Supplementary Information For

Hydroxychloride-triggered spinel composite electrode for energy-efficient and long-lasting brine electrolysis hydrogen production

Zhao Cai[1,2], Mingyang Wei,[1,3] Yuzhe Cao,[1] Usama Muhammd Ladan,[4] Xiaolei Yuan,[5] and Chenggang Zhou[1,3]**

[1] Faculty of Materials Science and Chemistry, China University of Geosciences, Wuhan 430074, China

[2] State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou 350002, China

[3] Shenzhen Research Institute, China University of Geosciences, Shenzhen 518000, China

[4] Department of Pure and Industrial Chemistry, Sokoto State University, Sokoto 840101, Nigeria

[5] School of Chemistry and Chemical Engineering, Nantong University, Nantong 226019, China

*E-mail: caizhao@cug.edu.cn (Z. Cai); cgzhou@cug.edu.cn (C. Zhou).

Supplementary Figures

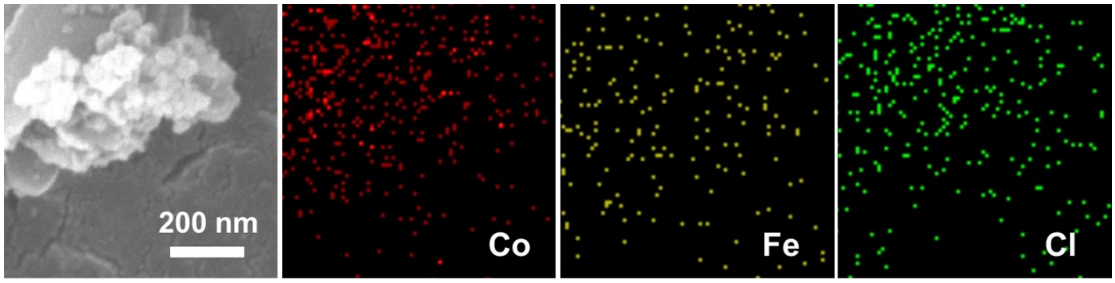

Figure S1 SEM and EDS elemental mapping images of of the $Co_2(OH)_3Cl@CoFe_2O_4$ electrode.

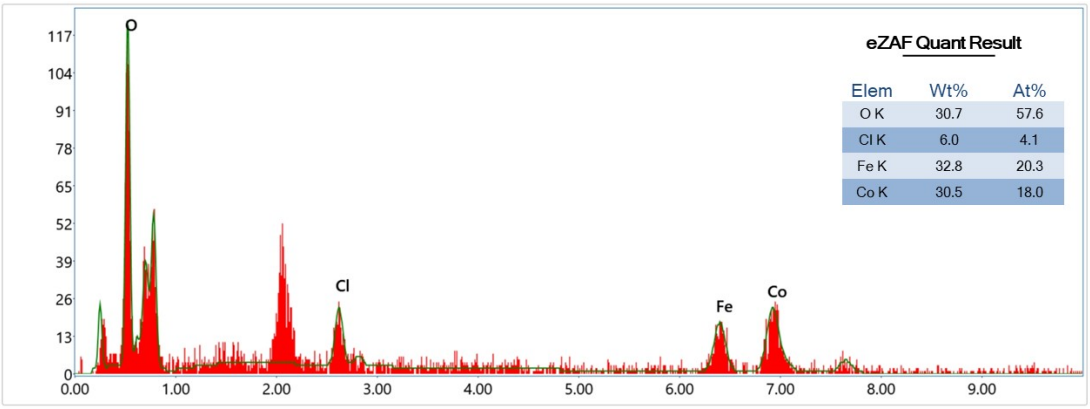

Figure S2 EDS spectrum of the $Co_2(OH)_3Cl@CoFe_2O_4$ electrode, suggesting a $Co_2(OH)_3Cl$: $CoFe_2O_4$ mol ratio of 4:10.

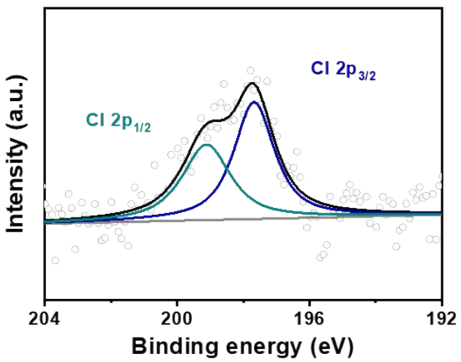

Figure S3 Cl 2p XPS spectra of the $Co_2(OH)_3Cl@CoFe_2O_4$ electrode.

Figure S4 O 1s XPS spectra of the $Co_2(OH)_3Cl$@$CoFe_2O_4$ electrode.

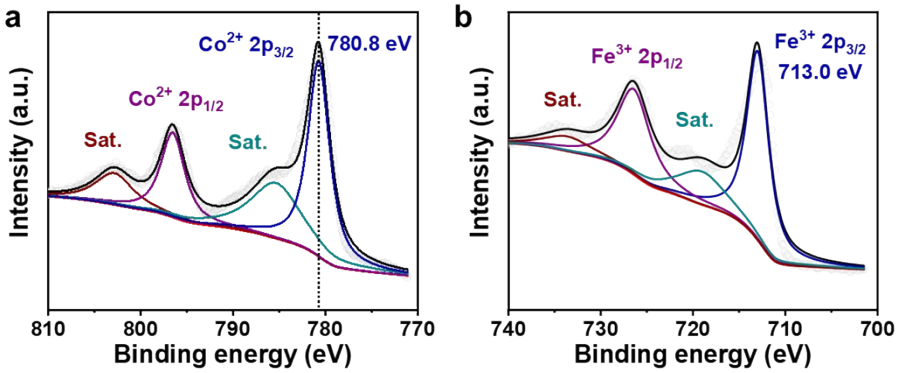

Figure S5 (a) Co 2p and (b) Fe 2p XPS spectra of the $CoFe_2O_4$ material.

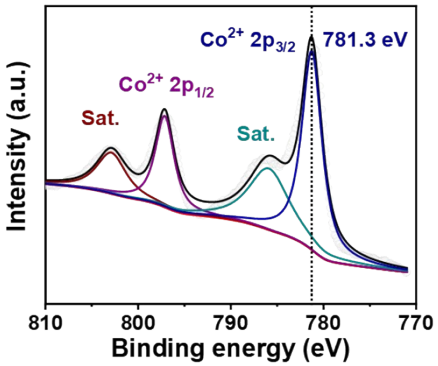

Figure S6 Co 2p XPS spectra of the $Co_2(OH)_3Cl$ material.

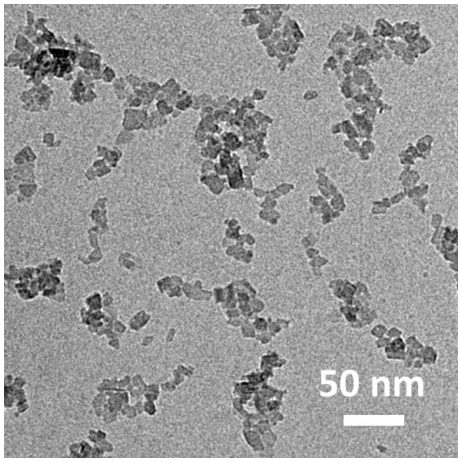

Figure S7 TEM image of the $Co_2(OH)_3Cl$ catalysts, suggesting an average particle size of ~13 nm.

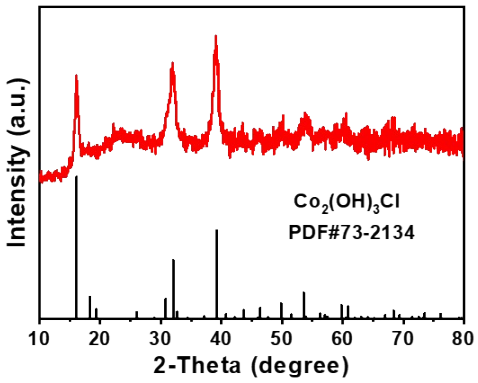

Figure S8 XRD analysis of the $Co_2(OH)_3Cl$ catalysts.

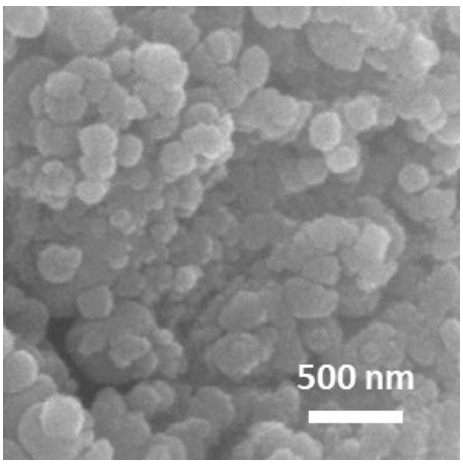

Figure S9 SEM image of the $CoFe_2O_4$ catalysts, suggesting an average particle size of ~200 nm.

Figure S10 XRD pattern of the $CoFe_2O_4$ catalysts.

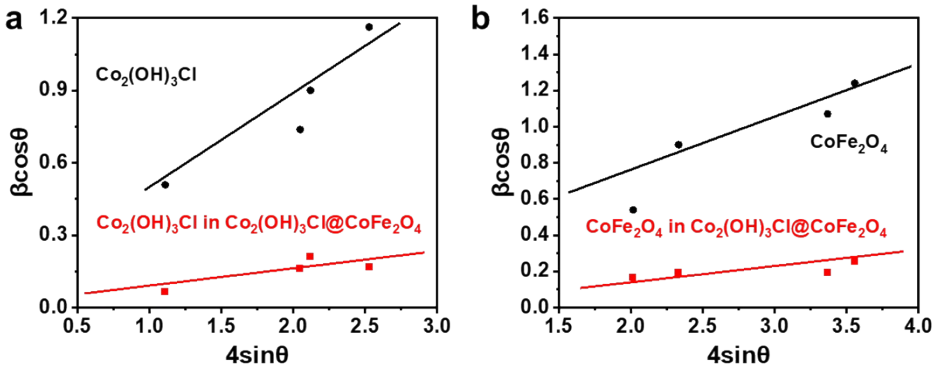

Figure S11 Williamson-Hall plots of as-prepared (a) $Co_2(OH)_3Cl$ and $Co_2(OH)_3Cl$ in $Co_2(OH)_3Cl@CoFe_2O_4$ composite electrode, and (b) $CoFe_2O_4$ and $CoFe_2O_4$ in $Co_2(OH)_3Cl@CoFe_2O_4$ composite electrode.

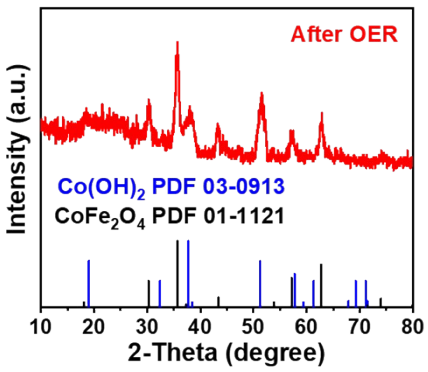

Figure S12 XRD analysis of the $Co_2(OH)_3Cl@CoFe_2O_4$ electrode after 100 h of OER at 100 mA cm^{-2}.

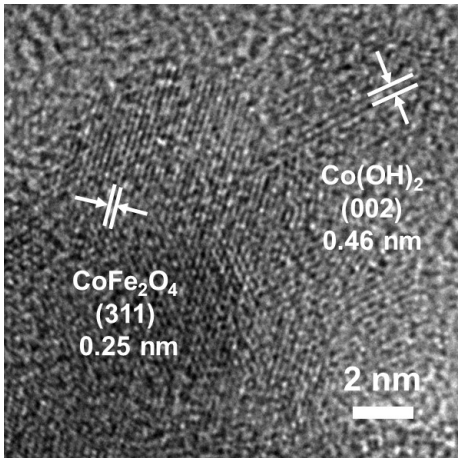

Figure S13 HRTEM image of the $Co_2(OH)_3Cl@CoFe_2O_4$ electrode after 100 h of OER at 100 mA cm^{-2}.

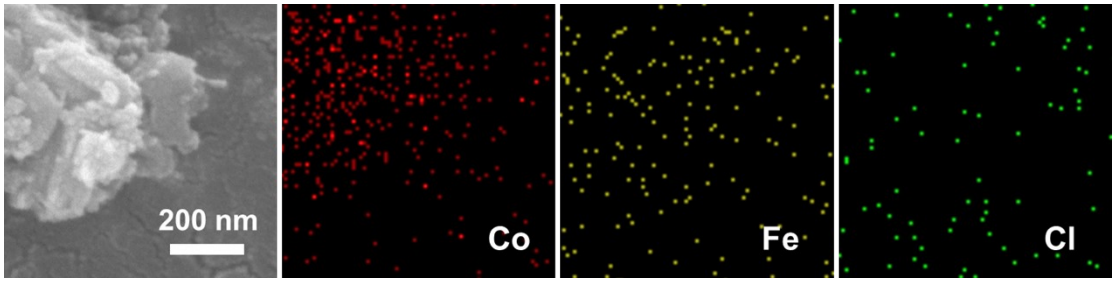

Figure S14 SEM and EDS elemental mapping images of of the $Co_2(OH)_3Cl@CoFe_2O_4$ electrode after 100 h of OER at 100 mA cm^{-2}.

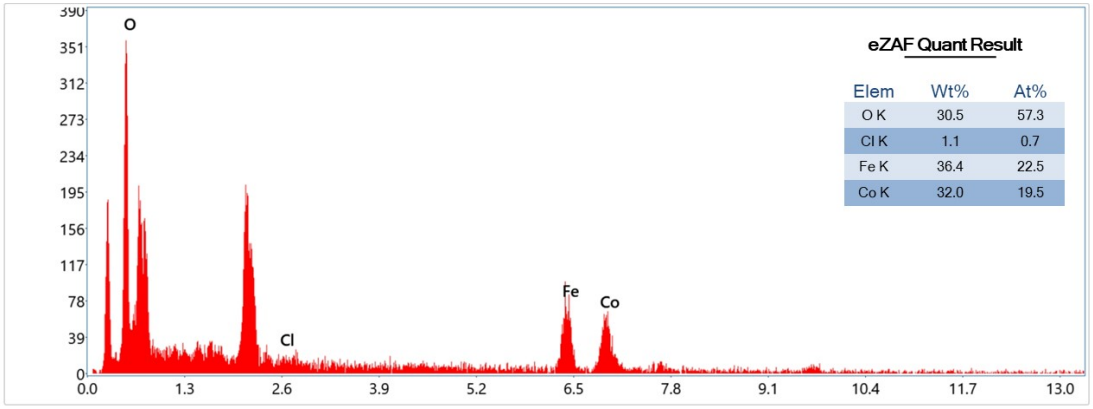

Figure S15 EDS spectrum of the $Co_2(OH)_3Cl@CoFe_2O_4$ electrode after 100 h of OER at 100 mA cm^{-2}, suggesting that very tiny amount of Cl^- was presented.

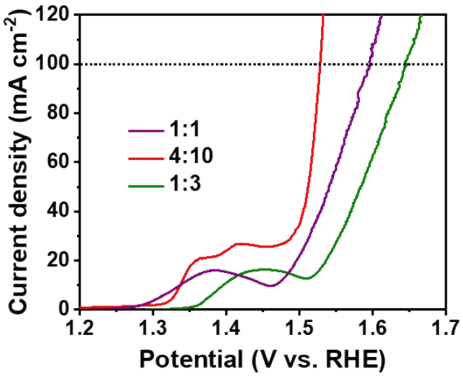

Figure S16 OER polarization curves of the composite electrodes with different $Co_2(OH)_3Cl$:$CoFe_2O_4$ ratios of 1:1, 4:10, and 1:3 in 1 M NaCl + 0.5 M NaCl electrolyte.

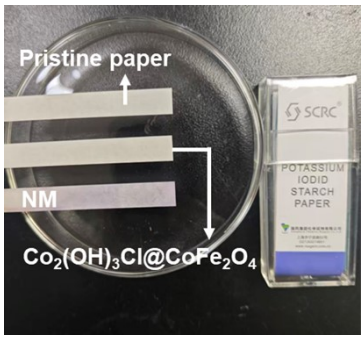

Figure S17 Digital image of potassium iodide starch papers wetted by the seawater electrolyte in NM||NM and NM||$Co_2(OH)_3Cl@CoFe_2O_4$ electrolyzers after 100 h of electrolysis at 100 mA cm^{-2}.

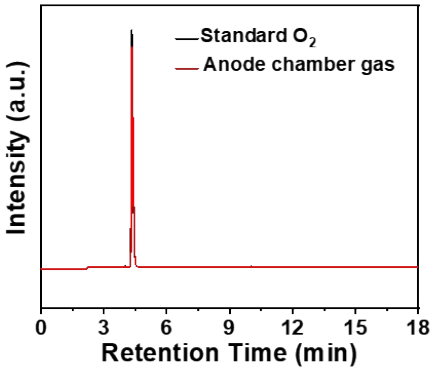

Figure S18 Gas chromatography result of the produced gas in the anode chamber of NM||$Co_2(OH)_3Cl@CoFe_2O_4$ electrolyzer.

Supplementary Table

Table S1. Comparison of the overpotential of $Co_2(OH)_3Cl@CoFe_2O_4$ electrode at the OER current density of 100 mA cm^{-2} with the high-performance Co-based electrodes in recent publications.

Materials	Overpotentials @100mA cm^{-2}	Electrolytes	References
$Co_2(OH)_3Cl@CoFe_2O_4$	295 mV	1 M KOH + 0.5 M NaCl	This work
$Co(OH)_2$/NF	375 mV	1 M KOH	*Int. J. Hydrogen Energ.*, **2023**, 48, 23877-23884
$Co(OH)_2$	420 mV	1 M KOH	*Int. J. Hydrogen Energ.*, **2024**, 56, 242-247
CoFe LDH/NF	320 mV	1 M KOH	*Appl. Catal. B-Environ.,* **2019**, 244, 583-593
CoFe LDH	340 mV	1 M KOH + 0.5 M NaCl	*ACS Appl. Energy Mater.,* **2022**, 5, 11483-11497
NiCo LDH	431 mV	1 M KOH + 0.5 M NaCl	*J. Alloy. Compd.*, **2024**, 1002, 175389
NiCo LDH/NF	440 mV	1 M KOH + 0.5 M NaCl	*New J. Chem.*, **2022**, 46, 7999-8009
NiMoCo LDH/NF	330 mV	1 M KOH + 0.5 M NaCl	*New J. Chem.*, **2022**,46, 7999-8009
MnCo LDH/NF	370 mV	1 M KOH	*Fuel*, **2024**, 364, 130961
NiCoFe LDH/CC	390 mV	1 M KOH	*J. Mater. Chem. A*, **2018**, 6, 3224-3230

Table S2. Comparison of the operation voltage of the NM||V-LDH@NM electrolyzer at 100 mA cm^{-2} with the high-performance brine electrolyzers in recent publications.

Electrolyzers	Operation voltages@100 mA cm^{-2}	Electrolytes	References
Ni||$Co_2(OH)_3Cl$@$CoFe_2O_4$	1.72 V	1 M NaOH + 0.5 M NaCl	This work
Cr-Cu_2S||Cr-Cu_2S	1.75 V	1 M NaOH + 0.5 M NaCl	*Int. J. Hydrogen Energ.,* **2023**, 49, 1113-1122
Y-NiMo/MoO_{2-x}||NiFe LDH	1.84 V	3M NaOH + seawater	*Nat. Commun.,* **2025**, 16, 773
$Fe_{0.09}Ni_{0.91}O_xH_y$||P-$Fe_{0.09}Ni_{0.91}MoO_4$	1.73 V	1 M NaOH + 1 M NaCl	*Appl. Catal. B-Environ.*, **2024**, 364, 124861
Ni||Ni_xCr_yO	1.75 V	1 M NaOH + seawater	*Angew. Chem. Int. Ed.*, **2023**, 62, e202309854
Ni_2S||Eu_2O_3/$FeNi_2S_4$	1.90 V	1 M KOH + seawater	*J. Am. Chem. Soc.,* **2025**, 147, 17190-17200
Pt/C||RuO_2	2.00 V	1 M NaOH + 0.5 M NaCl	*Nat. Commun.,* **2023**, 14, 3607
Cu_2S||FeCoP	1.95 V	1 M KOH + 0.5 M NaCl	*Nanoscale*, **2026**, DOI: 10.1039/D5NR04925C
Ni(Co)MoO_4/MoO_2^-|| (NiFe)OOH/GO	1.72 V	1 M KOH + seawater	*J. Mater. Chem. A,* **2025**, 13, 24753-24763
Pt/Ti||IrO_2/Ti	2.50 V	1 M NaOH + 0.5 M NaCl	*Angew. Chem. Int. Ed.*, **2025**, 64, e202422840
CoZnCr@Mo_2TiC_2||CoZnCr @Mo_2TiC_2	1.76 V	1 M KOH + seawater	*J. Mater. Chem. A,* **2025**, 13, 41752-41763

Table S3. Comparison of the energy consumptions of the as-assembled electrolyzers at different operating current densities.

	100 mA cm^{-2}	**1 A cm^{-2}**
Ni||Ni	4.57 KWh Nm^{-3}	/
Ni||$Co_2(OH)_3Cl$@$CoFe_2O_4$	4.13 KWh Nm^{-3}	4.90 KWh Nm^{-3}