# **Supplementary Information**

In-Situ Electrochemical Activation of Co(OH)2@Ni(OH)2 Heterostructure for Efficient

Ethanol Electrooxidation Reforming and Innovative Zinc-Ethanol-Air Battery

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### **Experimental Section**

#### Materials

2-methylimidazole (99%), Ni(NO)<sub>3</sub>·6H<sub>2</sub>O (98%), Co(NO)<sub>3</sub>·6H<sub>2</sub>O (98%), urea (CO(NH<sub>2</sub>)<sub>2</sub>, 99%), ammonium fluoride (NH<sub>4</sub>F, 99%), deuteroxide (D<sub>2</sub>O, 99.99%) were purchased from Aladdin. Ethanol (EtOH, 99.7%), methanol (MeOH, 99.5%), potassium hydroxide (KOH, 95%), acetic acid (99.99%) were purchased from Macklin. All water was ultra-pure water from the HITECH system (18.2 M $\Omega$ ).

#### Synthesis

#### Synthesis of Ni-doped ZIF-67 Precursor

Ni-doped ZIF-67 was synthesized by the traditional solution method<sup>1</sup> with slight changes. First, 0.5 mmol of Ni(NO<sub>3</sub>)<sub>2</sub> and 9.5 mmol of Co(NO<sub>3</sub>)<sub>2</sub> were dissolved in 250 mL MeOH, labeled as solution A, then 40 mmol of 2-methylimidazole was dissolved in 250 mL MeOH, labeled as solution B. Then solution B was poured into solution A with unremitting magnetic stirring for 1 h until the solution was uniform and purple. The solution was allowed to age for 24 h naturally. The product was collected by centrifuging and washing with deionized water (DIW) and absolute ethanol 3 times respectively and dried overnight at 80 °C.

## Synthesis of $Co(OH)_2$ ( $OH)_2$ Heterostructure

In a typical procedure, 80 mg Ni-doped ZIF-67 precursor, 2 mmol NH<sub>4</sub>F, 20 mmol urea, and different amounts of Ni(NO<sub>3</sub>)<sub>2</sub> (0.5, 0.75, 1, 1.25, 1.5 mmol, the experimental group was 1.25 mmol) were directly mixed and dissolved in 40 mL DIW by magnetic stirring. The mixture was stirred for 30 minutes until the solution was uniform and transferred to a Teflon-lined stainless-steel autoclave. Then, the autoclave was put in an electric oven at 120 °C for 8 h. After that, the product was rinsed 3 times with DIW and absolute ethanol, respectively. Finally, the product was dried overnight at 80 °C. The as-synthesized Co(OH)<sub>2</sub>@Ni(OH)<sub>2</sub> heterostructure was named Co(OH)<sub>2</sub>@Ni(OH)<sub>2</sub>. For comparison, we also synthesized Ni(OH)<sub>2</sub> with similar conditions, except for adding 80 mg Ni-doped ZIF-67 precursor.

#### 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, mixed catalysts loaded carbon cloth as the positive electrode, and 6.0 M KOH (with 1.0 M EtOH) as electrolyte. The mixed catalyst was  $Co(OH)_2@Ni(OH)_2$  and FeNC (previous report<sup>2</sup>) mixed by the mass ratio of 1:1. The catalyst ink was sprayed onto the hydrophobic carbon cloth to obtain a mass loading of 2 mg cm<sup>-2</sup>. Instead of changing the electrolyte, ethanol was added every 12 hours to maintain the ethanol concentration of 1.0 M.

#### Characterization

The crystal structure was identified by X-ray diffraction (XRD) using the Miniflex600 diffractometer (Cu K $\alpha$ ,  $\lambda$ =1.54056 Å radiation). The field emission scanning electron microscope (FESEM, Ultra-55), scanning transmission electron microscope (STEM), and High-Resolution Transmission Electron Microscope (HRTEM, JEOL 2100F) were applied to characterize the morphology and structure of the materials. The chemical composition was analyzed by X-ray photoelectron spectroscopy (XPS, ESCALAB 250, Mg K $\alpha$ ) and X-ray absorption spectroscopy (XAS, Taiwan Light Source). The Brunauer-Emmett-Teller (BET) surface area and the pore size were conducted on the SSA-70000 specific surface and micropore analyzer. The analysis of experimental products was quantitatively detected by Nuclear Magnetic Resonance Spectroscopy (NMR, Bruker Ascend 600M). The identification of active species was recorded using the Laser confocal Raman Spectrometer (Raman, LabRAM HR Evolution).

#### Electrochemistry

The electrochemical measurements for EOR were studied with a three-electrode system on the electrochemical workstation (CHI 760 E) in 1.0 M KOH with 1.0 M EtOH (pH = 13.9) at room temperature. Carbon clothes  $(1.0 \times 1.0 \text{ cm}^2)$  consisting of as-prepared materials were used as the working electrodes. A carbon rod and saturated calomel electrodes (SCE) functioned as counter and reference electrodes, respectively. To prepare the working electrode, 5 mg of composite catalyst powder was dispersed in 1 mL ethanol and contained with 40 µL of 5 wt% Nafion solution, and the mixture was sonicated for 30 min to form a homogeneous catalyst ink, 200 µL of which was dropped onto the carbon cloth electrode at a catalyst loading of 1.000 mg cm<sup>-2</sup> and dried at room temperature. The SCE reference electrode was calibrated with respect to a reversible hydrogen electrode (RHE) using the following equation:  $E_{RHE} = E_{SCE} + 0.059 \times \text{pH} + 0.241 - 0.317 \times 10^{-3}(\text{T}-298) - 5.664 \times 10^{-6}(\text{T}-298)^{2.3,4}$ 

The linear sweep voltammograms (LSV) curves were performed at a sweep rate of 50 mV s<sup>-1</sup>. The polarization curves were iR-corrected according to the equation:  $E_c = E_m - I \times R_s$  ( $E_c$  is the corrected potential,  $E_m$  is the measured potential experimentally,  $R_s$  is the resistance from the electrolyte/contact resistance of the setup and measured by EIS). The chronoamperometry (CP) measurement is used to conduct long-term stability tests. The Faradic efficiency (FE) of acetate is calculated using the following equation:  $FE = (4 \times N_A \times e \times n)/Q \times 100 \%$  ( $N_A$  is Avogadro constant, e is the elementary charge, Q is the total passed charge). For temperature-dependent measurements, a sealed glass electrolyzer was suspended in a water bath with temperature control. The electrochemical activation energy ( $E_a$ ) for EOR can be estimated by using the Arrhenius relationship:  $\log(j) = -E_a / (\ln 10 \times R \times T)$  (j is the current density at 1.38 V, R is the universal gas constant, T is the temperature).

In-situ Raman measurements were recorded using the help of an electrochemical workstation (CHI 760 E). The potential-dependent spectra were recorded by stepping the potential with 0.1 V and maintaining it

for 90 s. The Raman electrochemical flow cell (K004, Tjaida) with 5 ml electrolyte was used for in-situ Raman characterizations.

#### **Computational Methods**

DFT calculations were performed with the open-source plane-wave code, Quantum Espresso<sup>5</sup>. In all calculations, the electronic exchange and correlation effects were described by generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) function. The Van der Waals interaction was taken into account for all calculation<sup>6</sup>. The plane-wave cutoff energy and k-point were set to "fine"<sup>7</sup>. The convergence of forces and energy on each atom during structure relaxation was set to  $0.03 \text{ eV} \text{ Å}^{-1}$  in force and  $10^{-5} \text{ eV}$  in energy, respectively. The vacuum space was more than 15 Å, large enough to avoid interplanar interactions. In order to improve the accuracy and precision of the overall calculation, the Hubbard U correction was applied to Ni and Co, and the U value of Ni and Co was chosen to be 3.1. The unit cells of Ni(OH)<sub>2</sub>, Co(OH)<sub>2</sub>, NiOOH, and CoOOH were in the R-3m1, P3m1, P3m1, and R3m symmetry groups, respectively. The hetero-interface model was built by NiOOH (001) and CoOOH (001) with a matching error of less than 5%. For computing the C<sub>2</sub>H<sub>5</sub>OH adsorption energy and CH<sub>3</sub>COOH desorption energy, layer slab models of pure Ni(OH)<sub>2</sub> (003), pure Co(OH)<sub>2</sub> (001), pure NiOOH (001), pure CoOOH (001), Ni(OH)<sub>2</sub>-Co(OH)<sub>2</sub> heterostructure and NiOOH-CoOOH heterostructure were constructed, respectively. All slab models were geometrically optimized and the top layers were allowed to relax.

The adsorption energies were calculated by  $\Delta E_{ads} = E_{ads+sur} - (E_{ads} + E_{sur})$ , where  $E_{ads+sur}$  represents the total energy of the adsorbate interacting with the surface,  $E_{ads}$  is the energy of the adsorbate in the gas phase, and  $E_{sur}$  is the energy of the bare surface. The adsorption-desorption process is assumed to be reversible and there is no barrier for adsorption, the desorption energy is equivalent to adsorption energy<sup>8</sup>. The desorption energies were calculated by  $\Delta E_{des} = (E_{des} + E_{sur}) - E_{des+sur}$ , where  $E_{des+sur}$  represents the total energy of the adsorbate interacting with the surface,  $E_{des}$  is the energy of the adsorbate in the gas phase, and  $E_{sur}$  is the energy of the bare surface.

The considered EOR occurring in an alkaline electrolyte (pH=14) are shown in the following steps<sup>9, 10</sup>:  $CH_3CH_2OH^* + OH^- \rightarrow CH_3CH_2O^* + H_2O + e^-$ ;  $CH_3CH_2O^* + OH^- \rightarrow CH_3CHO^* + H_2O + e^-$ ;  $CH_3CHO^* + OH^- \rightarrow CH_3CO^* + H_2O + e^-$ ;  $CH_3CO^* + OH^- \rightarrow CH_3COOH^* + e^-$ 

## **Supporting Figure**



Figure S1. TEM images and corresponding modeling images for Ni-doped ZIF-67 precursor.



Figure S2. SEM images of Co(OH)<sub>2</sub>@Ni(OH)<sub>2</sub> heterostructure.



Figure S3. TEM images for Ni(OH)<sub>2</sub>.



Figure S4. TEM images for Ni(OH)<sub>2</sub> without F doping.



Figure S5. HRTEM images and for Co(OH)<sub>2</sub>@Ni(OH)<sub>2</sub> heterostructure.



**Figure S6.** Element mapping images of Co, Ni, C and N elements in Ni-doped ZIF-67 precursor. Colour codes: Co(purple), Ni (green), C(blue), N (red).



**Figure S7.** Element mapping images of Ni, O, F, C, and N elements in Ni(OH)<sub>2</sub>. Colour codes: Ni (green), O(yellow), F(red), C(blue), N (purple).



**Figure S8.** Chronoamperometry curves of the  $Co(OH)_2@Ni(OH)_2$  at 1.5 V (vs. RHE) without iR-correction in 1 M KOH with 1 M ethanol.



Figure S9. Linear sweep voltammetry (LSV) activation curve of Ni(OH)<sub>2</sub> from segment 1 to segment 30.



Figure S10. LSV curves of  $Ni(OH)_2$  with and without F doping.



**Figure S11.** Cyclic voltammetry curve of the  $Co(OH)_2@Ni(OH)_2$  in (a) 1 M KOH with 1 M ethanol and (b) only 1 M KOH.



Figure S12. Multi-Potential Steps curve of the  $Co(OH)_2@Ni(OH)_2$  in (a) 1 M KOH with 1 M ethanol and (b) only 1 M KOH.



**Figure S13.** Nyquist plots of Ni(OH)<sub>2</sub>, Co(OH)<sub>2</sub>@Ni(OH)<sub>2</sub>, Ni-doped ZIF-67 at 1.4 V (vs. RHE) in 1 M KOH with 1 M ethanol.



Figure S14. Arrhenius plots (1.38 V) of Ni(OH)<sub>2</sub> and Co(OH)<sub>2</sub>@Ni(OH)<sub>2</sub>.



**Figure S15.** Cyclic voltammetry curve of the  $Co(OH)_2@Ni(OH)_2$  before and after the 3000 cycles of test between 0.8 V to 1.8 V without iR-correction in 1 M KOH with 1 M ethanol.



Figure S16. SEM images of Co(OH)<sub>2</sub>@Ni(OH)<sub>2</sub> heterostructure after stability test.



**Figure S17.** The statistical diagram of Faradic efficiency (FE) for 4e<sup>-</sup> EOR in the classical three-electrode system after 5 hours of constant voltage operation at 1.3, 1.4, 1.5, 1.6, 1.7, 1.8, 1.9, 2.0 V (vs. RHE) without iR-correction.



**Figure S18.** The corresponding statistical graph of  $Co(OH)_2$  @Ni(OH)<sub>2</sub> in the electrolyte of 1.0 M KOH containing 1.0 M EtOH or 3.0 M MeOH or 0.5 M urea.



Figure S19. CP curves for  $Pt/C//Co(OH)_2@Ni(OH)_2$  in a two-electrode system in 1.0 M KOH with/without 1.0 M EtOH.



**Figure S20.** Photographs of (a) Hybrid Water Electrolyzer and (b) Traditional Water Electrolyzer working at the current density of 50 mA cm<sup>-2</sup>.



Figure S21. Nyquist plots of batteries.



Figure S22. Faradic efficiency (FE) analysis diagram of reaction products for the zinc-ethanol-air battery.



Figure S23. XRD patterns of Ni-doped ZIF-67 precursor.



Figure S24. XRD patterns of the Co(OH)<sub>2</sub>@Ni(OH)<sub>2</sub>



**Figure S25.** XRD pattern for  $Co(OH)_2$  ( $OH)_2$  with 0.5, 0.75, 1.0, 1.25, 1.5 mmol Ni(NO<sub>3</sub>)<sub>2</sub> inputs for the one-pot process.



**Figure S26.** Linear sweep voltammetry polarization curves and Nyquist plots of Co(OH)<sub>2</sub>@Ni(OH)<sub>2</sub> with different amounts of Ni(NO<sub>3</sub>)<sub>2</sub> (0.5, 0.75, 1, 1.25, 1.5 mmol) in 1 M KOH with 1 M EtOH.



Figure S27. (a)  $N_2$  sorption isotherm, and (b) the corresponding pore size distribution of Ni(OH)<sub>2</sub> and Co(OH)<sub>2</sub>@Ni(OH)<sub>2</sub>.



Figure S28. Material specific surface area comparison, data from<sup>11-17</sup>.



**Figure S29.** (a) XRD pattern and of Ni(OH)<sub>2</sub>. High-resolution XPS spectra for (b) Ni2p of Ni(OH)<sub>2</sub>, (c) F1s of Co(OH)<sub>2</sub>@Ni(OH)<sub>2</sub>, and (d) F1s of Ni(OH)<sub>2</sub>.



Figure S30. HRTEM images of Co(OH)<sub>2</sub>@Ni(OH)<sub>2</sub> heterostructure after activation test.



Figure S31. Selected area electron diffraction (SAED) images of the  $Co(OH)_2$  ( $OH)_2$  ( $OH)_2$ ) before and after the activation test.



Figure S32. Element mapping images of Ni, O and Co elements for the  $Co(OH)_2@Ni(OH)_2$  after electrochemical activation. Colour codes: Ni (green), O(yellow), Co (red).



Figure S33. XRD patterns of the  $Co(OH)_2@Ni(OH)_2$  before and after activation test.



**Figure S34.** The corresponding EXAFS of  $Co(OH)_2$  ( $OH)_2$ ) before and after activation test in k space, q space, and fitting k space which is obtained by k<sup>2</sup>-weighted Fourier transform.



Figure S35. WT-EXAFS of Ni(OH)<sub>2</sub> reference sample.



**Figure S36.** Schematic illustration of all kinds of ethanol adsorption sites used for DFT calculations. The corresponding codes of the models are as follows: (a)  $Ni(OH)_2$ , (b) $Co(OH)_2$ , (c)  $Co(OH)_2$ @  $Ni(OH)_2$ , (d) NiOOH, (e) CoOOH and (f) CoOOH@NiOOH.



**Figure S37.** Schematic illustration of all kinds of acetic acid desorption sites used for DFT calculations. The corresponding codes of the models are as follows: (a) Ni(OH)<sub>2</sub>, (b)Co(OH)<sub>2</sub>, (c) Co(OH)<sub>2</sub>@ Ni(OH)<sub>2</sub>, (d) NiOOH, (e) CoOOH and (f) CoOOH@NiOOH.



**Figure S38.** Calculated ethanol adsorption energy and acetate desorption energy for hydroxyl oxygen (CH<sub>3</sub>CH<sub>2</sub>\*OH, dark colors) and  $\alpha$ -carbon (CH<sub>3</sub>\*CH<sub>2</sub>OH, light colors) adsorbed to different sites of Ni(OH)<sub>2</sub>, Co(OH)<sub>2</sub>, Co(OH)<sub>2</sub>@Ni(OH)<sub>2</sub>, NiOOH, CoOOH, and CoOOH@NiOOH.



**Figure S39.** Associated optimal structures adsorbed with the intermediates from different states of (a) NiOOH, (b) CoOOH and (c) CoOOH@NiOOH.



Figure S40. DFT-calculated EOR energy profiles for Co site and Ni site of CoOOH@NiOOH.



**Figure S41.** Structure representations of (a)  $Co(OH)_2$ , (b)  $Ni(OH)_2$ , and (c)  $Co(OH)_2@Ni(OH)_2$  as well as their corresponding calculated (d-f) charge density distribution plots.



Figure S42. Projected density of states (PDOS) and d-band of  $Co(OH)_2$ ,  $Co(OH)_2@Ni(OH)_2$  and  $Ni(OH)_2$ .

## **Supporting Table**

Element	XPS	ICP	EDS
Ni/Co	4.0:1	2.4:1	2.5:1

 Table S1. The ratio of elements obtained by different testing methods.

Electrocatalyst	Overpotential	Electrolyte	Source
Co(OH) <sub>2</sub> @Ni(OH) <sub>2</sub>	71 mV	1 M EtOH with 1 M KOH	This work
Ni(OH) <sub>2</sub>	163 mV	1 M EtOH with 1 M KOH	This work
OLC/Co-N-C	344 mV	1 М КОН	Ref. <sup>18</sup>
NiFe-MOF/G	258 mV	1 М КОН	Ref. <sup>19</sup>
Co <sub>0.85</sub> Se <sub>1</sub> -x@C	231 mV	1 М КОН	Ref. <sup>20</sup>
2D MOF-Fe/Co	238 mV	1 М КОН	Ref. <sup>21</sup>
NPC/FeCo@NCNT	339.5 mV	0.1 M KOH	Ref. <sup>22</sup>
CC-9NH <sub>3</sub> -3h	298 mV	1 М КОН	Ref. <sup>23</sup>
NiCo <sub>2-x</sub> Fe <sub>x</sub> O <sub>4</sub> NBs	274 mV	1 М КОН	Ref. <sup>24</sup>
CIF: FeNiMo	203 mV	1 М КОН	Ref. <sup>25</sup>

**Table S2.** Overpotential statistics of some state-of-the-art OER catalysts recently.

Sample	Bond	Ν	<b>R</b> (Å)	$\sigma^2 \times 10^3$ (Å <sup>2</sup> )	<b>R-factor</b>
Before Activation	Ni-(O-H)	5.93±0.39	2.04±0.01	8.08±0.98	0.0042297
	Ni-Ni	6.11±0.74	3.10±0.01	9.95±1.08	
After Activation	Ni-(O-H)	5.76±0.35	2.06±0.01	6.37±0.87	0 0000 405
	Ni-Ni	5.66±0.58	3.13±0.01	6.78±0.81	0.0032437

**Table S3.** Structural parameters of the  $Co(OH)_2$  @Ni(OH)<sub>2</sub> before and after activation obtained from EXAFS fitting.

N, coordination number; R, distance between absorber and backscatter atoms;  $\sigma^2$ , Debye-Waller factor;  $S_0^2$  is set to 0.85.

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