Electrochemically Enhanced Oxygen Evolution and Urea Oxidation Reactions with Advanced High-Entropy LDH Nanoneedles

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Experimental Section

Material synthesis

A high-entropy layered double hydroxide (LDH) sample was synthesized using a one-step hydrothermal method. To summarize, equimolar amounts (0.45 mmol each) of Fe $(NO_3)_3.9H_2O$, Zn $(NO_3)_2$. $6H_2O$, Co $(NO_3)_2$. $6H_2O$, Mn $(NO_3)_2\cdot 6H_2O$, and Cr $(NO_3)_3\cdot 9H_2O$ were dissolved in 40 mL of DI water along with 10 mmol of urea under continuous stirring for 1 hour, the pH adjusted to 10 by the addition of 1 M NaOH and 1 M Na_2CO_3. The resulting solution was then transferred into a 100 mL Teflon-lined stainless-steel autoclave and heated at 180 °C in an oven for 12 hours. After allowing the autoclave to naturally cool down, the sample was washed repeatedly using DI water and ethanol, followed by drying in a vacuum oven at 60 °C for 12 hours. This resulting sample was labeled as HE-FCCMZ LDH. For comparison, ternary (CoCrMn), and quaternary (FeCoCrMn) metal LDHs were also synthesized using the same method, with relevant metal precursors, and urea.

Characterization of HE-FCCMZ LDH

The dimensions and arrangement of the synthesized HE-FCCMZ LDH were evaluated using high-resolution transmission electron microscopy (HR-TEM) and scanning electron microscopy (SEM) images, along with energy-dispersive X-ray spectroscopy (EDX) obtained from JEOL JEM-2010 (operating at 200 kV) and ZEISS ULTRA PLUS, respectively. The crystalline nature of the prepared electrocatalyst was determined utilizing a X-ray diffractometer (HR-XRD, D8 SSS, Bruker, Germany) with Cu Kα radiation ($\lambda = 1.54$ Å). The confirmation of functional groups in the synthesized CoFe-LDH/MoS_2@NDCDs was carried out using JASCO FT-IR 460 Plus, covering a wavenumber range of 400–4000 cm−1. Electronic states of the prepared electrocatalyst were investigated using an XPS analyzer, specifically the ULVAC-PHI, PHI 5000 VersaProbe. The Brunauer-Emmett-Teller (BET) surface area of the HE-FCCMZ LDH was determined through nitrogen gas adsorption–desorption measurements conducted with ASAP 2020 equipment from Micromeritics, Norcross, GA, at the boiling point of liquid nitrogen (77.4 K).

Electrochemical studies

Electrochemical assessments, encompassing linear sweep voltammetry (LSV), Tafel analysis, chronopotentiometry, electrochemical impedance spectroscopy (EIS), and electrochemical active surface area (ECSA) evaluations, were carried out using a CHI6279E electrochemical workstation for each of the three reactions individually. These experiments employed standard three-electrode setup for the oxygen evolution reaction (OER). The HE-FCCMZ LDH, in their prepared state, were coated onto a nickel foam (NF) and utilized as the working electrode. The reference electrode employed was Hg/HgO, and the counter electrode was Pt wire. The coating procedure involved cutting a 1x1 cm^2 piece of nickel foam, subjecting it to sonication in acetone and then in 3 M HCl acid for approximately 20 minutes each. Following sonication, the nickel foam was thoroughly rinsed with deionized water and ethanol and dried completely. Subsequently, 10 mg of the synthesized HE-FCCMZ LDH and 20 µL of a 5% Nafion solution were mixed with an ethanol/water solution and evenly dropcasted onto the surface of the nickel foam, after which it was allowed to dry. A 1 M KOH solution served as the electrolyte for all the electrochemical reactions.

Linear sweep voltammetry and Tafel slope measurements

The linear sweep voltammetry (LSV) measurement for OER was conducted within specific potential ranges of 0 V to 1 V with scan rate of 10 mV/s. In accordance with equation S1, all potentials were converted to the reversible hydrogen electrode (RHE) scale without compensation for iR drop for both HER and OER.

$E\ (\text{vs.RHE}) = E\ (\text{vs. Hg/HgO}) + E_{Hg/HgO}(\text{ref}) + 0.0591\ V \times pH$ ------------- **(S1)**

$\eta = a + b \log |j|$---------------------- **(S2)**

The Tafel slope value was calculated from the **eqn. S2** where η is the overpotential, b and j are the Tafel slope and the current density, respectively.

Electrochemical impedance spectroscopy measurements

EIS was conducted over a frequency range of 10^5 to 0.1 Hz with a 5 mV amplitude, maintaining an open circuit potential (OCP). The acquired results were fitted using an appropriate equivalent circuit.

Chronopotentiometry

The stability and durability of the synthesized electrocatalyst were assessed through chronopotentiometric studies. The experiment involved maintaining a constant current density of 10 mA cm^{-2} over a duration of 60 hours.

Calculation of electrochemical active surface area

Cyclic voltammetry (CV) was employed to calculate the electrochemical active surface area by measuring the double-layer capacitance (C_{dl}). CV curves were obtained from the non-faradic region at various scan rates ranging from 10 to 100 mV/s. The double-layer capacitance was determined by analyzing the slope of the average current density versus scan rate through linear fit values, and it was directly linked to the electrochemical surface area (ECSA). Equation (S4) outlines the relationship between double-layer charging current density (j_{dl}), scan rate (ν), and the double-layer capacitance (C_{dl}).

$$j_{dl} = \nu \, C_{dl} \qquad \textbf{(S3)}$$

$$\mathrm{ECSA} = C_{dl} / C_s \qquad \textbf{(S4)}$$

From equation (S5), the ECSA was calculated using the double layer capacitance (C_{dl}) and C_s. where C_s is specific capacitance of the sample in identical electrolyte solution.

ECSA normalization

$$\textbf{Specific activity} = \mathbf{J_{ECSA}} = \frac{J_{\mathrm{geo}}}{\mathbf{ECSA}} \qquad \textbf{(S5)}$$

Calculation of Turn over Frequency (TOF)

TOF is simply defined as the number of moles of O_2 formed per unit time from a catalytic active site. The equation used to calculate the TOF value of a catalyst is provided below:

$$\mathbf{TOF} = \mathbf{j \times NA / F \times n \times \tau} \qquad \textbf{(S6)}$$

Here, J is the current density at a certain overpotential, NA is the Avogadro number, n is the number of electron transfer ($n = 4$), F is faraday constant and τ is the number active sites over the working electrode surface. The τ value can be calculated from the redox area curve, obtained from the CV at the highest possible scan rates.

Results and Discussion

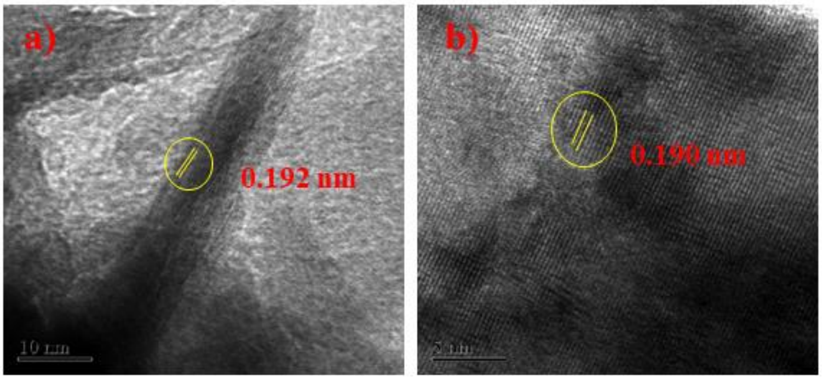

Fig S1. FE-TEM images of a) ME-FCCM LDH and b) LE-CCM LDH

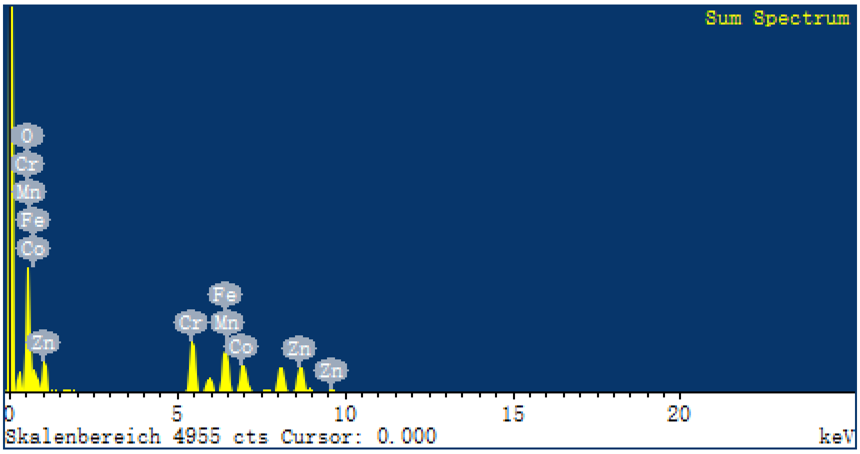

Fig. S2 EDX spectra of the HE-FCCMZ LDH

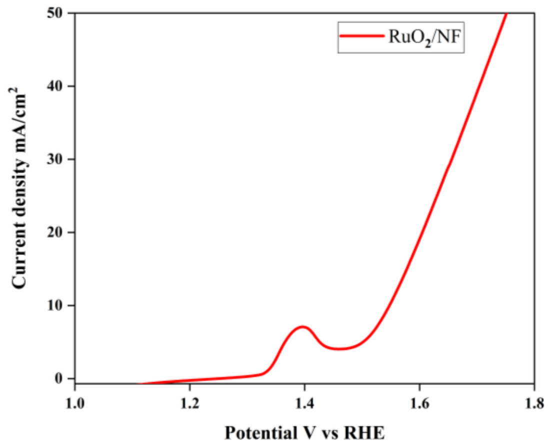

Fig. S3. LSV curve for RuO_2/NF in 1 M KOH

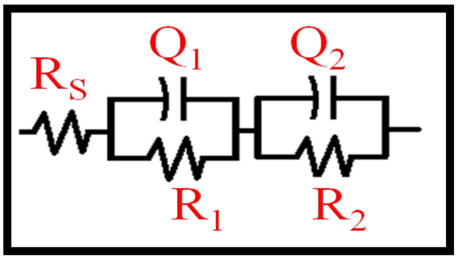

Fig. S4. Equivalent circuits for LE-CCM LDH, ME-FCCM LDH and HE-FCCMZ LDH

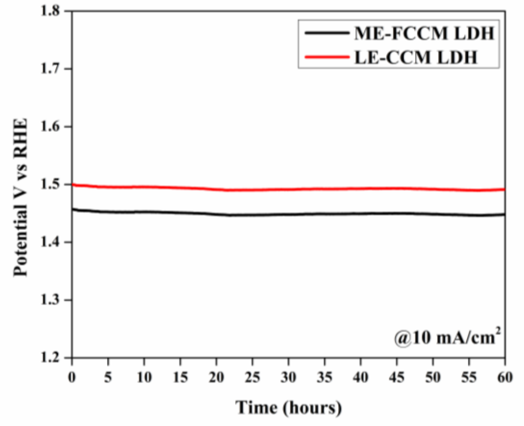

Fig. S5 Chronopotentiometry curves for ME-FCCM LDH and LE-CCM LDH for 60 hours of O_2 evolution

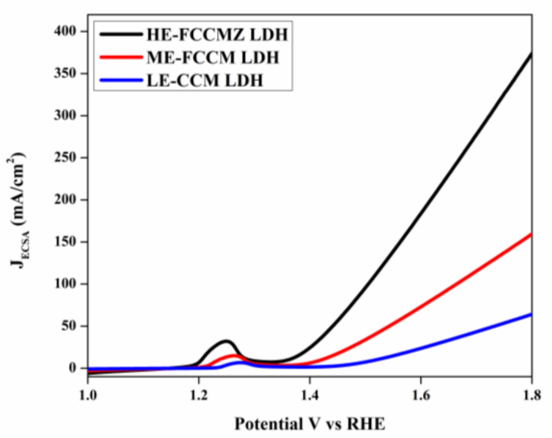

Fig. S6 LSV normalisation curves for HE FCCMZ LDH, ME-FCCM LDH and LE-CCM LDH

Table S1. Comparison of OER electrocatalysts characteristics with recent reports.

Materials	Current density (mA/cm^2)	Over potential (mV)	Tafel slope (mV/dec)	Stability (h)/Current density (mA/cm^2)	Ref
Au$_{SA}$-MnFeCoNiCu LDH	100 (10)	260 (213)	27.5	700/100	1
(FeCoNiCrMn)$_3$O$_4$ HEO	10	239	52.4	24/100	2
GaFeCoNiCr HEO nanosheet	10	240	37.9	250/10	3
HEOs-Ov	10	284	53	200/100	4
FeCoNiMnCuBOy HEO	10	259	66.1	55/10	5
NiAlPt-LDH@PHEA	10	227	25	100/1000	6
CoCuFeNiMnMo$_{1.5}$	10	375	140	72/10	7
Lix(FeCoNiCuZn)1-x HEAs	10	221	21.9	80/10	8
FeCox-HE LDH	10	295	61.79	40/10	9
HE-FCCMZ LDH	10	185	49.7	60/10	This work

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