Supporting information

High Entropy Layered Hydroxide for Efficient and Sustainable Seawater Oxidation

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Characterization

Powder XRD pattern of all samples were collected by using Rigaku Miniflex 600 XRD diffractometer (40 kV, 15 mA) with Cu kα radiation of wavelength 1.54 Å. The morphology of the as prepared sampled was characterized by SEM images which were collected from field emission scanning electron microscopy (FE-SEM, Carl Zeiss, Germany) operating at 5 kV. The elemental composition with atomic% of the materials were collected using an energy-dispersive X-ray spectrometer (EDS) associated with FE-SEM apparatus. In depth microstructural property of the samples were obtained by using High resolution transmission electron microscopy (FEI TECNAI 20 G2, Netherlands, 200 kV) characterisation technique. The TEM specimen was prepared by dispersing a little amount of powder sample (a few mg) into pure ethanol and a drop of homogeneous solution was deposited on carbon coated Cu grid. The surface composition and valance states of the samples were determined by using XPS technique recorded on SCIENTA R-3000 analyser with a monochromatic Al Ka source. A 2×10^{-10} torr vacuum ambit chamber was maintained during XPS analysis. The instrument was calibrated before use with Au and Ag foils. Charge neutralization was used for all measurements using a combination of low-energy Ar^+ ions and electrons, and also the charging effects were compensated by shifting binding energies based on the adventitious C 1s peak (284.8 eV). Raman spectra of the prepared samples was acquired using alpha300 RAS (WITec) Raman spectrometer. Infrared spectra of the samples were recorded using a Fourier transform

infrared (FTIR) spectrophotometer (SHIMADZU, IRPrestige-21, scan range: 400–4000 nm). The inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis was carried out with the help of Thermofisher, iCAP RQ Spectrometer taking 5 mL of solution and digested with aqua regia.

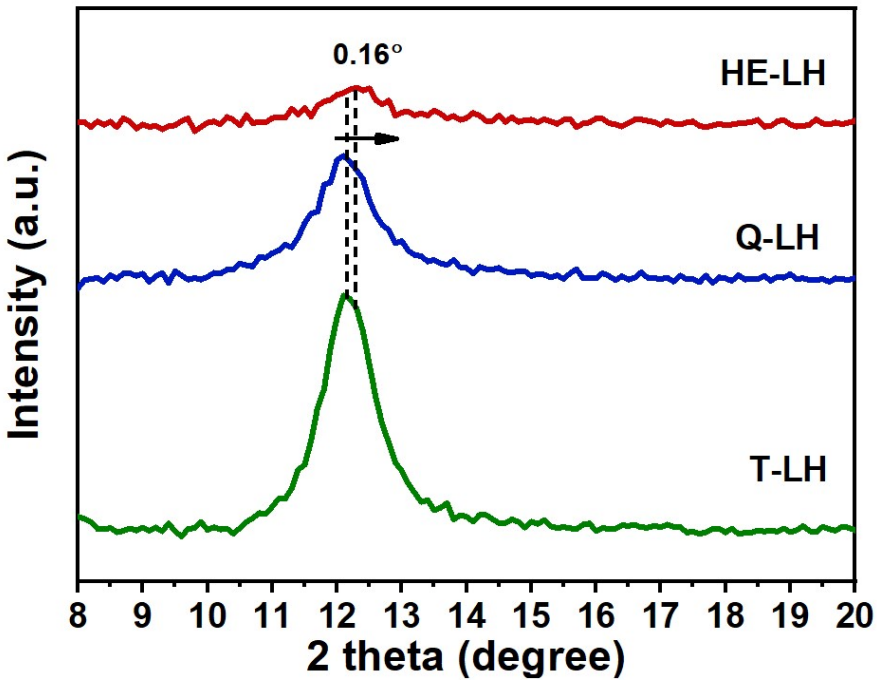

Fig. S1 Magnified view of XRD pattern of developed layered hydroxides corresponding to (003) plane.

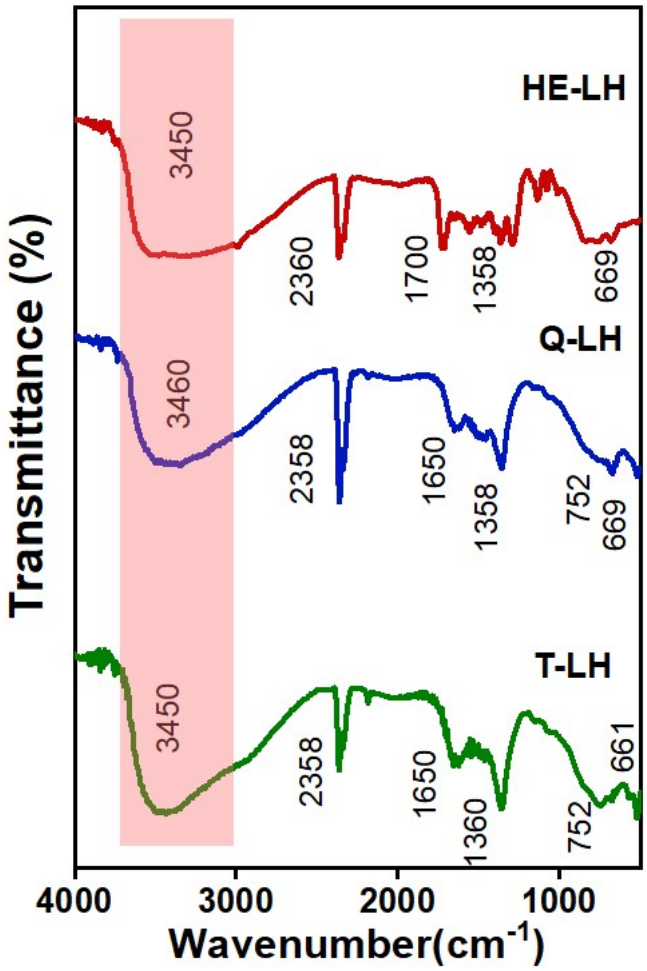

Fig. S2 FTIR spectrum of HE-LH, Q-LH and T-LH.

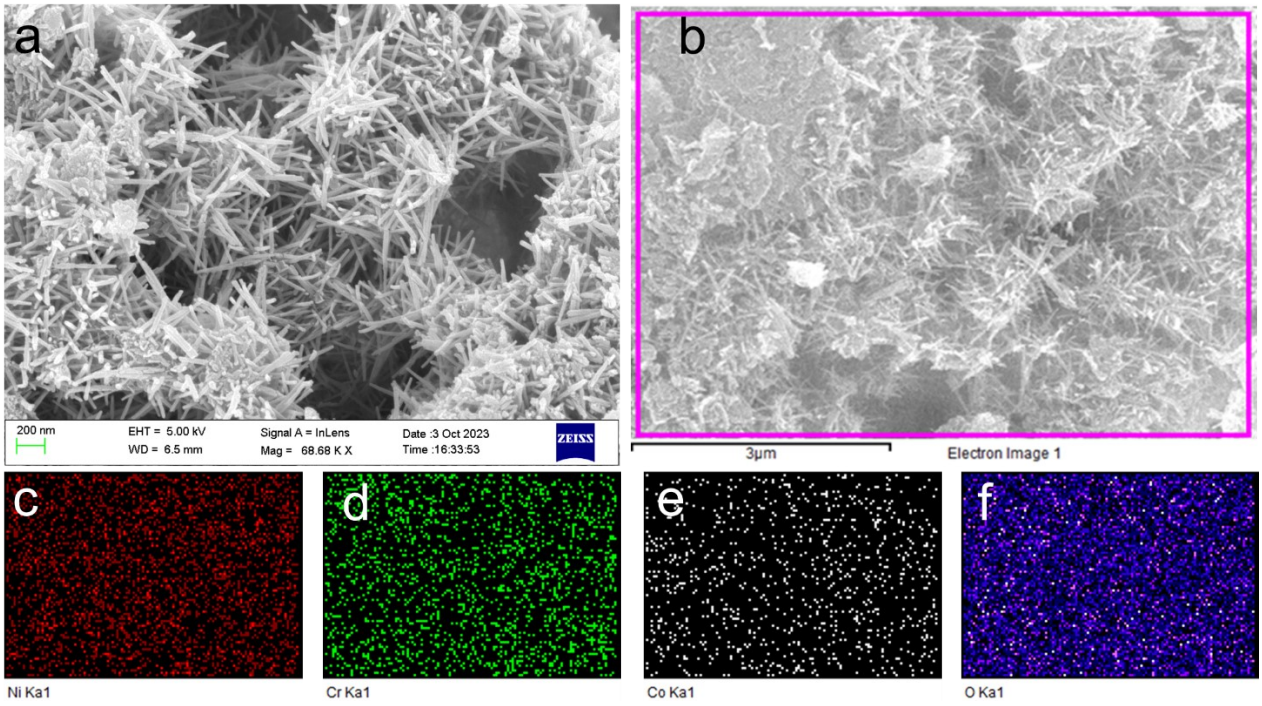

Fig. S3 SEM and EDX mapping of T-LH sample.

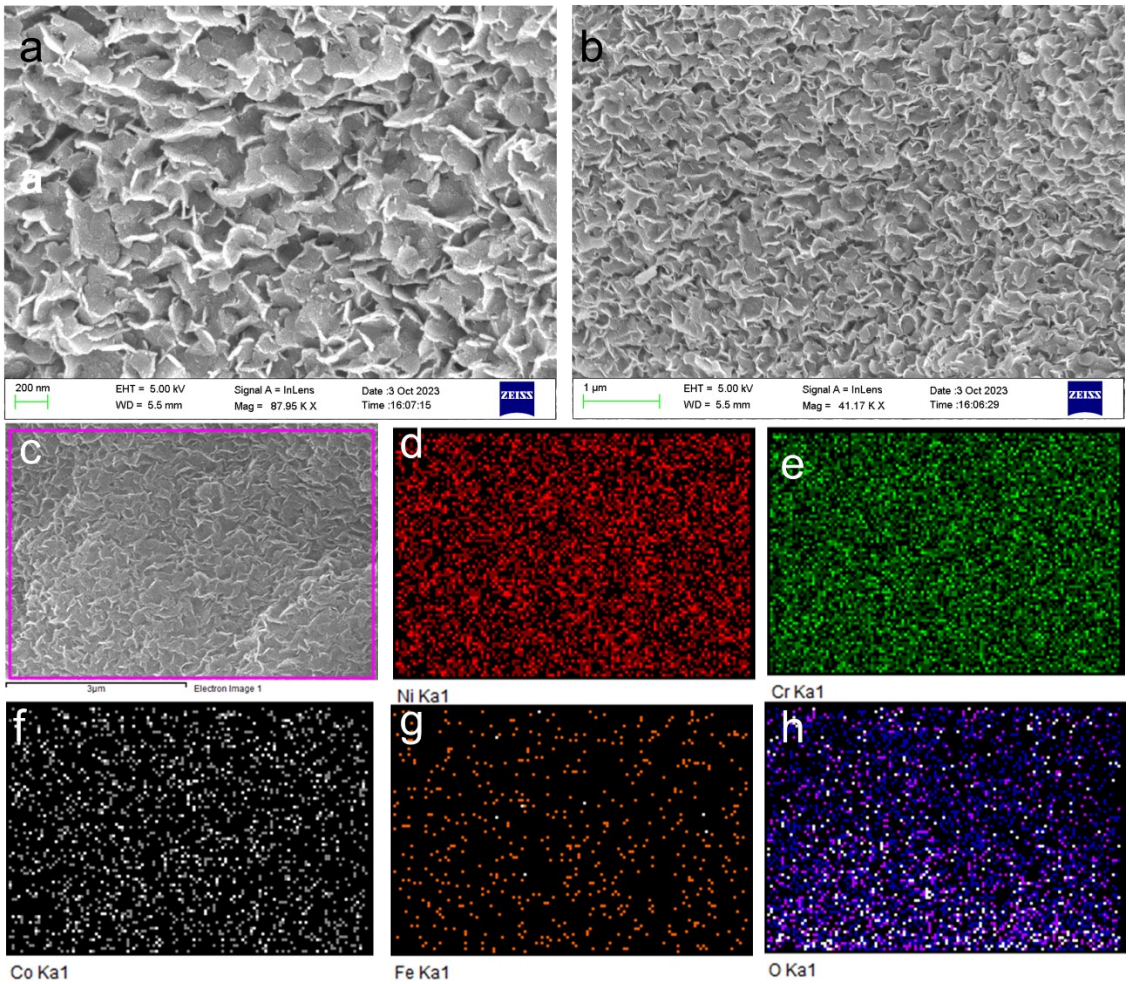

Fig. S4 SEM and EDX elemental mapping of Q-LH sample.

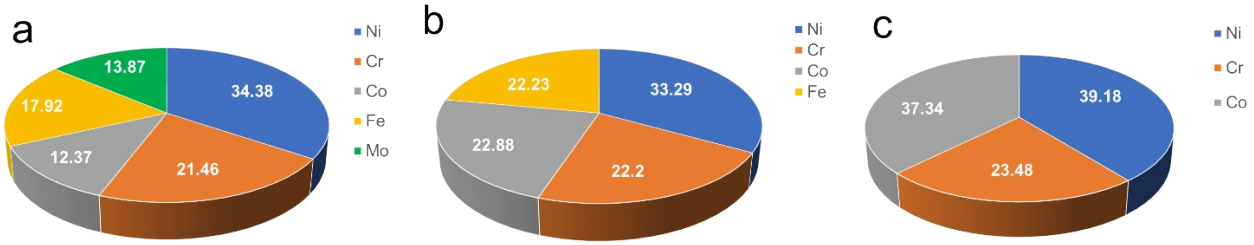

Fig. S5 Atomic percentage of various metals present in (a) HE-LH, (b) Q-LH and (c) T-LH obtained from EDX analysis.

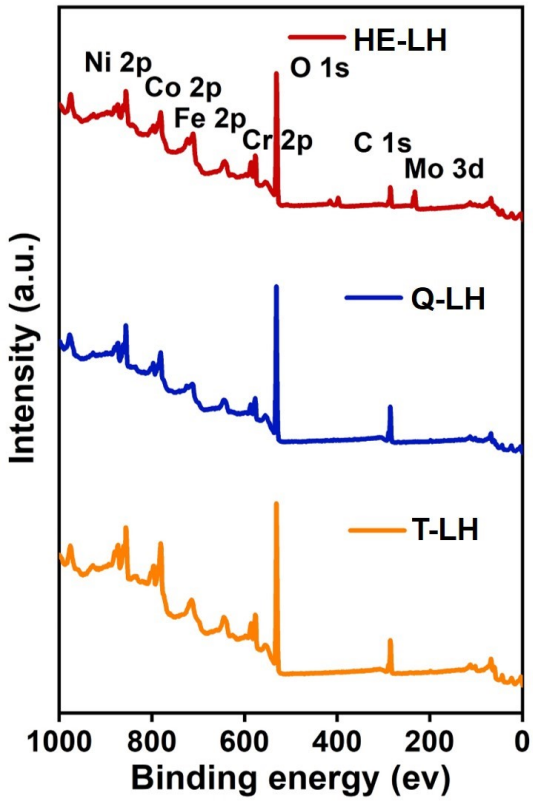

Fig. S6 XPS survey of HE-LH, Q-LH and T-LH.

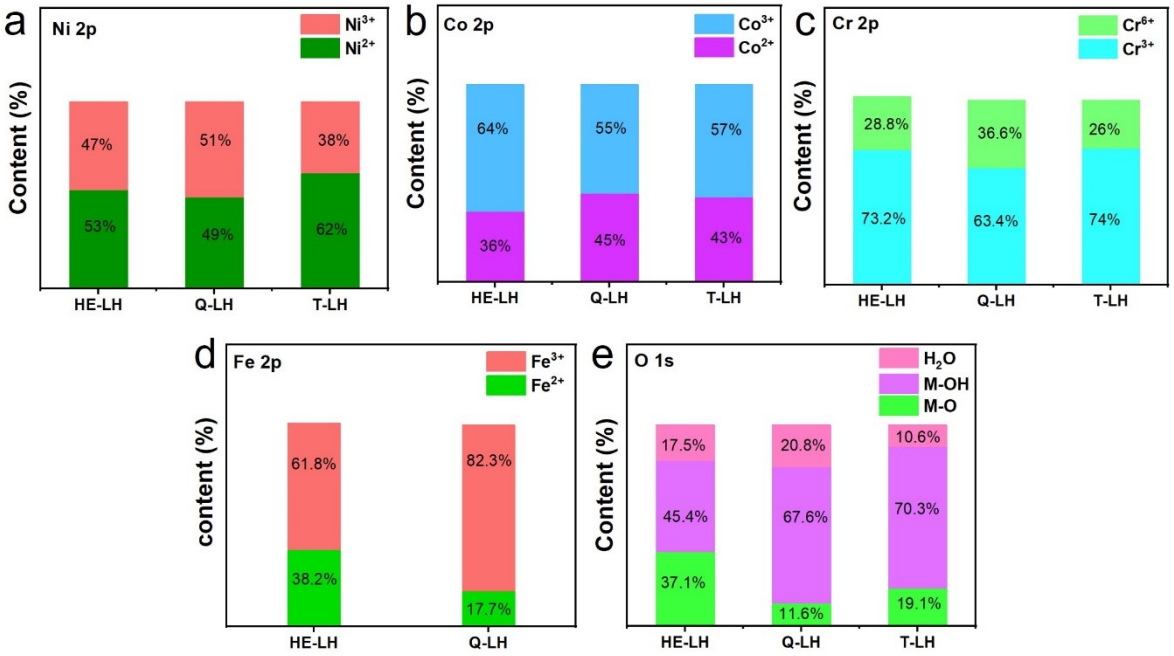

Fig. S7 Percentage content of different states of elemental species for HE-LH, Q-LH and T-LH obtained from XPS peak areas.

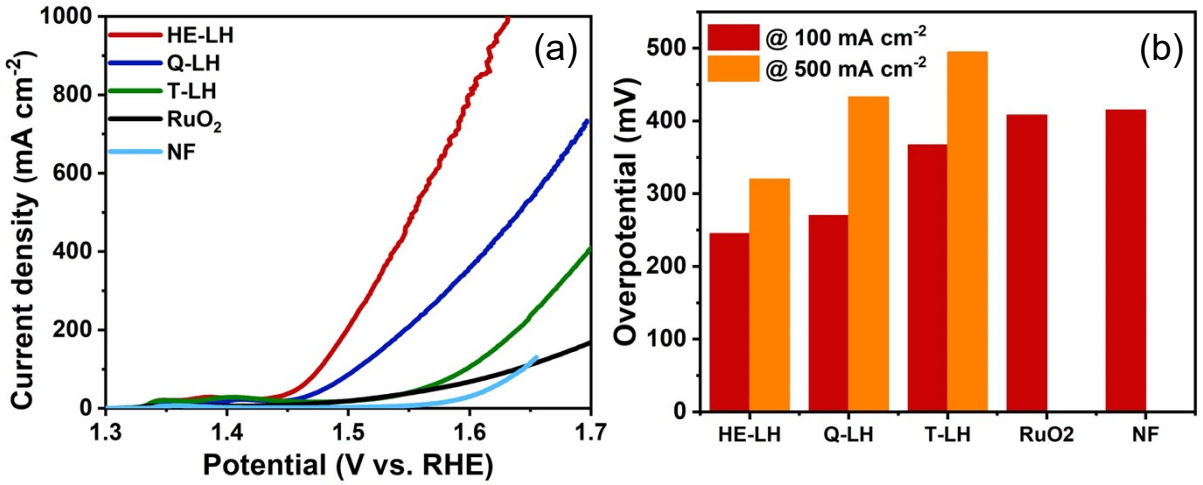

Fig. S8 Comparative LSV curves for developed electrocatalysts, conventional RuO_2 and bare Ni foam taken at 5 mV s^{-1} scan rate and (b) corresponding overpotential comparison at different current densities.

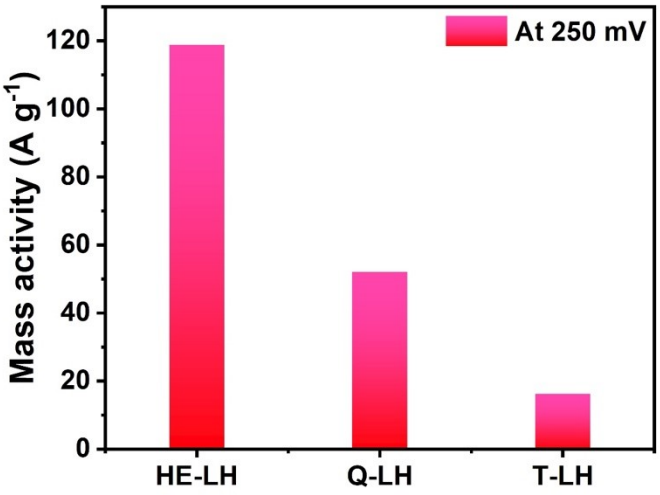

Fig. S9 Mass activity of different electrocatalysts in 1 M KOH electrolyte.

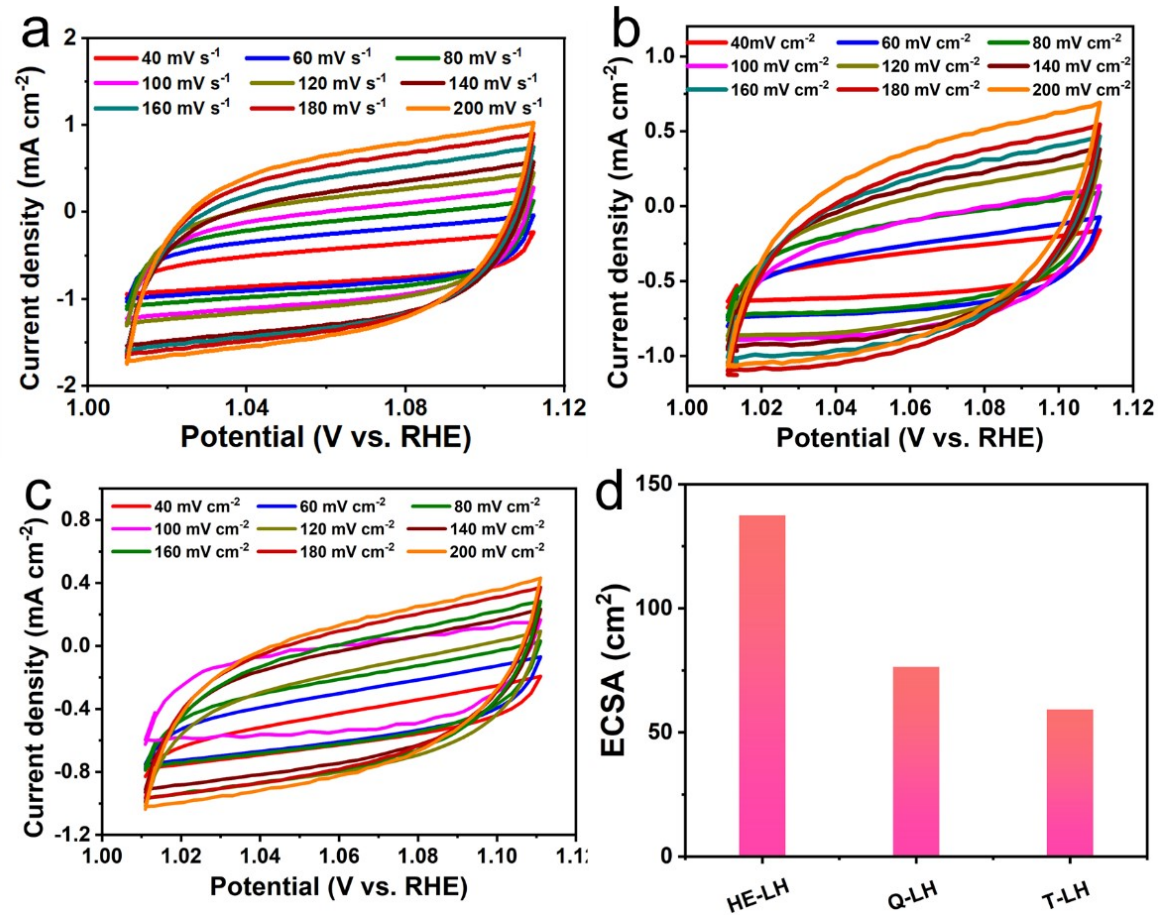

Fig. S10 CV curves recorded at different scan rates in non-Faradaic region for (a) HE-LH, (b) Q-LH and (c) T-LH in 1 M KOH electrolyte.

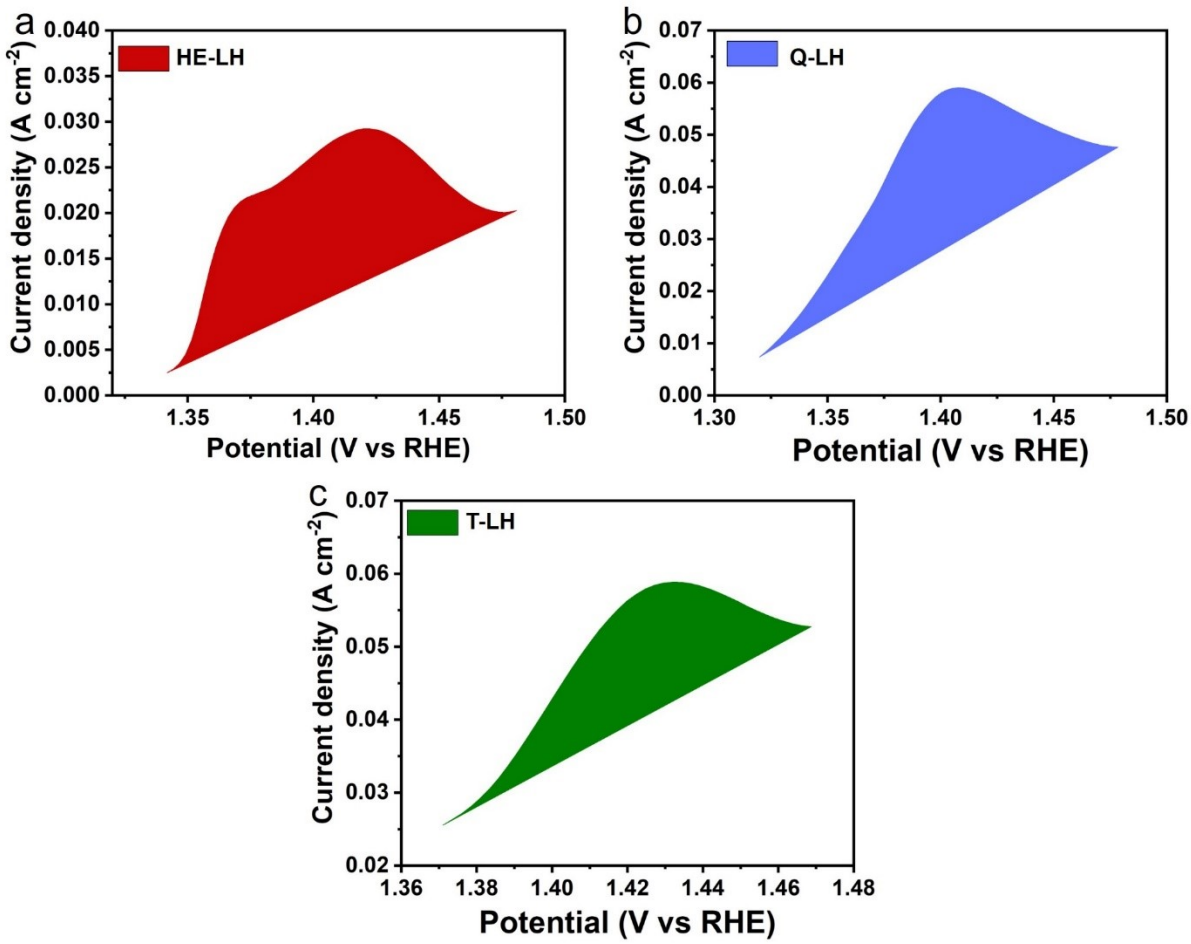

Fig. S11 Oxidation peak area of the CV curves taken at 20 mV s^{-1} scan rates for (a) HE-LH, (b) Q-LH and (c) T-LH electrocatalysts in 1 M KOH electrolyte medium.

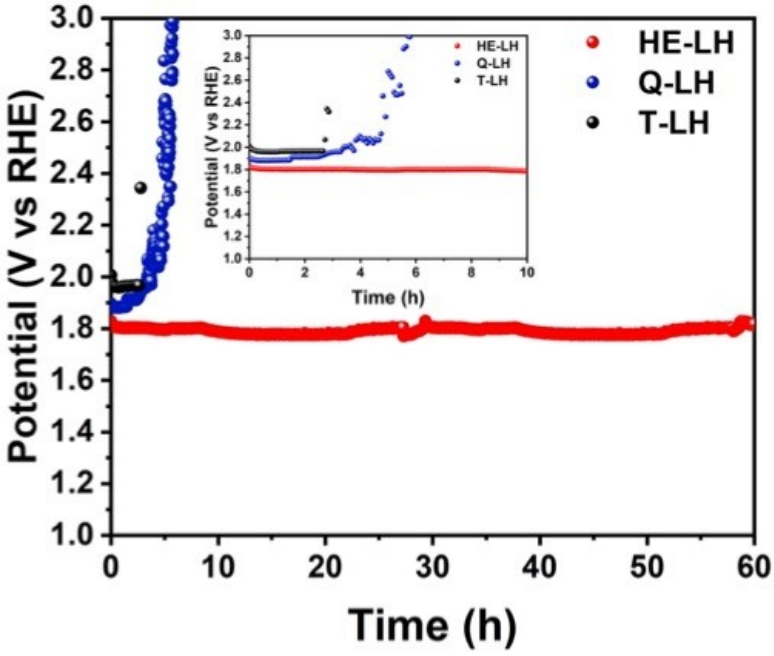

Fig. S12 CP stability tests of electrocatalysts at a fixed current density of 500 mA cm^{-2}.

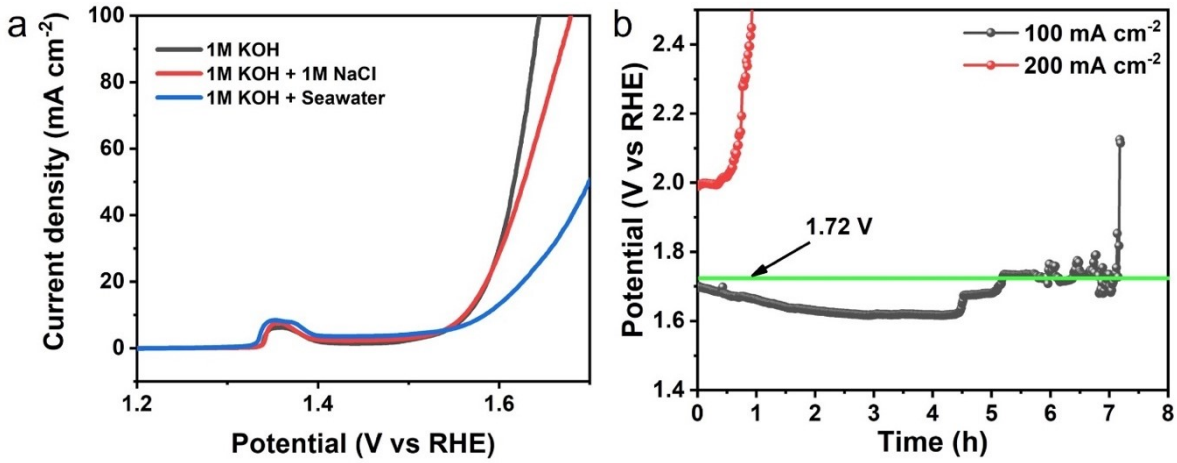

Fig. S13 (a) LSV curve of bare Ni foam in 1M KOH, 1M KOH + 1M NaCl and 1M KOH + seawater electrolyte medium. (b) CP study at different current densities in 1M KOH + 1M NaCl electrolyte.

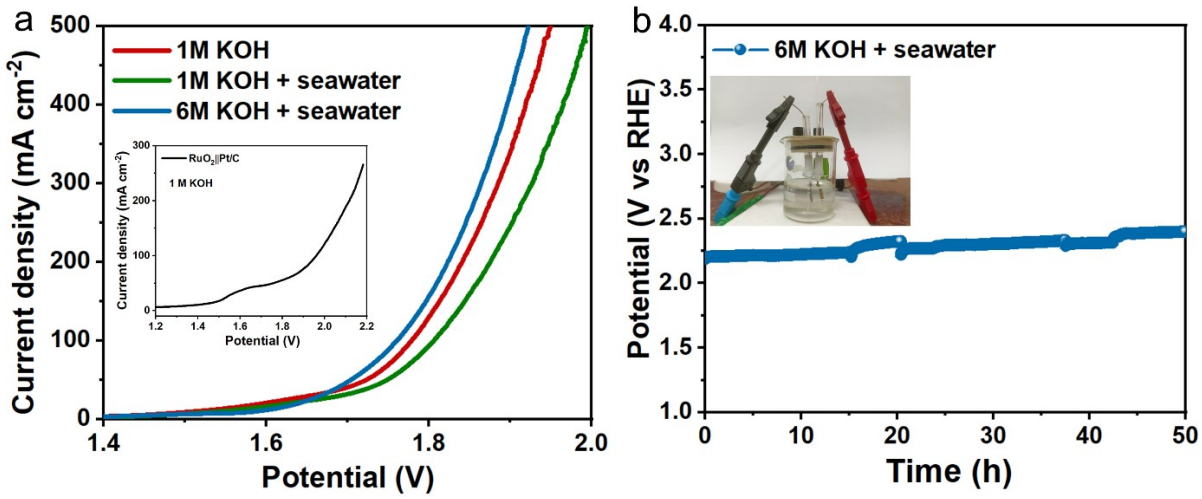

Fig. S14 Overall water splitting using HE-LH || Pt/C two-electrode setup. (a) LSV polarization curve for overall water/seawater electrolysis in 1 M KOH, 1 M KOH + seawater and 6 M KOH + seawater electrolyte (Inset: LSV polarization curve for RuO_2 || Pt/C system in 1 M KOH electrolyte). (b) Long term stability test at high current density of 500 mA cm^{-2} current density in 6 M KOH + seawater electrolyte**.**

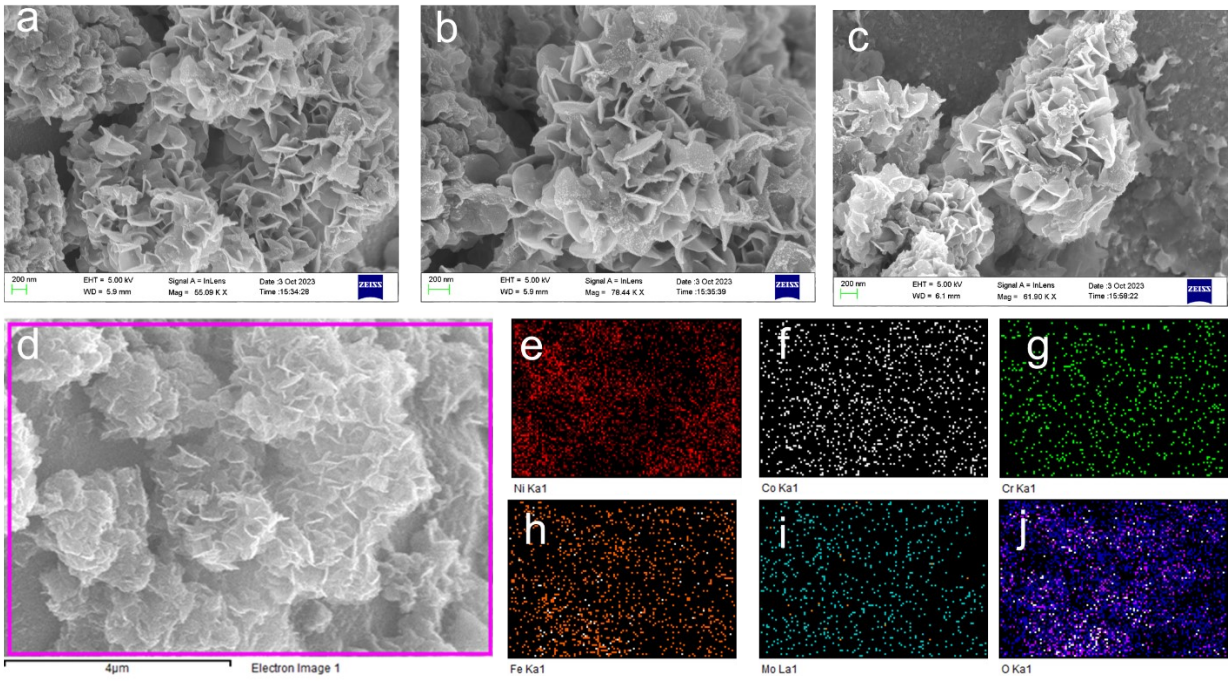

Fig. S15 SEM (a-c) and EDX elemental mapping (e-j) of HE-LH after long term stability test for OER in 1 M KOH + seawater electrolyte.

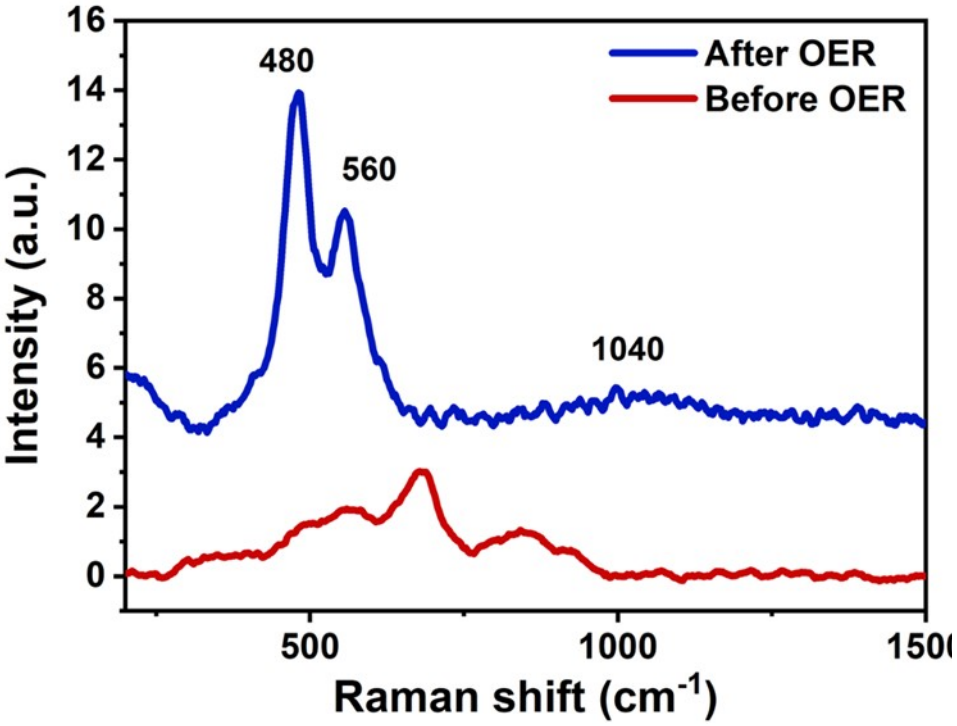

Fig. S16 Raman spectra of HE-LH before and after long term stability in real alkaline seawater.

Table S1. Reaction parameters and precursor concentrations used for developing LHs and LTH.

Electrocatalysts	Reaction Temp/Time	Ni (mM)	Cr (mM)	Co (mM)	Fe (mM)	Mo (mM)	Total Precursor Conc. (mM)
HE-LH	120 °C/12h	5	5	3	5	7	25
Q-LH		5	5	5	5	0	20
T-LH		5	5	5	0	0	15

Table S2. Calculated microstructural parameters from XRD analyses for different electrocatalysts.

Electrocatalysts	Microstrain (ε) × 10^3	Dislocation density (ρ in nm^{-2})
HE-LH	0.63	0.0284
Q-LH	0.60	0.0265
T-LH	0.49	0.0181

Table S3. Fitted data of EIS spectroscopy of various electrocatalysts taken at overpotential of 250 mV for OER in 1M KOH electrolyte solution.

Electrocatalyst	R_s (ohm)	R_{ct} (ohm)
HE-LH	0.96	0.58
Q-LH	0.92	2.61
T-LH	1.01	4.02
RuO_2	1.02	16.03

Table S4. Potentiodynamic polarization (PD) parameters of HE LH, Q-LH and T-LH in 1 M KOH + 1 M NaCl electrolyte.

Electro catalysts	**E_{corr} (V)**	**I_{corr} (A cm^{-2})**	**β_a (V/dec)**	**β_c (V/dec)**	**R_p ($\Omega.cm^2$)**	**Corrosion rate (mm/year)**
HE-LH	0.89	2.7×10-8	1.78	0.21	14088	0.135
Q-LH	0.873	6.3×10-8	0.85	0.40	7996	0.647
T-LH	0.862	7.39×10-8	0.44	0.28	5440	1.36

Table S5 Fitted simulation EIS result with R_s, R_c, R_{ct}, Y and n parameters of different electrocatalysts in 1 M KOH + 1 M NaCl electrolyte.

Catalysts	**R_s (Ω cm^2)**	**R_c (Ω cm^2)**	**Y_1 (Ω^{-1} cm^{-2})**	**n_1**	**R_{ct} (Ω cm^2)**	**Y_2 (Ω^{-1} cm^{-2})**	**n_2**
HE-LH	1.19	5.701	0.502×10^{-3}	0.765	18817	0.29×10^{-3}	0.942
Q-LH	1.34	1.9	0.707×10^{-3}	0.89	18407	1.5×10^{-3}	0.91
T-LH	1.30	1.2	3.19×10^{-3}	0.72	11547	3.016×10^{-3}	0.8

Table S6. XPS peak intensity ratios of HE LH before and after prolonged stability test in 1 M KOH + seawater electrolyte.

Electrocatalysts	**Ni^{3+}/Ni^{2+}**	**Cr^{6+}/Cr^{6+}**	**Co^{3+}/Co^{2+}**	**Fe^{3+}/Fe^{2+}**	**M-OH/M-O**
Before	0.79	0.35	1.68	0.72	1.13
After	1.41	1.04	1.05	1.55	3.54

Table S7. ICP-AES analysis of electrolytes before and after long term stability of HE-LH at 500 mA cm^{-2} in 1 M KOH + seawater electrolyte.

Metals	**Concentrations (ppm)**	
	Before	**After**
Cr	0	0.06
Fe	0	0
Co	0	0
Ni	0	0
Mo	0	0.03

Table S8. Comparison of OER performance between HE-LH and recently reported OER electrocatalysts in alkaline freshwater and seawater electrolyte.

Electrocatalysts	**Electrolyte**	**Current density (mA cm^{-2})**	**Overpotential (mV)**	**Tafel slope (mV dec^{-1})**	**Durability**	**Ref.**
HE-LH	1 M KOH	100	242	36.9	120	This work
		500	320			
	1 M KOH + seawater	100	258			
		500	417		180	
	6 M KOH + seawater	100	281			
		500	290		140	
NiFe-CuCo LDH	1 M KOH	100	262	48.3	100	S1
		500	300			
	1 M KOH + seawater	100	315		100	

	6 M KOH + seawater	500 100 500	355 281 290		100 100 500	
S-(NiFe)OOH	1 M KOH 1 M KOH + seawater	100 100 500	281 300 398	48.9	100 100 100	S2
CoFeNiCrV LDH	1 M KOH	10	232	38.6	20	S3
CoCrV LTH	1 M KOH 1 M KOH + seawater	100 100	320 395	39	110 24	S4
NiFe LDH@NF	1 M KOH	10 100	184 256	56.68	84	S5
Ce@NiCo LDH	1 M KOH	50	250	98	24	S6
NiFe oxyhydroxide	1 M KOH + 0.5 M NaCl	100	280	51.5	100	S7
Ni_2P/Fe_2P	1 M KOH 1 M KOH + seawater	100 100	261 305	58	48 36	S8
CoCrFeNiMo HEA	1 M KOH	10	220	59	24	S9
FeCoNiMnMo HEA	1 M KOH + 0.6 M NaCl	10	237	51.2	200	S10
B-Co_2Fe LDH	1 M KOH 1 M KOH + seawater	100 100 500	246 310 376	39.2	100 100 100	S11
NiMoN/NiFeN	1 M KOH	100 500	277 337	58.6	48	S12
NiMoN/NiFeN	1 M KOH + seawater	100 500	307 369		---	S12
NiFeCrMnCoOOH	1 M KOH 1 M KOH + 0.5 M NaCl	10 10	201 223	31 42	25 25	S13
RuO_2/NiFeOOH	1 M KOH 1 M KOH + seawater	10 100	187.6 273.5	31.9 -----	100 100	S14
c-NF//a-NF-LDH	1 M KOH + 0.5 M NaCl	100	300	65	100	S15
NiFe-LDH@ $FeNi_2S_4$	1 M KOH 1 M KOH + 0.5 M NaCl	100 100	240 261	29.4 56.3	12 20	S16

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