Supporting Information

Upcycling Spent NCM Cathodes into Gradient Electrocatalysts for Enhanced Stability in Direct Seawater Splitting

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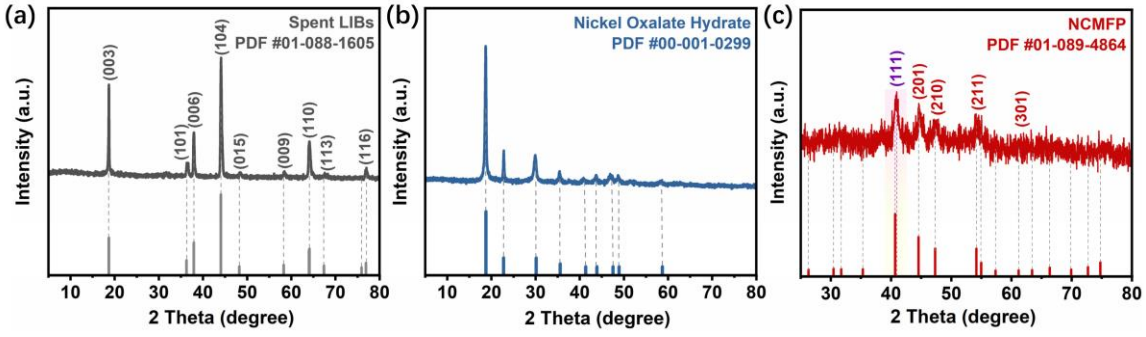


Figure S1. (a) XRD pattern of Spent LIBs, (b) NiMnCoFe-oxalate salts, and (c) NCMFP.

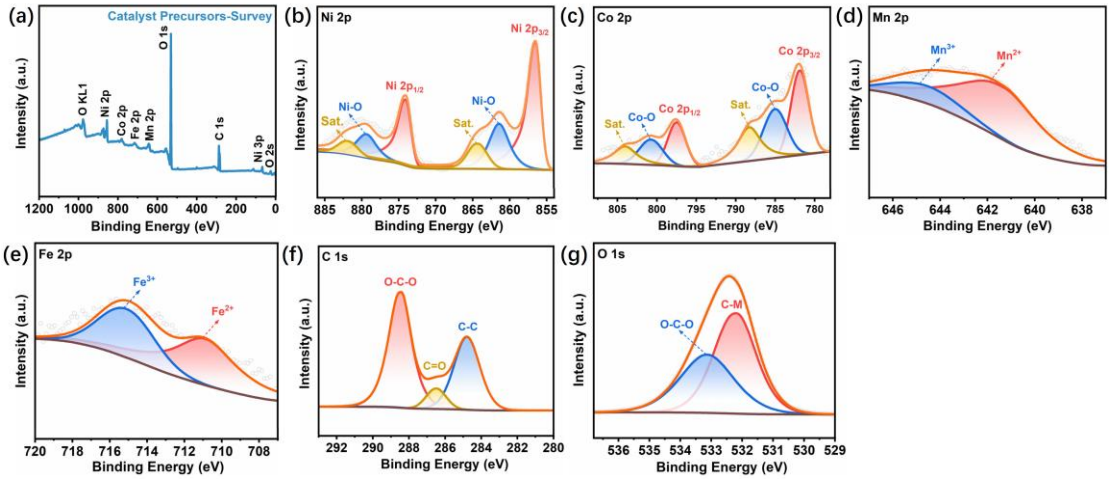


Figure S2. XPS spectra of NiMnCoFe-oxalate salts as prepared: (a) Survey spectrum, (b) Ni 2p, (c) Co 2p, (d) Mn 2p, (e) Fe 2p, (f) C 1s, (g) O 1s.

Table S1: Table of Metal Concentration in the NCMFP:

Metal Element	Elemental Spectral Lines	Normalized Concentration (%)
Ni	Ni 231.604 r	79.98
Co	Co 228.615 r	12.80
Mn	Mn 257.610 r	6.98
Fe	Fe 259.940 r	0.24

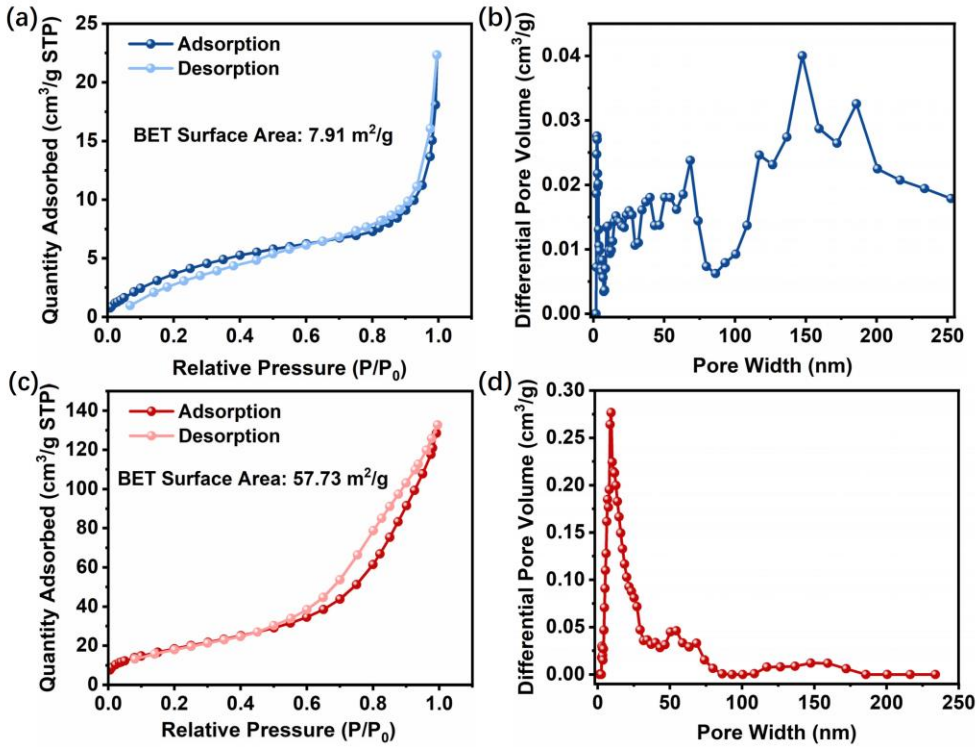


Figure S3. (a) N_2 adsorption-desorption curves of NiMnCoFe-oxalate salts, (b) Pore size distribution curve of NiMnCoFe-oxalate salts. (c) N_2 adsorption-desorption curves of NCMFP, (d) Pore size distribution curve of NCMFP.

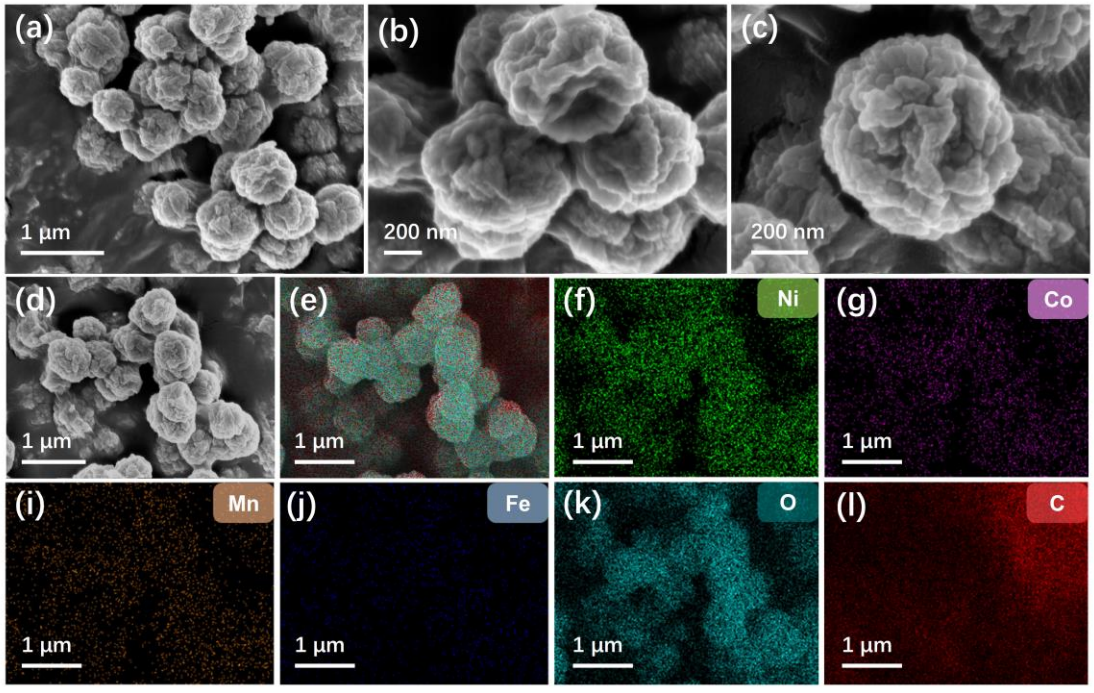


Figure S4. (a-c) SEM images of NiMnCoFe-oxalate salts at different magnifications, (d-l) SEM image and the corresponding elemental mappings of NiMnCoFe-oxalate salts.

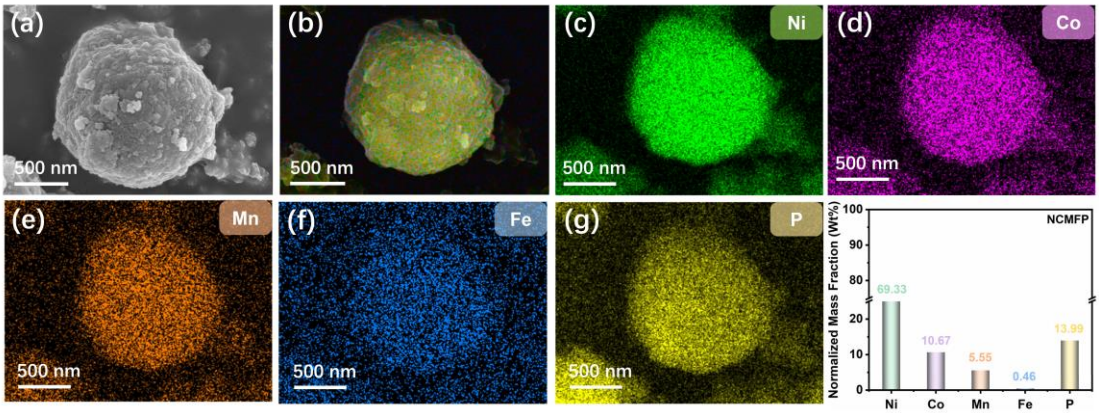


Figure S5. (a) SEM images of NCMFP, (b-g) the corresponding elemental mappings of NCMFP and the SEM-EDS data of area scan on NCMFP particle.

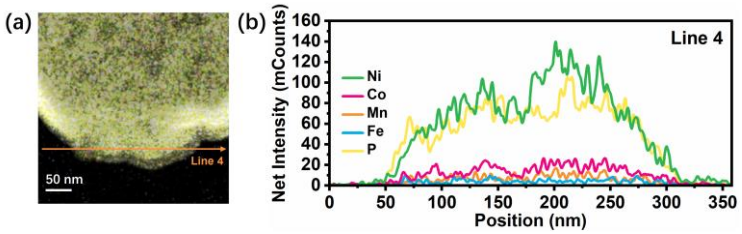


Figure S6. (a) Transverse line scan of NCMFP particles and (b) corresponding data.

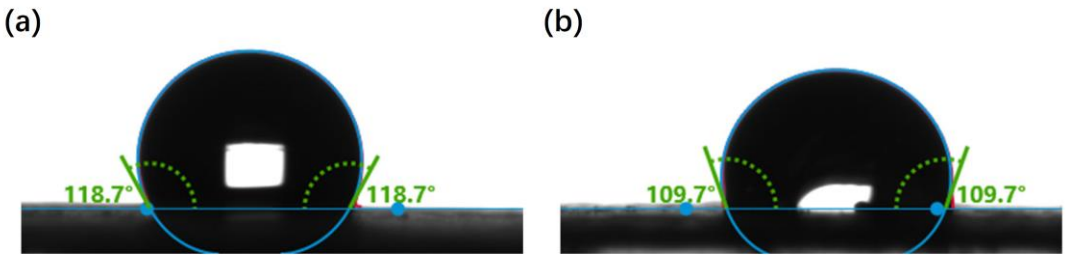


Figure S7. Contact angle test. (a) Contact angle of pure carbon paper. (b) Contact angle of NCMFP on carbon paper.

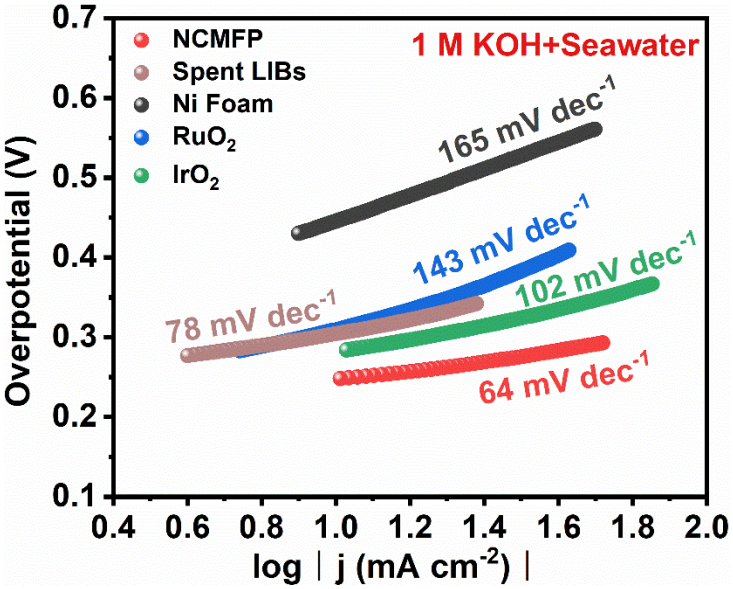
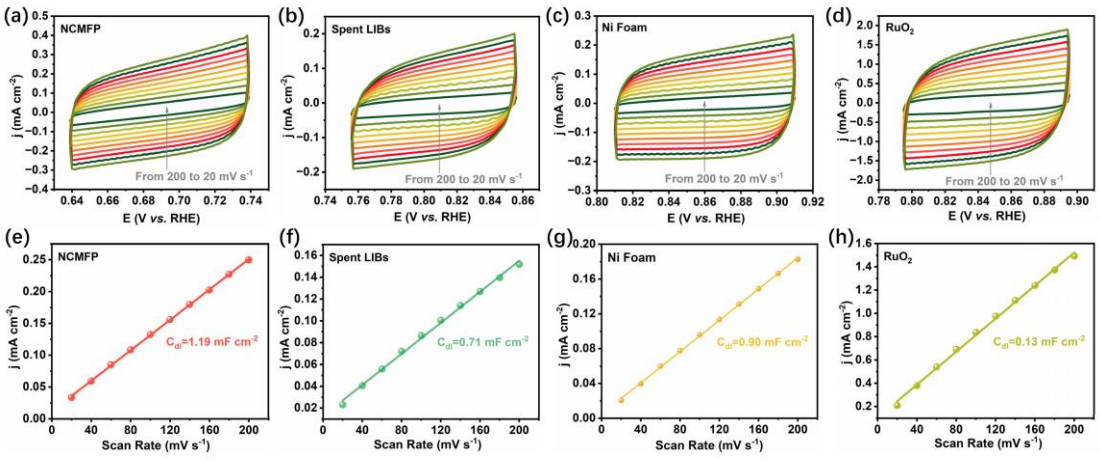


Figure S8. Tafel plots in 1 M KOH + Seawater.



Calculation of ECSA for each catalyst:

ECSA = C_{dl}/C_s, where C_s is the specific capacitance for a flat surface (40 μF cm^{-2}).

ECSA $_{NCMFP}$ = 1.19 mF cm^{-2}/40 μF cm^{-2} = 29.75 cm^2

ECSA $_{Ni\ Foam}$ = 0.90 mF cm^{-2}/40 μF cm^{-2} = 22.5 cm^2

ECSA $_{RuO_2}$ = 0.13 mF cm^{-2}/40 μF cm^{-2} = 7.50 cm^2

ECSA $_{Spent\ LIBs}$ = 0.71 mF cm^{-2}/40 μF cm^{-2} = 17.75 cm^2

Figure S9. Cyclic voltammetry (CV) curves and linear fitting of double layer capacitance (C_{dl}) versus CV scan rate were used to estimate the electrochemically active surface area (ECSA) of different catalysts. The CV curves were measured in the scan rate range of 20 mV s^{-1} to 200 mV s^{-1} with an interval of 20 mV s^{-1}.

Table S2: Under the conditions of 1 M KOH + Seawater, the detailed data obtained from the fitted electrochemical impedance spectroscopy (EIS) are as follows:

Element	Rs (Ω)	CPE-T	CPE-P	Rct (Ω)	Wo
NCMFP	1.213	0.0010207	0.73512	17.77	0.40909
Spent LIBs	1.194	0.0051592	0.76266	14.39	0.43886
Ni Foam	1.108	0.0012648	0.73929	19.83	0.47063

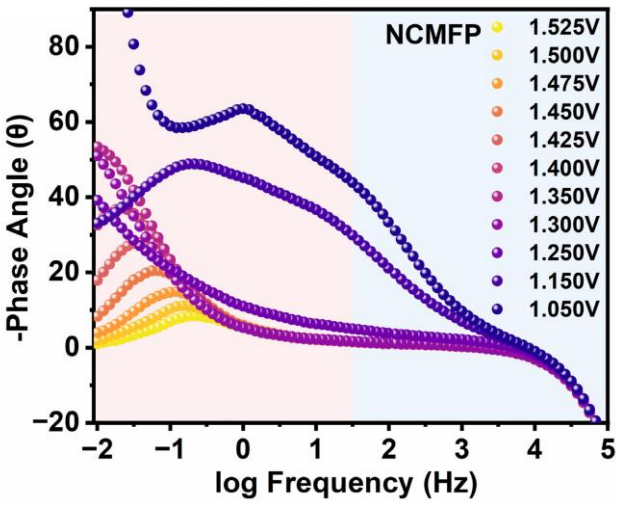


Figure S10. Bode plots at different potentials in alkaline saline electrolyte.

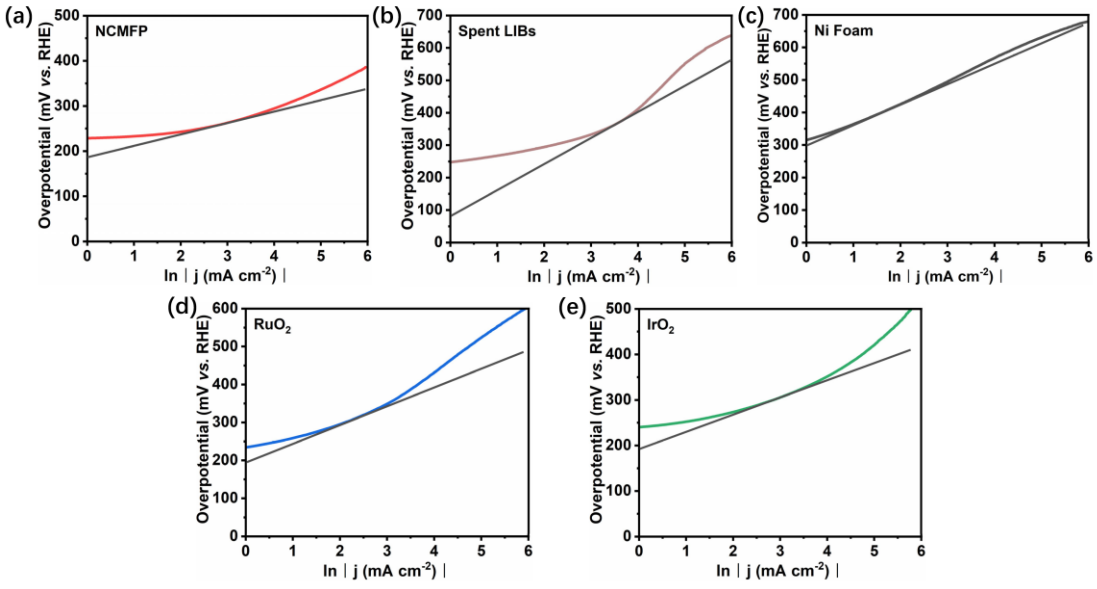


Figure S11. Tafel plots of (a) NCMFP, (b) Spent LIBs, (c) Ni Foam, (d) RuO_2 and (e) IrO_2.

Table S3: Comparison of overpotential values required at different current density between the NCMFP catalyst and other recently reported transition-metal-based OER electrocatalysts.

No.	Catalyst	Electrolyte	j (mA cm^{-2})	η (mV)	Reference
1	**NCMFP**	**1 M KOH+Seawater**	**10 50 100 150 200**	**245 290 310 335 350**	**This Work**
2	NiFe-CuCo LDH	1 M KOH+Seawater	100	318	*Proceedings of the National Academy of Sciences 119.18 (2022): e2202382119*
3	Fe-Ni$(OH)_2$/Ni_3S_2	1 M KOH+0.5 M NaCl	10	269	*Nano Research 14 (2021): 1149-1155*
4	NiFe hydroxide/NiS_x-Ni	1 M KOH+0.5 M NaCl	100	330	*Proceedings of the National Academy of Sciences 116.14 (2019): 6624-6629*
5	NiFe LDH	1 M NaOH+Seawater	100	333	*Angewandte Chemie 133.42 (2021): 22922-22926*
6	Cu@Co-CoO/Rh	1 M KOH+0.5 M NaCl	10	260	*Small* 17.50 (2021): 2103826
7	NiCo LDH/NiCoP	1 M KOH+0.5 M NaCl	50	350	*Chemical Engineering Journal* 411 (2021): 128538
8	Ni_3S_2/Co_3S_4	1 M KOH+0.5 M NaCl	100	360	*Applied Catalysis B: Environmental* 291 (2021): 120071
9	V doped CoCr LDH	1 M NaOH+Seawater	10	320	*Chemical Communications* 58.8 (2022): 1104-1107
10	B-Co_2Fe LDH	1 M KOH+0.5 M NaCl	200	350	Nano Energy 2021,83, 105838
11	NiP_x/HA	1 M KOH+0.5 M NaCl	200	392	*Small* 19.11 (2023): 2205689
12	NiCoHPi@Ni_3N/NF	1 M KOH+Seawater	150	370	*ACS Applied Materials & Interfaces* 14.19 (2022): 22061-22070
13	CoFeLDH@Ni_2P/NF	1 M KOH+0.5 M NaCl	150	350	*Journal of Colloid and Interface Science* 659 (2024): 821-832
14	NiO/Ni_3S_2@Ni_5P_4/NF	1 M KOH+Seawater	150	365	*International Journal of Hydrogen Energy* 51 (2024): 1373-1380
15	NiNS/NF	1 M KOH+Seawater	100	404	*Journal of materials chemistry A* 7.14 (2019): 8117-8121

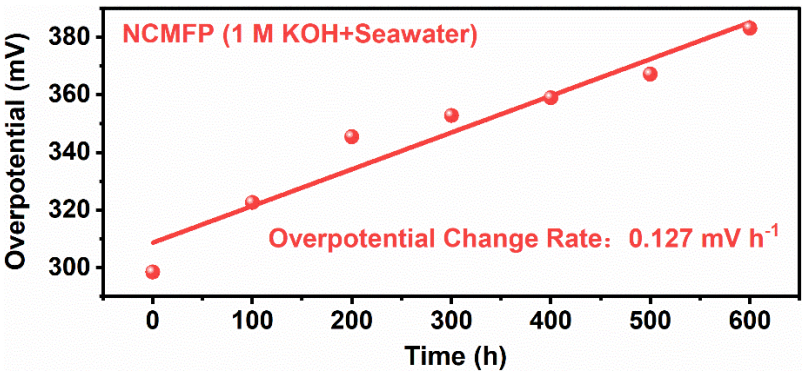


Figure S12. Average overpotential change rate in long-term stability test.

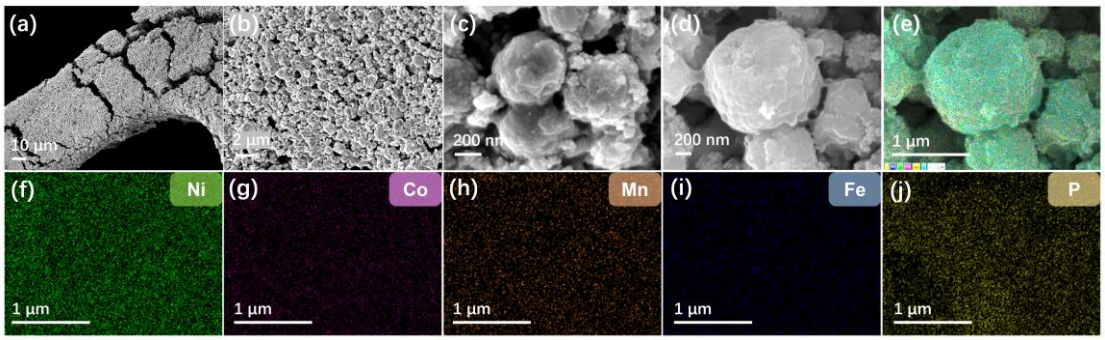


Figure S13. SEM images of NCMFP after long-term stability test, and the corresponding elemental mapping.

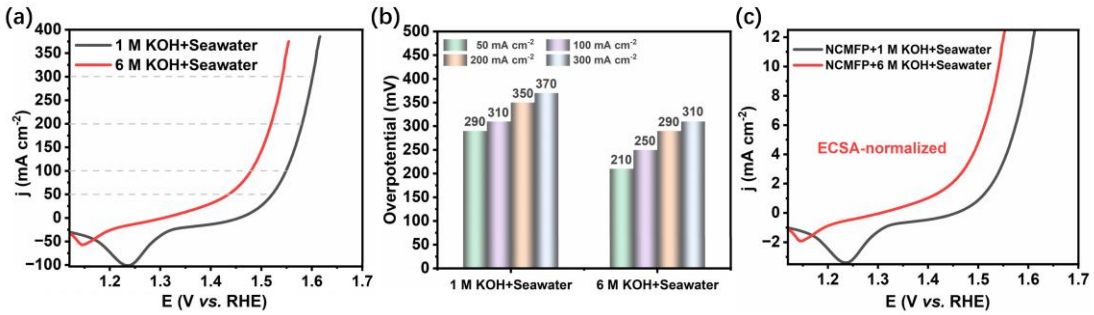


Figure S14. (a) Comparison of OER polarization curves in 1 M KOH + Seawater and 6 M KOH + Seawater electrolytes. (b) Comparisons of the overpotential required at 50 mA cm^{-2}, 100 mA cm^{-2}, 200 mA cm^{-2}, and 300 mA cm^{-2}, respectively. (c) OER polarization curves in 1 M KOH + Seawater and 6 M KOH + Seawater electrolytes through normalizing the electrochemical activity via ECSA.

Table S4: Under the conditions of 6 M KOH + Seawater, the detailed data obtained from the fitted electrochemical impedance spectroscopy (EIS) are as follows:

Element	Rs (Ω)	CPE-T	CPE-P	Rct (Ω)	Wo
NCMFP	0.59465	0.00026156	0.87454	1.965	0.35401
Spent LIBs	0.63265	0.00034921	0.88519	2.265	0.34471
Ni Foam	0.49140	0.04863800	0.64265	12.98	0.52237

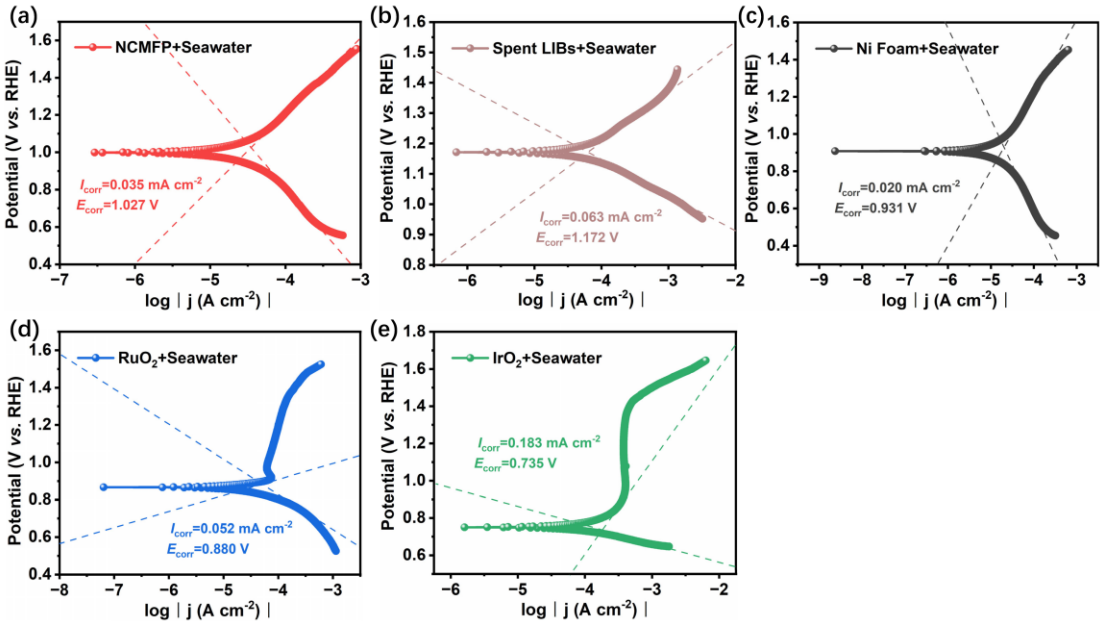


Figure S15. Corrosion polarization curve comparison in real seawater electrolyte.

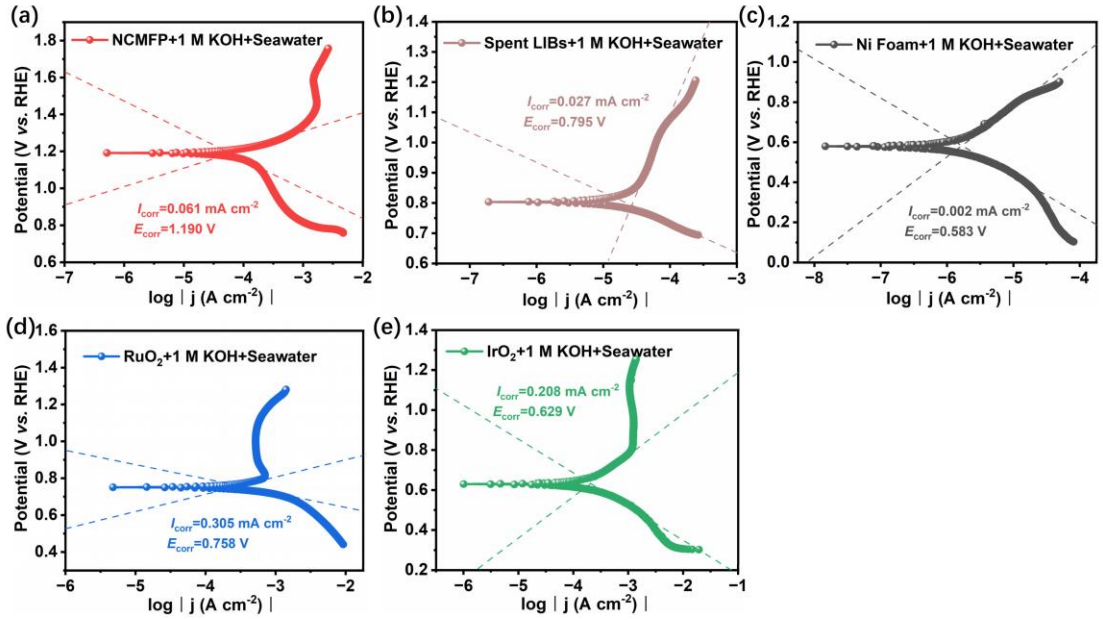
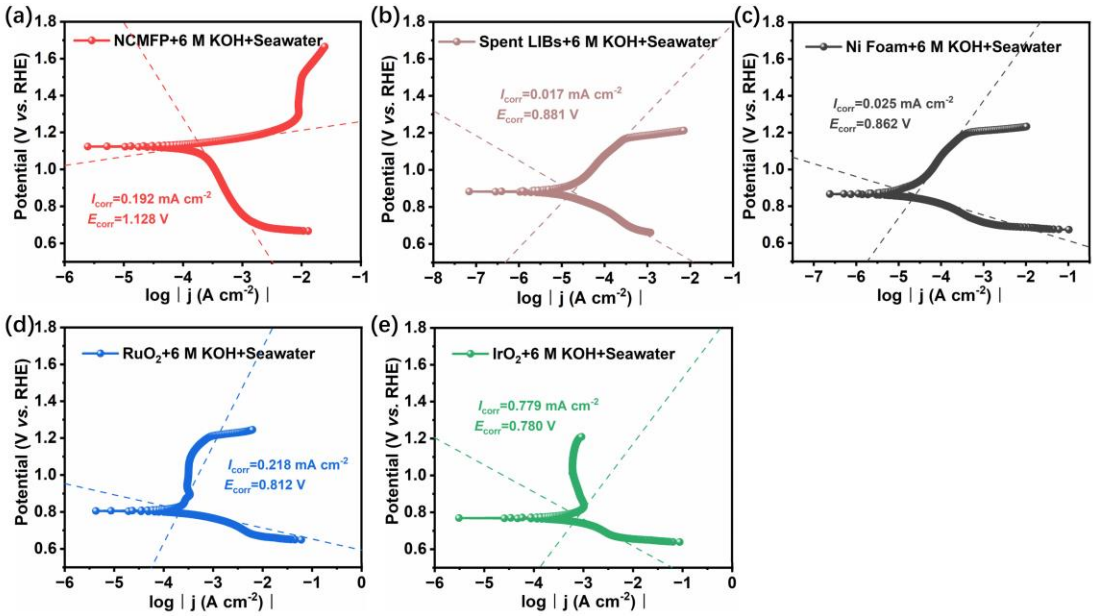


Figure S16. Corrosion polarization curve comparison in 1 M KOH + Seawater electrolyte.



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121 **Figure S17**. Corrosion polarization curve comparison in 6 M KOH + Seawater electrolyte.

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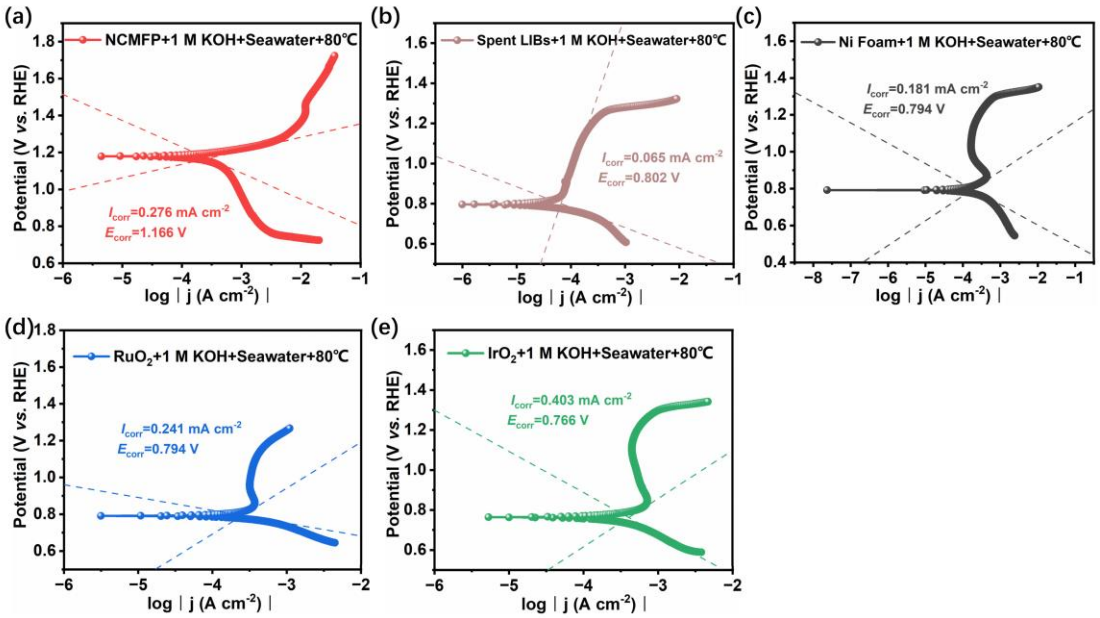

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124 **Figure S18**. Corrosion polarization curve comparison in 6 M KOH + seawater + 80°C

125 electrolyte.

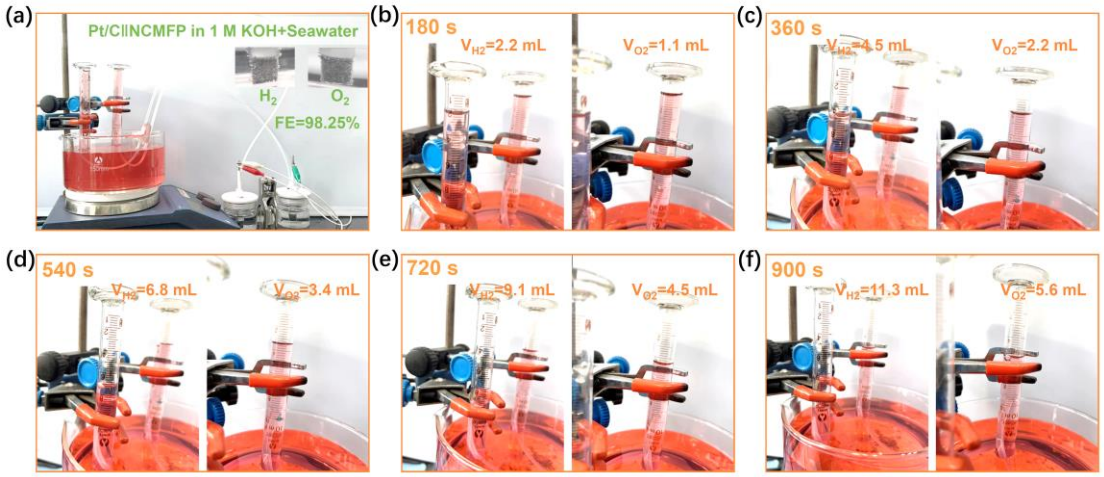

Figure S19. (a) Magnified photo of the electrolyzer, inset: magnified photo of the electrodes during electrolysis, drainage device for collecting the produced hydrogen and oxygen. (b-f) Generators for producing hydrogen and oxygen.

Table S5: Cost Required for Synthesizing One Gram of Final Product:

Ref.	Drug List	Chemical Function	Market Unit Price of the Drug	Unit Price of the Drug(RMB/ml or RMB/g)	Drug Usage Amount (Solid)	Drug Usage Amount (Liquid)	Cost Required for Synthesizing One Gram of Final Product
1	HNO_3 - Nitric Acid	Cleaning	0.42 RMB/ml	0.42		50	39.0
	Li2CO3 - Lithium Carbonate	Adjusting the ratio of Li to TM (Transition Metal)	3.60 RMB/g	3.60	5		
	DI- Deionized Water	Cleaning	DI Water	0.00		——	
2	NMP- N-Methyl-2-pyrrolidone	Used as a solvent, helping to separate the cathode powder (containing degraded NCM, PVDF, and conductive impurities) from the aluminum foil in cathode sheets.	0.52 RMB/ml	0.52		50	94.5
	DI Water- Deionized Water	Used for washing the separated cathode powder to remove residual NMP and other impurities.	DI Water	0.00		——	
	EG- Ethylene Glycol	Used as a dispersion medium for dispersing degraded NCM material and lithium hydroxide (LiOH).	0.5699 RMB/ml	0.57		70	
	TBT- TitaniumIV Butoxide	Used as an additive to improve the performance of NCM material, with addition amounts of 3wt%, 5wt%, and 7wt% of the weight of the NCM material.	0.27 RMB/mL	0.27		0.262	
	Ethanol	Used to dilute deionized water and mix with TBT in a ratio of 1:3.	0.15 RMB/mL	0.15		150	
	LiOH- Lithium Hydroxide	Mixed with degraded NCM material to adjust the lithium content, ensuring the stoichiometric ratio of the regenerated material.	25.18 RMB/g	25.18	0.2388		
3	DMC- Dimethyl Carbonate	Used for cleaning the positive and negative electrodes to remove residual electrolyte.	2.20 RMB/ml	2.20		10	66.0
	NMP- N-Methyl-2-pyrrolidone	Used as a solvent to help dissolve polyvinylidene fluoride (PVDF) binder and separate the cathode active material.	0.52 RMB/ml	0.52		50	
	- Water	Reacts with residual lithium in waste graphite to extract lithium ions.	DI Water	0.00		——	
	Li_2CO_3- Lithium Carbonate	Used in the regeneration process, mixed with lithiated NCM powder to adjust the molar ratio of lithium to transition metal	3.59 RMB/g	3.59	5		
4	DMC- Dimethyl Carbonate	Used for cleaning electrodes to remove residual electrolyte.	2.20 RMB/ml	2.20		30	98.2
	NMP- N-Methyl-2-pyrrolidone	Used to dissolve the cathode binder and separate the active material.	0.52 RMB/ml	0.52		50	
	LiOH- Lithium Hydroxide	Used in the hydrothermal lithiation process.	25.18 RMB/g	25.18	0.2388		
	KOH- Potassium Hydroxide	Used in conjunction with LiOH for the hydrothermal lithiation process.	0.95 RMB/ml	0.95	0.2388		
	Deionized Water	Used for cleaning the processed NCM523 powder.	DI Water	0.00		——	
5	LiOH·H2O - Lithium Hydroxide Monohydrate	Used as a lithium source in the regeneration process of the cathode material, helping to restore the lithium content in the material.	25.18 RMB/g	25.18	0.84		134.3
	NaCl - Sodium Chloride	Used as an auxiliary agent, potentially playing a role in the sintering process, such as promoting interactions between particles or improving the conductivity of the material.	0.25 RMB/g	0.25	0.56		
	. DMC - Dimethyl Carbonate	Used for cleaning the cathode material to remove residual electrolyte.	2.20 RMB/ml	2.20		50	
	. Li2CO3 - Lithium Carbonate	Used under certain conditions as a substitute for LiOH, serving as a lithium source in the regeneration process.	3.60 RMB/g	3.60	0.84		
6	Oxalic Acid Solution 0.6 M	Used to react with S-NCM powder for selective leaching or dissolution.	0.46 RMB/g	0.46	13.51		14.8
	CoC_2O_4 - CobaltII Oxalate	Added to the precursor to adjust the composition of the final material.	2.076 RMB/g	2.08	0.315		
	MnC_2O_4 - ManganeseII Oxalate	Same as above, used to adjust the composition.	0.52 RMB/g	0.52	0.315		
	$Li_2C_2O_4$ - Lithium Oxalate	Same as above, used to provide a lithium source.	6.60 RMB/g	6.60	0.525		
	Sb_2O_5 - Antimony Pentoxide	Used for doping the regenerated NCM material to introduce antimony.	12.18 RMB/g	12.18	0.105		
	Li_2CO_3 - Lithium Carbonate	Added to compensate for potential lithium loss during the regeneration process.	3.60 RMB/g	3.60	0.84		
7	LiOH·H_2 O - Lithium Hydroxide Monohydrate	Mixed with degraded NCA cathode material to provide a lithium source and compensate for lithium loss.	25.18 RMB/g	25.18	0.84		24.7
	$Na2SO_4$ - Sodium Sulfate	Used as a eutectic salt to help achieve uniform mixing and sintering.	0.98 RMB/g	0.98	0.56		
	Deionized Water	Used to rinse the regenerated material to remove residual salts.	DI Water	0.00		——	
	Li_2CO_3 - Lithium Carbonate	Used as a substitute for LiOH to provide a lithium source during the processing of NCM523.	3.60 RMB/g	3.60	0.84		
This Work	NMP- N-Methyl-2-pyrrolidone		0.52 RMB/ml	0.52		15	18.2
	Oxalic Acid		0.46 RMB/g	0.46	13.51		
	Sodium Hypophosphite Monohydrate		0.21 RMB/g	0.21	20		

References

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