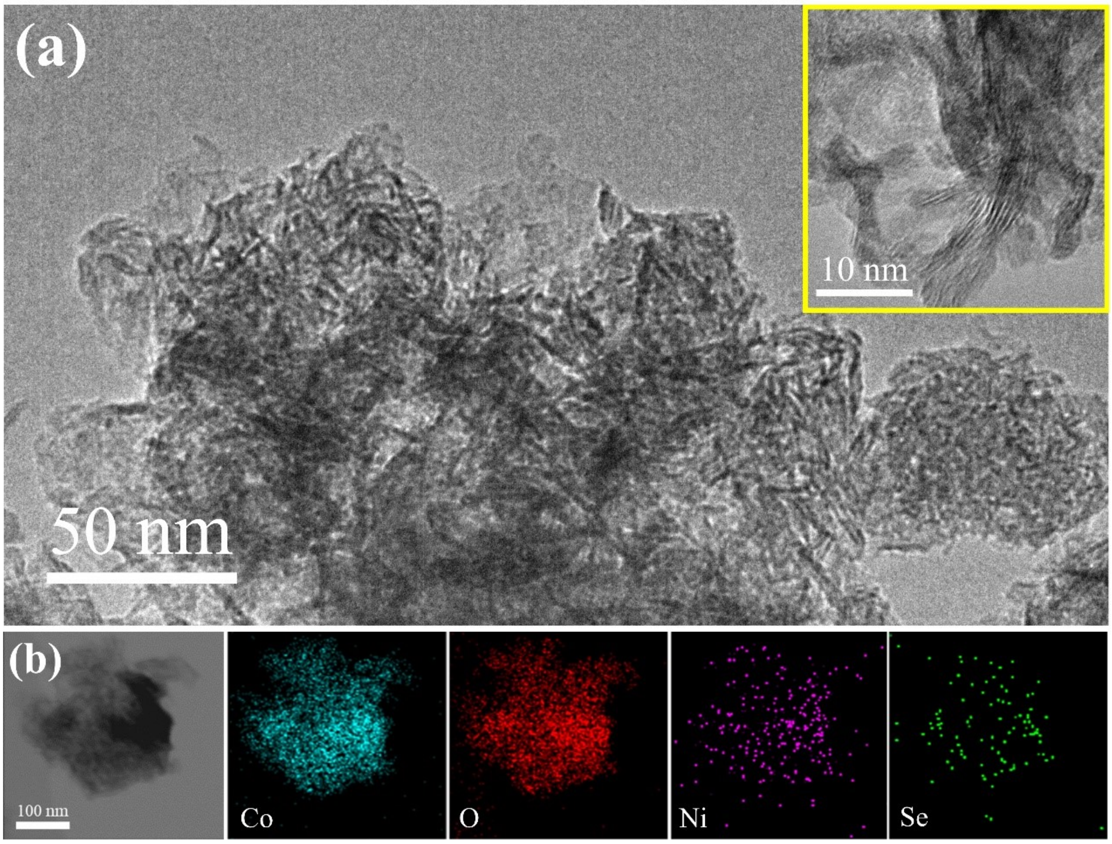

Figure. S12 (a) HRTEM image of Ni-m-$CoSeO_3$ after chronopotentiometry test. **(b)** Energy dispersive X-ray spectroscopy (EDS) elemental maps of Co, O, Ni and Se.

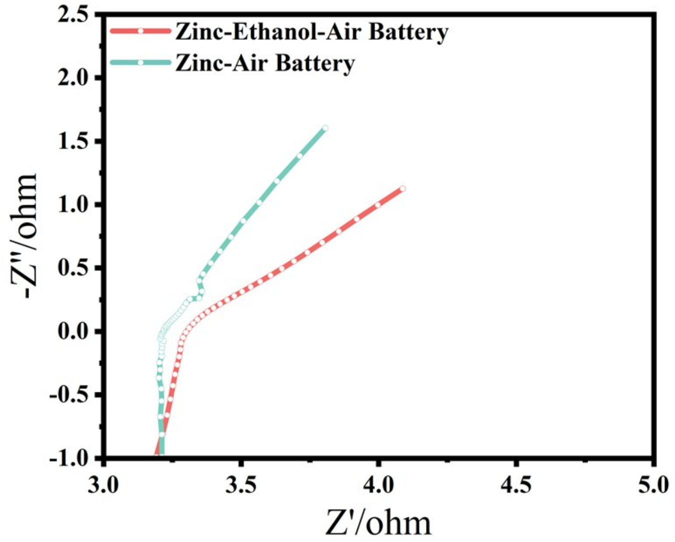

Figure. S13 Nyquist plots of Zinc-Ethanol-Air Battery and Zinc-Air Battery.

Table S1 XPS peak table for Ni-m-$CoSeO_3$ treated at 160 °C.

Peak	Position/ B. E.	FWHM/ eV	Area / P	Atomic %
C1s	284.82	2.25	65761.9	42.77
O1s	530.44	2.57	98275.9	22.43
N1s	399.49	2.26	9596.95	3.5
Se3d	53.91	1.86	13961.05	6.59
Co2p	780.6	5.87	98972.16	5.58
Ni2p	856.0	3.69	60154.23	1.42

Table S2 XPS peak table for m-$CoSeO_3$ treated at 160 °C.

Peak	Position/ B. E.	FWHM/ eV	Area / P	Atomic %
C1s	284.81	280.85	27436.32	1.91
O1s	531.16	526.75	36083.79	2.25
N1s	399.8	394.7	2840.85	2.23
Se3d	54.41	48.9	5603.49	1.89
Co2p	781.41	774.5	13991.19	5.81

Table S3 XPS peak table for Ni-m-$CoSeO_3$ treated at 140 °C.

Peak	Position/ B. E.	FWHM/ eV	Area / P	Atomic %
C1s	284.79	2.09	73737.74	60.77
O1s	531.23	2.98	74153.36	21.45
N1s	399.71	2.23	12523.92	5.79
Se3d	54.51	2.07	3144	1.88
Co2p	781.41	3.85	49728.02	3.56

Table S4 XPS peak table for Ni-m-$CoSeO_3$ treated at 180 °C.

Peak	Position/ B. E.	FWHM/ eV	Area / P	Atomic %
C1s	284.8	2.28	56381.64	36.46
O1s	530.74	2.27	86174.92	19.56
N1s	399.7	1.53	7599.42	2.76
Se3d	53.99	1.9	19335.1	9.08
Co2p	779.95	6.13	100696.98	5.65

Table S5 ICP table for Ni-m-$CoSeO_3$ and m-$CoSeO_3$ treated at 160 ℃.

Ni-m-$CoSeO_3$ (37.5 ppm)	Concentration average	Relative Content	m-$CoSeO_3$ (250 ppm)	Concentration average	Relative Content
Co	8.801 ppm	23.47%	Co	58.126 ppm	23.25%
Ni	1.282 ppm	3.42%	Ni	-0.02 ppm	0%
Se	20.829 ppm	55.54%	Se	121.36 ppm	48.54%

Table S6 Content of Co^{2+} and Co^{3+} derived from XPS results of Ni-m-$CoSeO_3$ and m-$CoSeO_3$ treated at 160 °C.

	Area of peak for Co^{2+} 2p3/2 / P	Relative content of Co^{2+}	Area of peak for Co^{3+} 2p3/2 / P	Relative content of Co^{3+}
Ni-m-$CoSeO_3$	37626.61	63.29%	21823.44	36.71%
m-$CoSeO_3$	32904.66	70.38%	13848.82	29.62%

Reference

1. G. R. Salvi and A. J. deBethune, *Journal of The Electrochemical Society*, 1961, **108**, 672.
2. M. A. Trosheva, M. A. Buckingham and L. Aldous, *Chemical Science*, 2022, **13**, 4984-4998.