Supporting Information

Bifunctional Pt–Co₃O₄ Electrocatalysts for Simultaneous Generation of Hydrogen and Formate via Energy-Saving Alkaline Seawater/Methanol Co-Electrolysis

Kun Xiang, ^{a,b} Zhongxin Song, ^a Dan Wu, ^a Xiaohui Deng, ^a Xuewan Wang, ^a Wen You, ^c Zhikun Peng, ^d Lei Wang, ^a Jing-Li Luo, ^a and Xian-Zhu Fu*^a

Corresponding Author

Prof. Xian-Zhu Fu

E-mail: xz.fu@szu.edu.cn



Fig. S1 The cyclic voltammetry (CV) of p-Co₃O₄/CP and Pt-Co₃O₄/CP at a scan rate of 100 mV s^{-1} in 1.0 M KOH.



Fig. S2 (a-c) SEM images of carbon paper (CP). (d-f) SEM images of α -Co(OH)₂/CP.



Fig. S3 (a-b) SEM images of p-Co₃O₄/CP.



Fig. S4 (a) The CV curves of p-Co₃O₄/CP, (b) Pt-Co₃O₄/CP electrode, and (c) the plots of current density at 0.96 V as a function of scan rates for p-Co₃O₄/CP and Pt-Co₃O₄/CP electrode in 1.0 M NaOH.



Fig. S5 (a) Anodic and (b) cathodic LSV curves of Pt-Co(OH)₂/CP in 1.0 M NaOH, 1.0 M NaOH+3.5% NaCl, and 1.0 M NaOH+3.5% NaCl+2.0 M MeOH, respectively.



Fig. S6 (a) Anodic and (b) cathodic LSV curves of H-Pt-Co₃O₄/CP in 1.0 M NaOH, 1.0 M NaOH+3.5% NaCl, and 1.0 M NaOH+3.5% NaCl+2.0 M MeOH, respectively. (c) Anodic and (d) cathodic specific mass activities of Pt-Co₃O₄/CP and H-Pt-Co₃O₄/CP in 1.0 M NaOH+3.5% NaCl+2.0 M MeOH".



Fig. S7 (a-b) Anodic and cathodic polarization curves of p-Co₃O₄/CP in 1 M NaOH, 1 M NaOH+3.5% NaCl, and 1 M NaOH+3.5% NaCl+2 M MeOH, respectively. (c-d) Anodic and cathodic polarization curves of OV-Co₃O₄/CP in 1 M NaOH, 1 M NaOH+3.5% NaCl, and 1 M NaOH+3.5% NaCl+2 M MeOH, respectively.



Fig. S8 (a) Tafel slopes for the anodic reaction in 1 M NaOH + 3.5% NaCl + 2 M MeOH on p-Co₃O₄/CP, OV-Co₃O₄/CP, Pt-Co₃O₄/CP, Pt-Co(OH)₂/CP and H-Pt-Co₃O₄/CP. (b) EIS recorded at 0.65 V (vs RHE) in 1 M NaOH + 3.5% NaCl + 2 M MeOH on: p-Co₃O₄/CP, OV-Co₃O₄/CP, Pt-Co₃O₄/CP, Pt-Co(OH)₂/CP and H-Pt-Co₃O₄/CP. (c) EIS recorded on Pt-Co₃O₄/CP at a single potential in the HER range (-60 mV vs. RHE) in 1 M NaOH, 1 M NaOH + 3.5% NaCl, 1 M NaOH + 3.5% NaCl + 2 M MeOH and 1 M NaOH + 3.5% NaCl + 2 M MeOH + 0.1 M HCOONa.



Fig. S9 The polarization curves of Pt-Co₃O₄/CP electrode with different concentrations of methanol in alkaline seawater.



Fig. S10 The polarization curves of Pt-Co₃O₄/CP and commercial electrocatalysts (20% Pt/C and RuO₂) electrodes in methanol/alkaline seawater.



Fig. S11 The LSV curves of p-Co₃O₄/CP and OV-Co₃O₄/CP with 2.0 M methanol for overall simulated alkaline seawater splitting.



Fig. S12 The calibration curves of (a) Cl⁻and (b) HCOO⁻.



Fig. S13 The contents of Cl⁻ at various cell voltages.



Fig. S14 (a-b) The cathodic and anodic polarization curves for Pt-Co₃O₄/CP electrode in 1 M NaOH +3.5% NaCl+ 2 M MeOH and 1 M NaOH + 2 M MeOH, respectively. (c) LSV curves of symmetric Pt-Co₃O₄/CP cell in 1 M NaOH +3.5% NaCl+ 2 M MeOH and 1 M NaOH + 2 M MeOH, respectively.



Fig. S15 (a-c) SEM images of Pt-Co₃O₄/CP at the anode after long-term test; (d-f) SEM images of Pt-Co₃O₄/CP at the cathode after long-term test.



Fig. S16 (a-b) Fitted Co 2p XPS spectra of Pt-Co₃O₄/CP after long-term test at the anode and cathode, respectively. (c-d) Fitted O 1s XPS spectra of Pt-Co₃O₄/CP after long-term test at the anode and cathode, respectively. (e-f) Fitted Pt 4f XPS spectra of Pt-Co₃O₄/CP after long-term test at the anode and cathode, respectively.

Table S1. Comparison of the HER performance with other state-of-the-art electrocatalysts in in

 methanol-containing electrolyte.

Electrocatalysts	Overpotential (mV) η @10 mA cm ⁻²	Electrolyte	Ref.
NC@CuCo ₂ N _x /CF	105 mV	1.0 M KOH+15 mM BA	Adv. Funct. Mater. 2017, 27, 1704169
Co _{0.83} Ni _{0.17} /AC	193 mV	1.0 M KOH+10 mM BA	New J. Chem. 2018, 42, 6381
Rh-NSs	56 mV	1.0 M KOH + 1.0 M Isopropanol	Nanoscale 2019, 11, 9319
Co-S-P	167 mV	1.0 M KOH+1.0 M Ethanol	Inorg. Chem. Front., 2020, 7, 4498
CoxP@NiCo-LDH/NF	100 mV	1.0 M KOH+0.5 M MeOH	J. Energy Chem. 2020, 50, 314.
Co(OH)2@HOS	148 mV	1.0 M KOH+3.0 M MeOH	Adv. Funct. Mater. 2020, 30, 1909610
Ni _{0.33} Co _{0.67} (OH) ₂ /NF	187 mV	1.0 M KOH+0.5 M MeOH	ChemSusChem 2020, 13, 914.
Pt-Co ₃ O ₄ /CP	50 mV	1.0 M KOH+2 M MeOH	This work