Supporting Information

Table S1 Electrolyte.

Serial number	H_2O (mL)	KOH (M)	tert−butanol (mM)	Quinoxaline (mM)	Tetrahydroquinoxaline (mM)	$K_4[Fe(CN)_6]$ (mM)
Electrolyte 1	35	1	–	–	–	–
Electrolyte 2	35	1	–	15	–	–
Electrolyte 3	35	1	51	–	–	–
Electrolyte 4	35	1	51	15	–	–
Electrolyte 5	35	1	–	–	15	–
Electrolyte 6	35	1	–	10	–	–
Electrolyte 7	35	1	–	–	–	100

Table S2 Electrochemical system.

Electrochemical system	Counter electrode	Working electrode	Reference electrode	Electrolyte of working electrode	Electrolyte of counter electrode
Electrochemical system 1 (ES 1)	Pt	NF	Hg/HgO	35 mL Electrolyte 1	35 mL Electrolyte 1
Electrochemical system 2 (ES 2)	Pt	CoO/NF	Hg/HgO	35 mL Electrolyte 1	35 mL Electrolyte 1
Electrochemical system 3 (ES 3)	Pt	Co_2NiO_4/NF	Hg/HgO	35 mL Electrolyte 1	35 mL Electrolyte 1
Electrochemical system 4 (ES 4)	Pt	NF	Hg/HgO	35 mL Electrolyte 2	35 mL Electrolyte 1
Electrochemical system 5 (ES 5)	Pt	CoO/NF	Hg/HgO	35 mL Electrolyte 2	35 mL Electrolyte 1
Electrochemical system 6 (ES 6)	Pt	Co_2NiO_4/NF	Hg/HgO	35 mL Electrolyte 2	35 mL Electrolyte 1
Electrochemical system 7 (ES 7)	Pt	Co_2NiO_4/NF	Hg/HgO	35 mL Electrolyte 3	35 mL Electrolyte 1
Electrochemical system 8 (ES 8)	Pt	Co_2NiO_4/NF	Hg/HgO	35 mL Electrolyte 4	35 mL Electrolyte 1
Electrochemical system 9 (ES 9)	Pt	NF	Hg/HgO	35 mL Electrolyte 1	35 mL Electrolyte 1
Electrochemical system 10 (ES 10)	Pt	CoO/NF	Hg/HgO	35 mL Electrolyte 1	35 mL Electrolyte 1
Electrochemical system 11 (ES 11)	Pt	Co_2NiO_4/NF	Hg/HgO	35 mL Electrolyte 1	35 mL Electrolyte 1
Electrochemical system 12 (ES 12)	Pt	NF	Hg/HgO	35 mL Electrolyte 5	35 mL Electrolyte 1
Electrochemical system 13 (ES 13)	Pt	CoO/NF	Hg/HgO	35 mL Electrolyte 5	35 mL Electrolyte 1
Electrochemical system 14 (ES 14)	Pt	Co_2NiO_4/NF	Hg/HgO	35 mL Electrolyte 5	35 mL Electrolyte 1
Electrochemical system 15 (ES 15)	GF	Co_2NiO_4/NF	Hg/HgO	35 mL Electrolyte 6	35 mL Electrolyte 7

Table S3 Electrochemical parameters from EIS at −0.3 V (*vs*. RHE) of the catalysts.

	NF	CoO/NF	Co_2NiO_4/NF
R1 (ohm)	1.00	1.24	1.19
R2 (ohm)	1.80	1.69	0.89

Table S4 Electrochemical parameters from EIS at 1.5 V (*vs*. RHE) of the catalysts.

	NF	CoO/NF	Co_2NiO_4/NF
R1 (ohm)	0.97	0.92	0.96
R2 (ohm)	95.84	23.99	5.97

Table S5 Summary of electrocatalysts for nitrogen-containing heterocyclic organic compounds.

Catalyst	Reaction substrate	Temperature (°C)	Solvent	Potential (V *vs*. RHE)	Conversion (%)	Selectivity (%)	Ref.
Co_2NiO_4/NF	quinoxaline	25	1 M KOH	−0.3	99.84	99.15	
Co-F	quinoline	25	1 M KOH + dioxane	−0.2	99	94	[1]
Co_3O_4	quinoxaline	25	1 M KOH + dioxane	−0.13	98.2	99.3	[2]
RuP_2/Ni_2P	quinoline	25	1 M KOH + dioxane	−0.15	97%	99%	[3]
NiCoP/NF	quinoline	25	1 M KOH + dioxane	−0.2	95%	99%	[4]
P-WO_3/NF	quinoxaline	25	1 M KOH	−0.2	90	99	[5]
$MoNi_4$/NF	quinoxaline	25	1 M KOH	−0.5	99	99	[6]
RuNi/NF	quinoline	25	1 M KOH + dioxane	−0.25	99	99	[7]
$Cu(OH)_2$@NiCo-MOF	quinoline	25	1 M KOH + dioxane	−0.3	99.5	100	[8]
CuNWs	quinoline	25	1 M KOH	−0.375	100	100	[9]
Pd/NF	quinoxaline	25	1 M KOH	−0.2	95	100	[10]
$CuCo_2O_4$/NF	quinoxaline	25	1 M KOH	−0.18	93	99	[11]

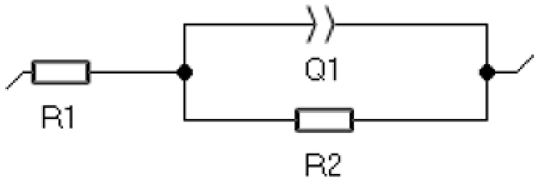

Fig. S1 Equivalent circuit diagram. R_1 represents solution resistance, R_2 represents charge transfer resistance, Q_1 represents constant phase element.

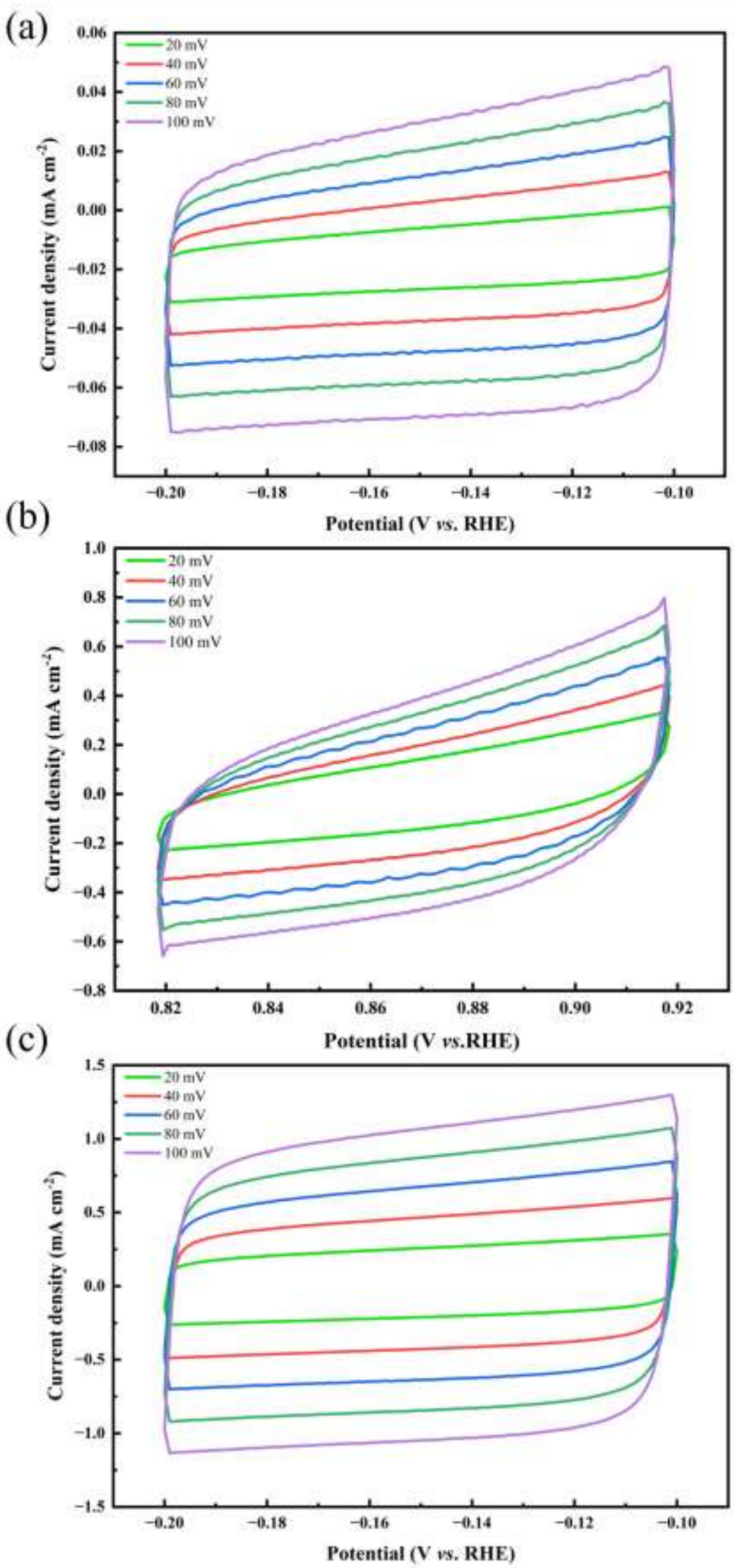

Fig. S2 CV curves of (a) NF in ES 1, (b) CoO/NF in ES 2, and (c) Co_2NiO_4/NF in ES 3.

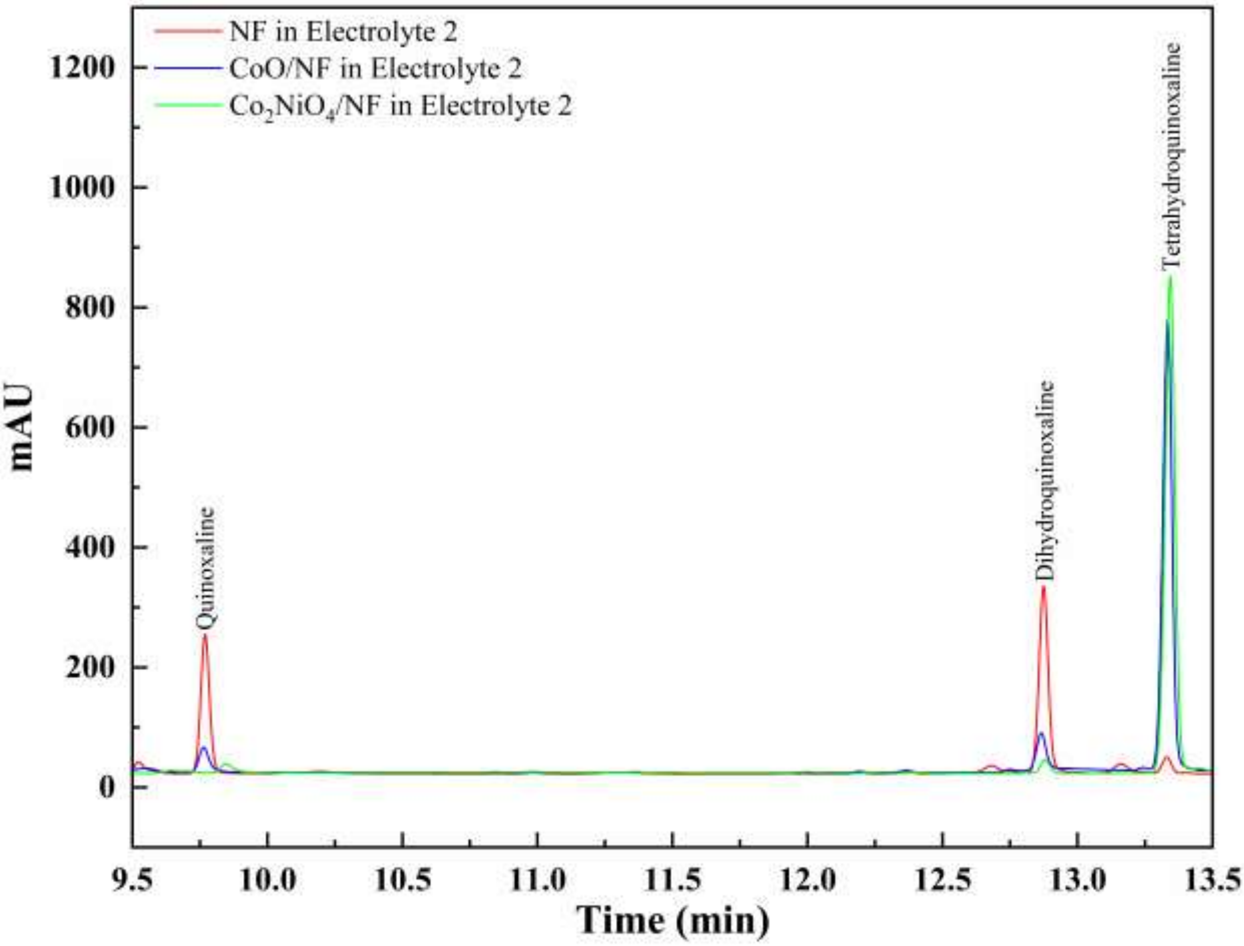

Fig. S3 GC tests for ECH of NF, CoO/NF, and Co_2NiO_4/NF in Electrolyte 2.

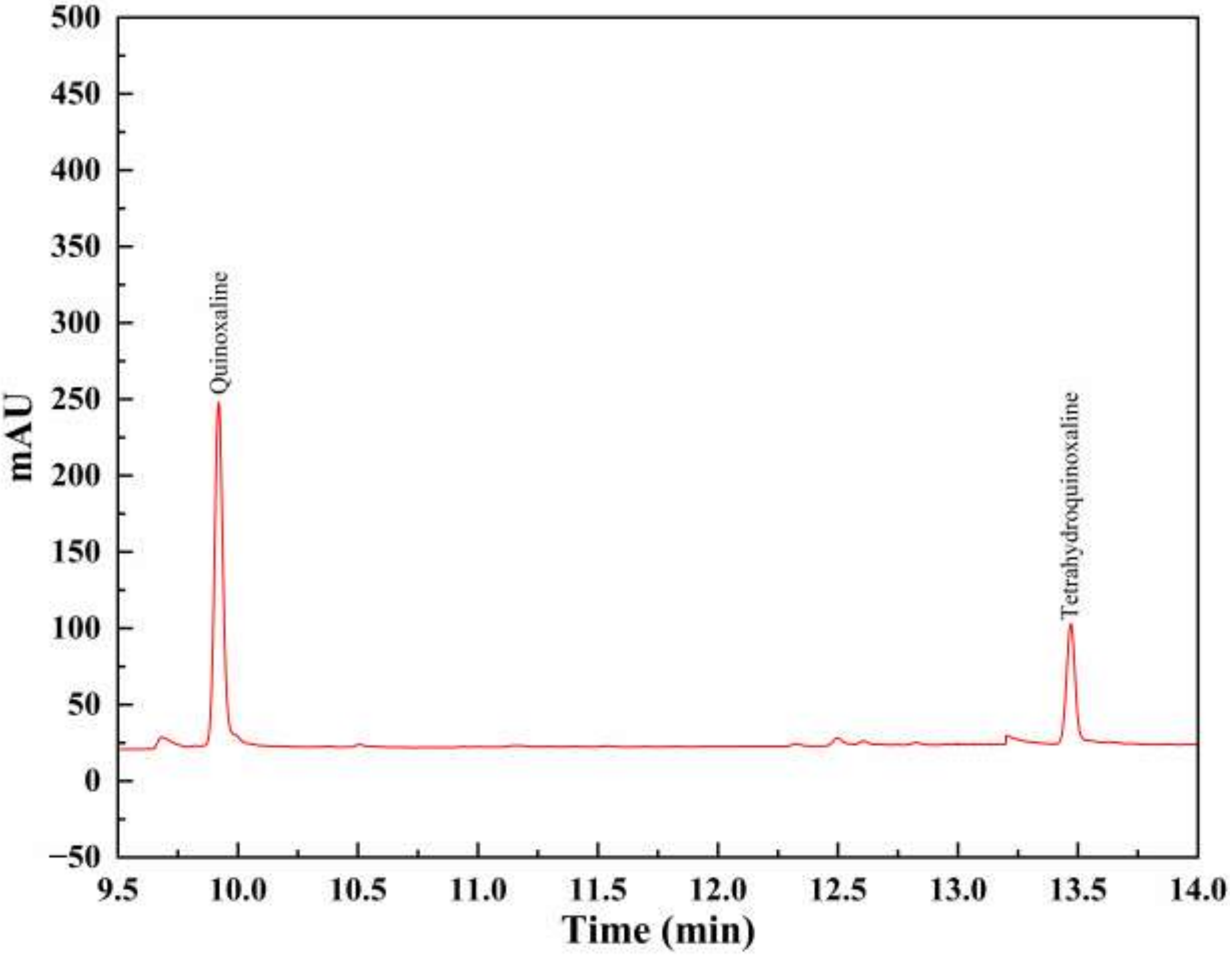

Fig. S4 GC tests for ECH of Co_2NiO_4/NF in ES 8.

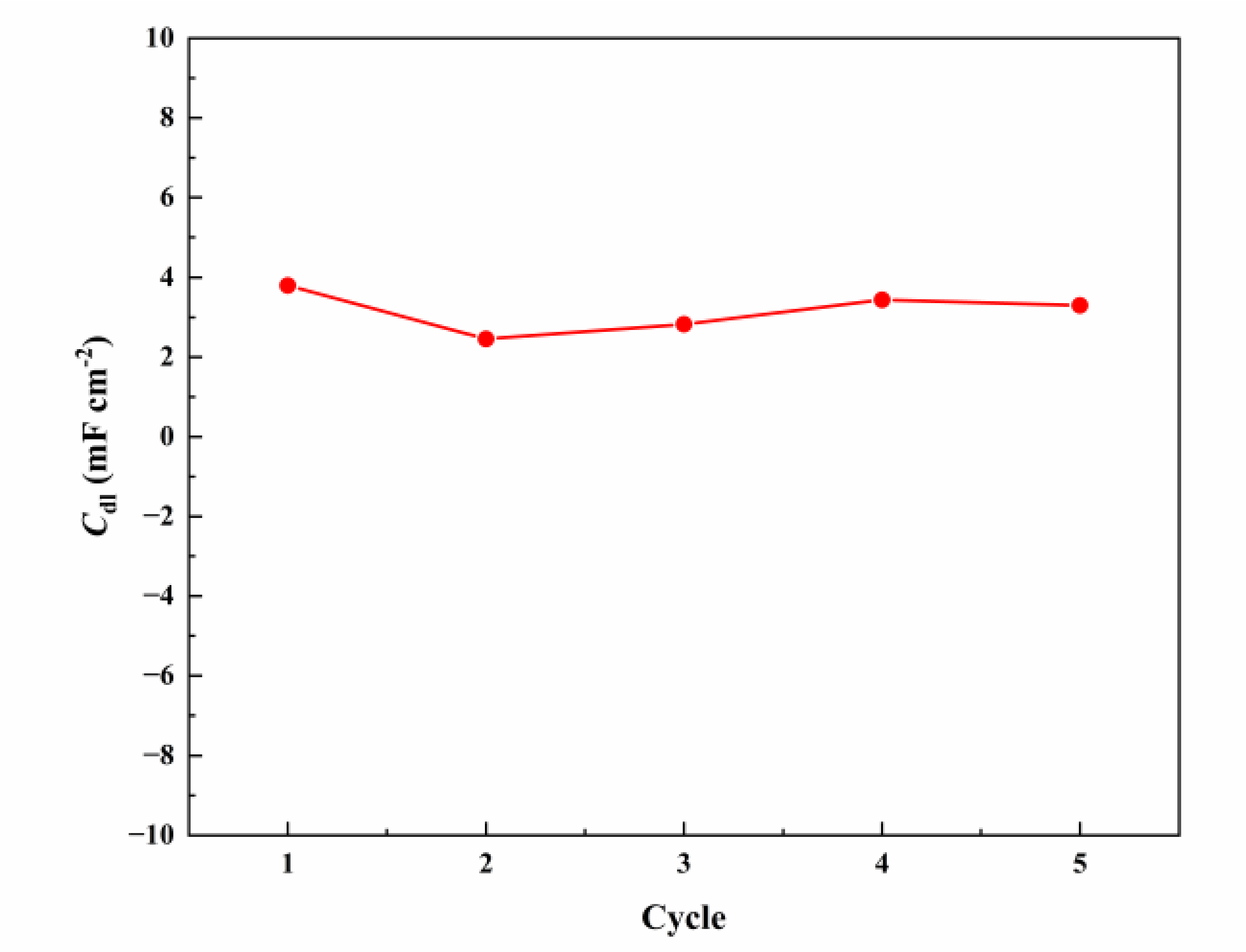

Fig. S5 C_{dl} for ECH of Co_2NiO_4/NF with 5 cycles.

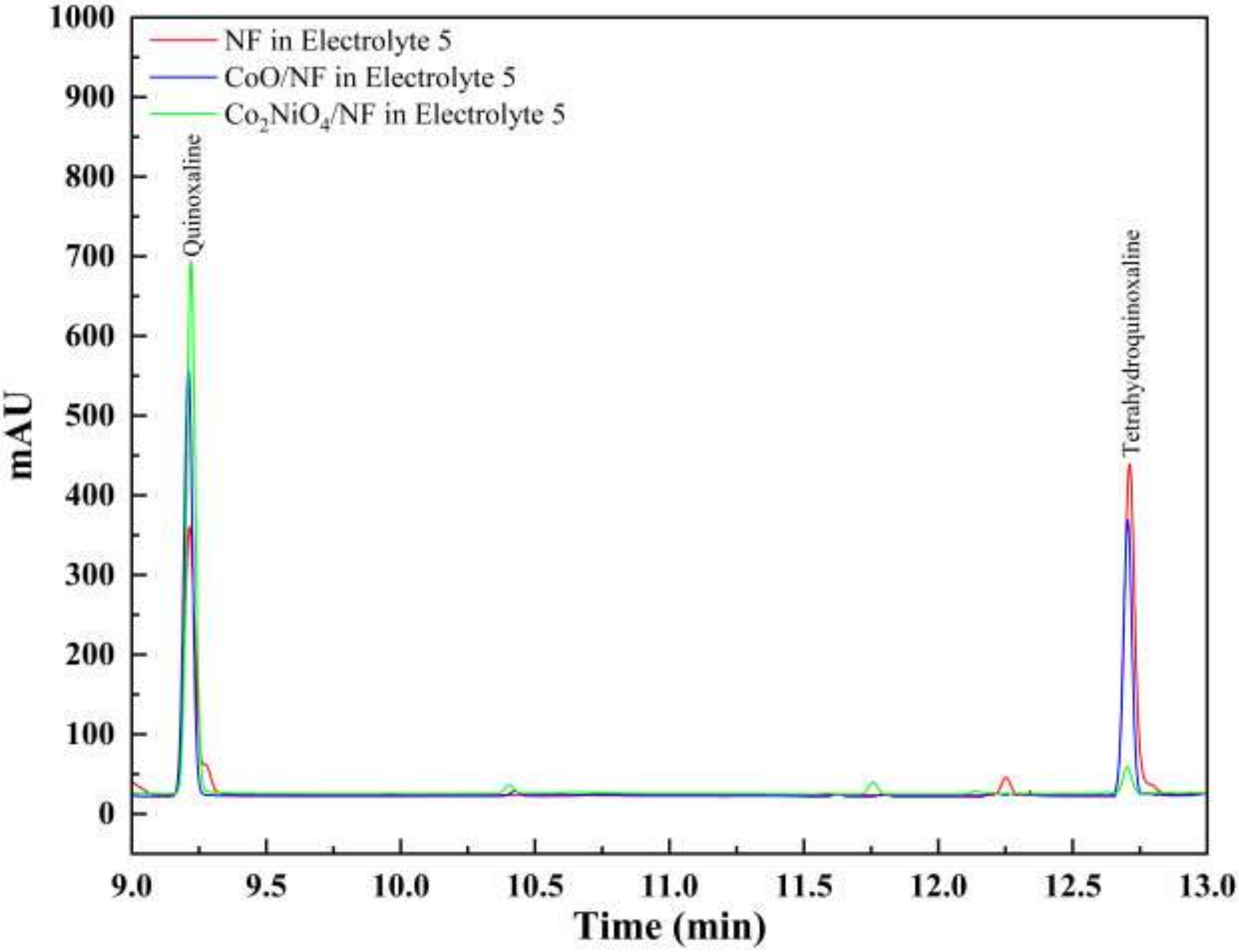

Fig. S6 GC tests for ECD of NF, CoO/NF, and Co_2NiO_4/NF in Electrolyte 5.

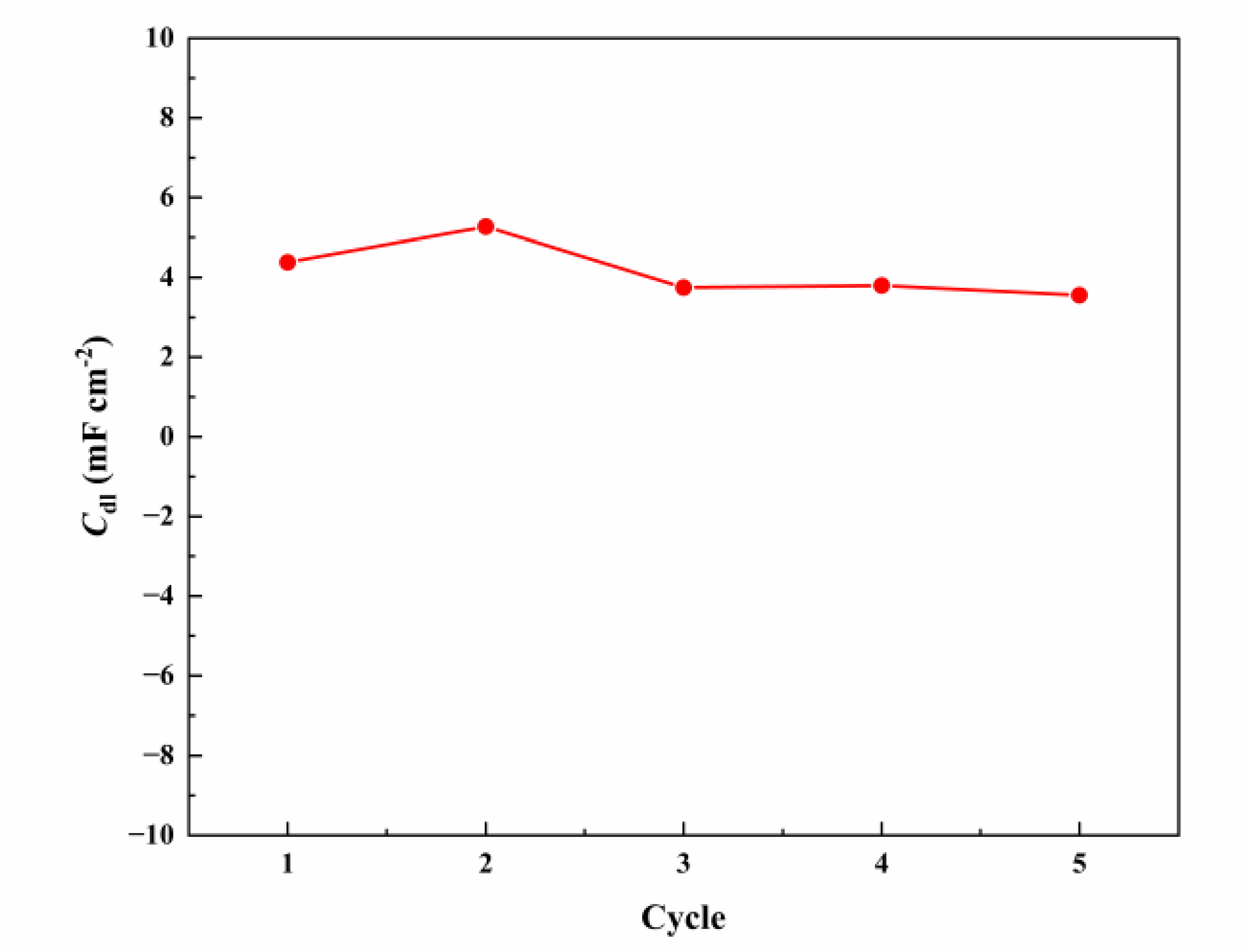

Fig. S7 C_{dl} for ECD of Co_2NiO_4/NF with 5 cycles.

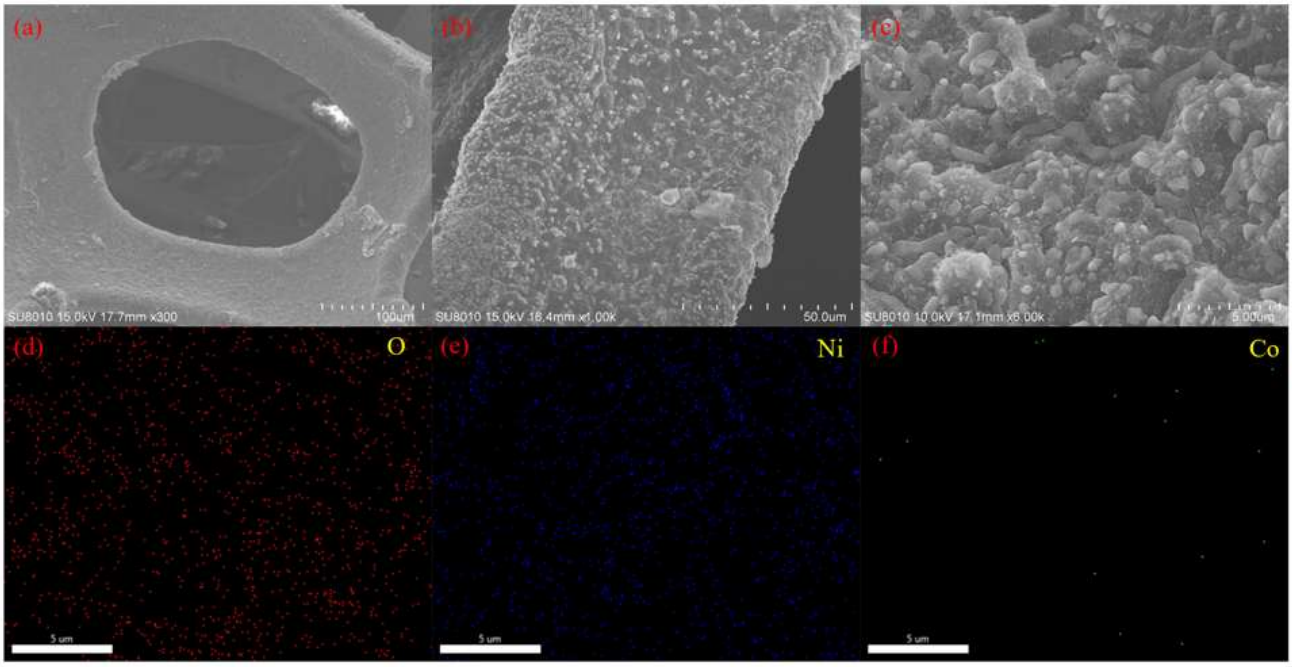

Fig. S8 (a–c) SEM images and (d–f) EDS mapping of Co_2NiO_4/NF after 10 charge−discharge cycles in flow batteries.

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