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Supporting Information

Boosting Oxygen Evolution via Lattice Oxygen Activation in High-Entropy Perovskite Oxides

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Materials and Methods

Chemical Materials

Lanthanum(III) nitrate hexahydrate ($La(NO_3)_3\cdot 6H_2O$), praseodymium(III) nitrate hexahydrate ($Pr(NO_3)_3\cdot 6H_2O$), cobalt(II) nitrate hexahydrate ($Co(NO_3)_2\cdot 6H_2O$), iron(III) nitrate nonahydrate ($Fe(NO_3)_3\cdot 9H_2O$), nickel nitrate hexahydrate ($Ni(NO_3)_2\cdot 9H_2O$), urea (CH_4N_2O), and citric acid monohydrate ($C_6H_8O_7\cdot H_2O$) were supplied by Adamas Chemical Reagent Co., Ltd.. Strontium (II) nitrate ($Sr(NO_3)_2$), potassium hydroxide (KOH, AR), and Nafion (5 wt %) were purchased from Aladdin Chemical Reagent. All the chemicals were used without further purification.

Material Synthesis

1 mmol stoichiometric amounts of ($La(NO_3)_3\cdot 6H_2O$) , ($Pr(NO_3)_3\cdot 6H_2O$), $Sr(NO_3)_2$, $Fe(NO_3)_3\cdot 9H_2O$, $Co(NO_3)_2\cdot 6H_2O$, and $Ni(NO_3)_2\cdot 6H_2O$ were dissolved in 20 mL of deionized water and stirred for 15 min. Then 7.5 mmol of citric acid monohydrate and 80 mmol urea were added to the above solution. The mixture was then stirred continuously at 90 °C in an oil

bath until the crystal water was completely evaporated. The obtained product was ground, placed in a porcelain boat, and then annealed in a tubular furnace at 1000 °C (5 °C min^{-1}) in air for 3 h to yield (LaPrSr)(FeCoNi)O_3.

Materials Characterization

Powder X-ray diffraction (XRD) analysis was conducted using a Bruker AXS D8 Advance X-ray diffractometer with Cu-Kα radiation (λ= 1.5406 Å). Scanning electron microscopy (SEM) images were performed with a Zeiss Auriga microscope equipped with an energy dispersive spectroscope analyses (EDS) detector operating at 20 kV. Transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM) imaging, and electron energy loss spectroscopy (EELS) analysis were obtained using a field emission gun FEI™ Tecnai F20 microscope with a Gatav Quantum filter at 200 kV. X-ray photoelectron spectra (XPS) measurements were obtained using a SPECS system equipped with an Al anode XR50 source operating at 150 W and a Phoibos 150 MCD-9 detector.

Electrochemical Measurements

The performance of the prepared catalysts for the oxygen evolution reaction (OER) was evaluated in a standard three-electrode setup by CHI760E electrochemical workstation in 1.0 M KOH solution. A Hg/HgO and platinum wire were employed as reference and counter electrodes, respectively. The catalyst ink was produced by ultrasonically dispersing 4 mg of the catalyst powder in 750 µL isopropanol, 230 µL deionized water and 20 µL of 5 wt% Nafion solution. The working electrode was prepared by drop-casting 5 µL of the fresh catalyst ink onto a glassy carbon (GC, 3mm in diameter) electrode and naturally dried in air. Linear sweep voltammetry (LSV) was conducted at a scan rate of 5 mV s^{-1} from 0 to 1.0 V (vs. Hg/HgO) in O_2-saturated 1.0 M KOH electrolyte. All the presented data were corrected with 90% iR-compensation. Electrical impedance spectroscopy (EIS) was measured in a frequency range from 100 kHz to 0.01 Hz at 5 mV and recorded at 1.55 V. The electrochemical double-layer capacitance (C_{dl}) curves of catalysts were measured by cyclic voltammetry in a non-Faradaic region (0.90–1.00 V vs. RHE) at varied scan rates of 20 to 200 mV s^{-1} based on the following equation: $C_{dl} = \Delta j/v$, where Δj ($\Delta j = (j_a - j_c)/2$) and v are the current density (at 0.95 V, mA cm^{-2}) and scan rate (mV s^{-1}), respectively. The long-term durability was tested using chronopotentiometry (CP) at a constant current density of 10 mA cm^{-2} for 60 h without iR compensation and LSVs after continuous cyclic voltammetry tests (1.3 V to 1.7 V) for 2000 cycles at 0.2 V s^{-1}.

Zn–Air batteries assembly

The catalytic ink was sprayed on the hydrophobic carbon paper uniformly with a mass loading of 0.5 mg/cm^2. This carbon paper was used as the air cathode while a polished Zn foil was used as the anode. The two electrodes were assembled into a ZAB, while a 6 M KOH and 0.2 M zinc acetate aqueous solution was used as the electrolyte. Charge–discharge polarization curves and open circuit voltage measurements were determined by CHI760E electrochemical workstation. The galvanostatic test was performed using a Neware BTS4008 battery test system. The specific capacities were determined using the galvanostatic discharge profiles standardized to the consumed mass of Zn.

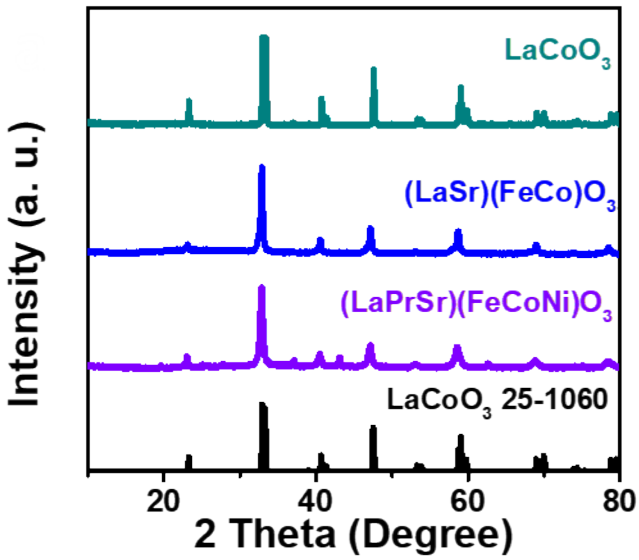

Figure S1. XRD pattern of prepared $(LaPrSr)(FeCoNi)O_3$, $(LaSr)(FeCo)O_3$, $LaCoO_3$

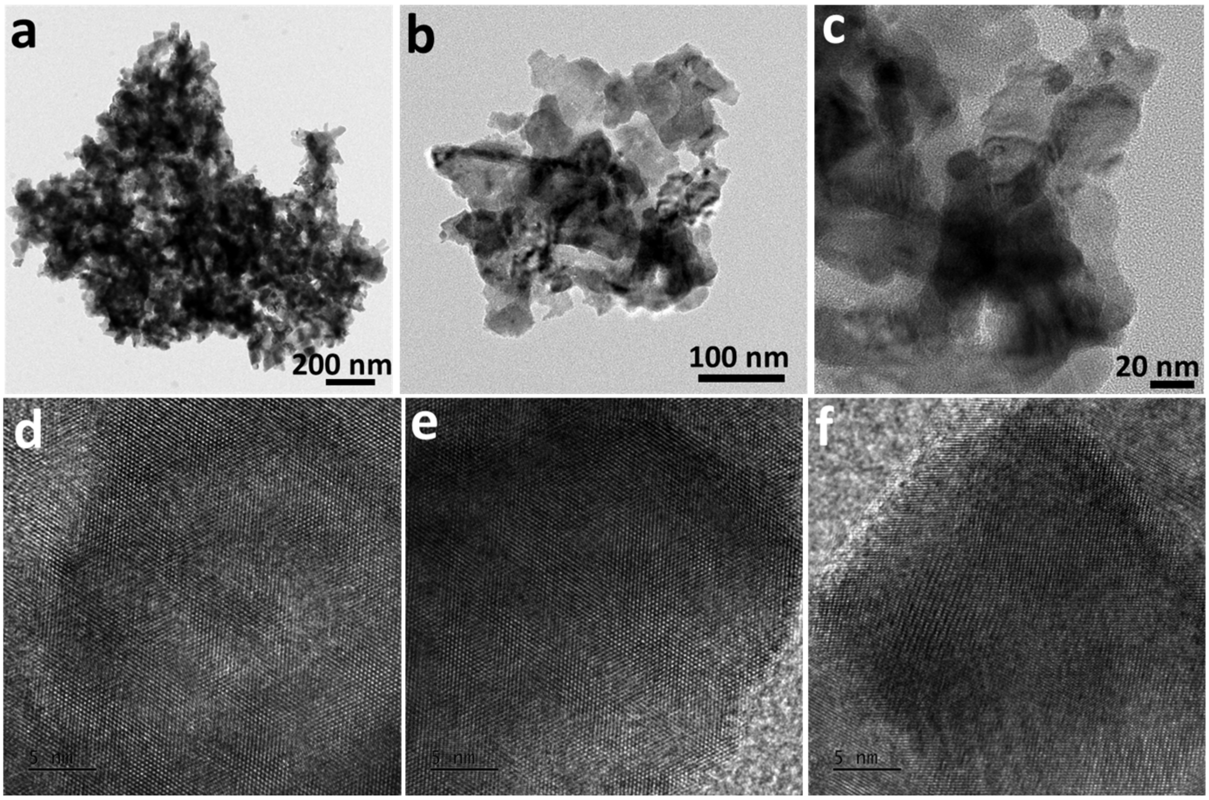

Figure S2. TEM and HRTEM images of LPSFCNO

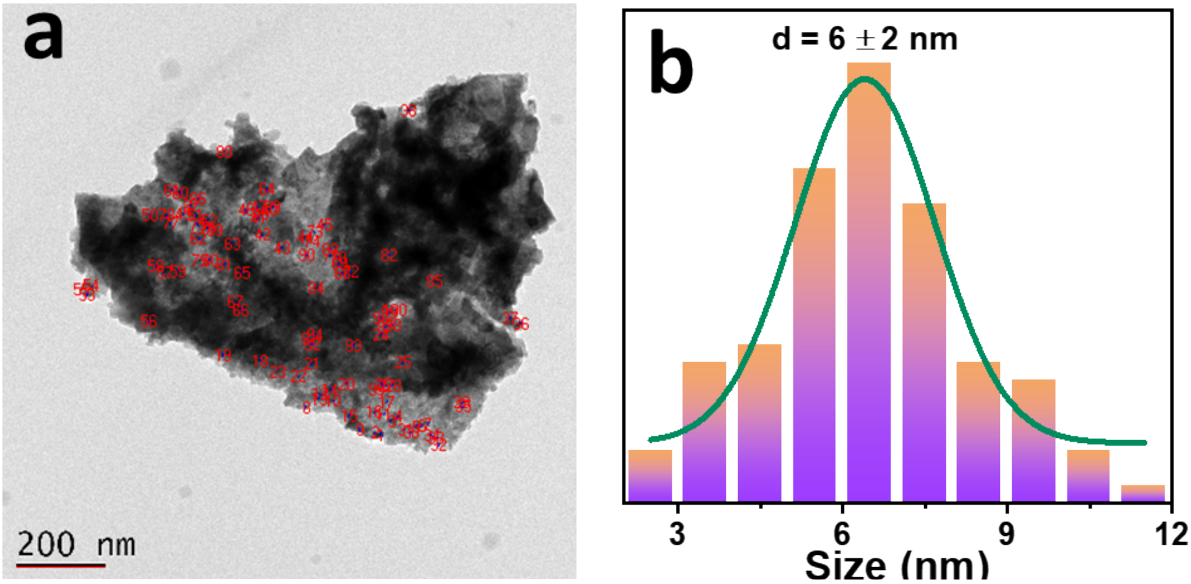

Figure S3. Marked TEM and particle size distribution images of LPSFCNO

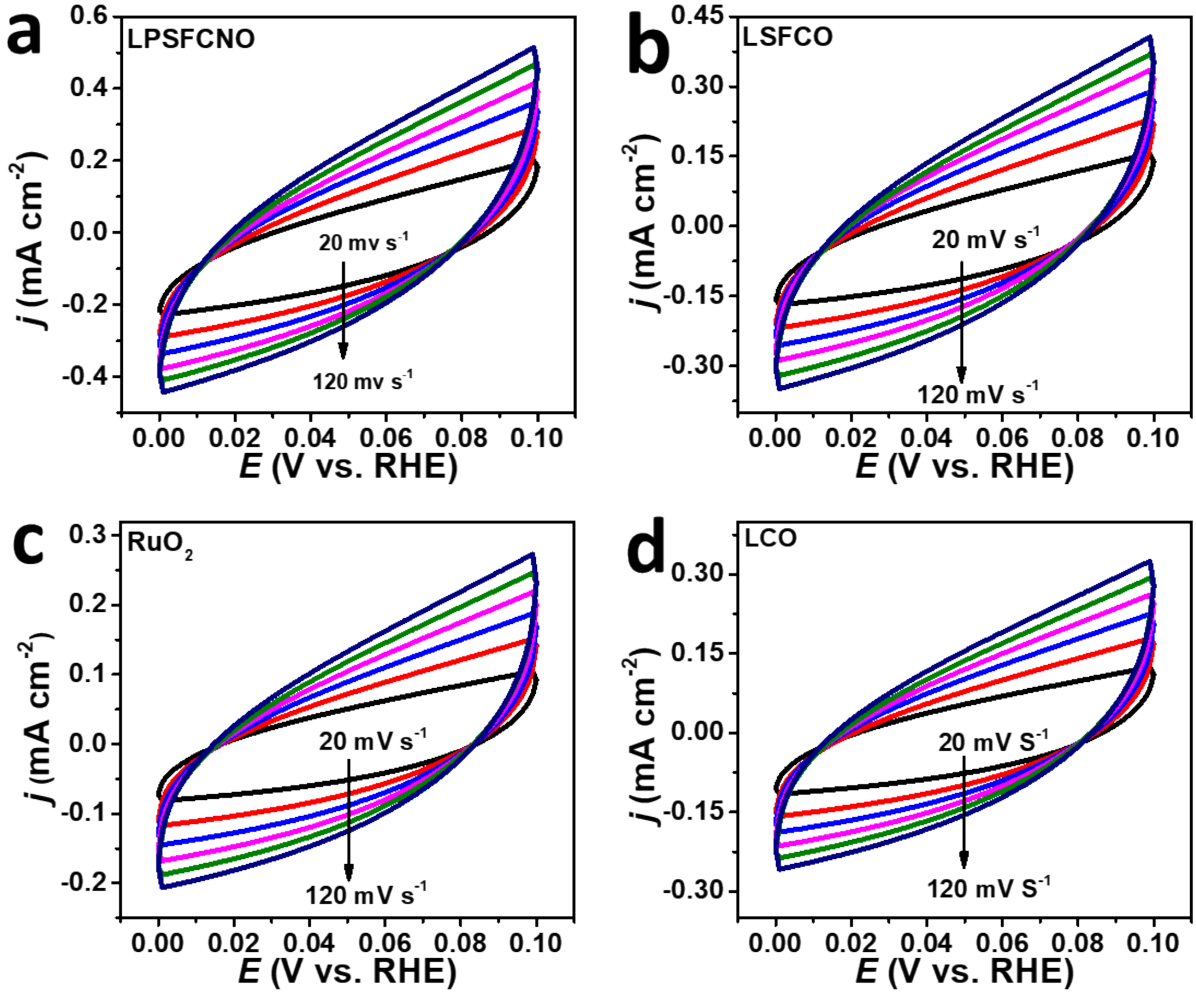

Figure S4. Cyclic voltammograms of a) LPSFCNO; b) LSFCO; c) RuO_2 and d) LCO in the non-faradaic region of 0.00-0.10 V vs. RHE at various scan rates.

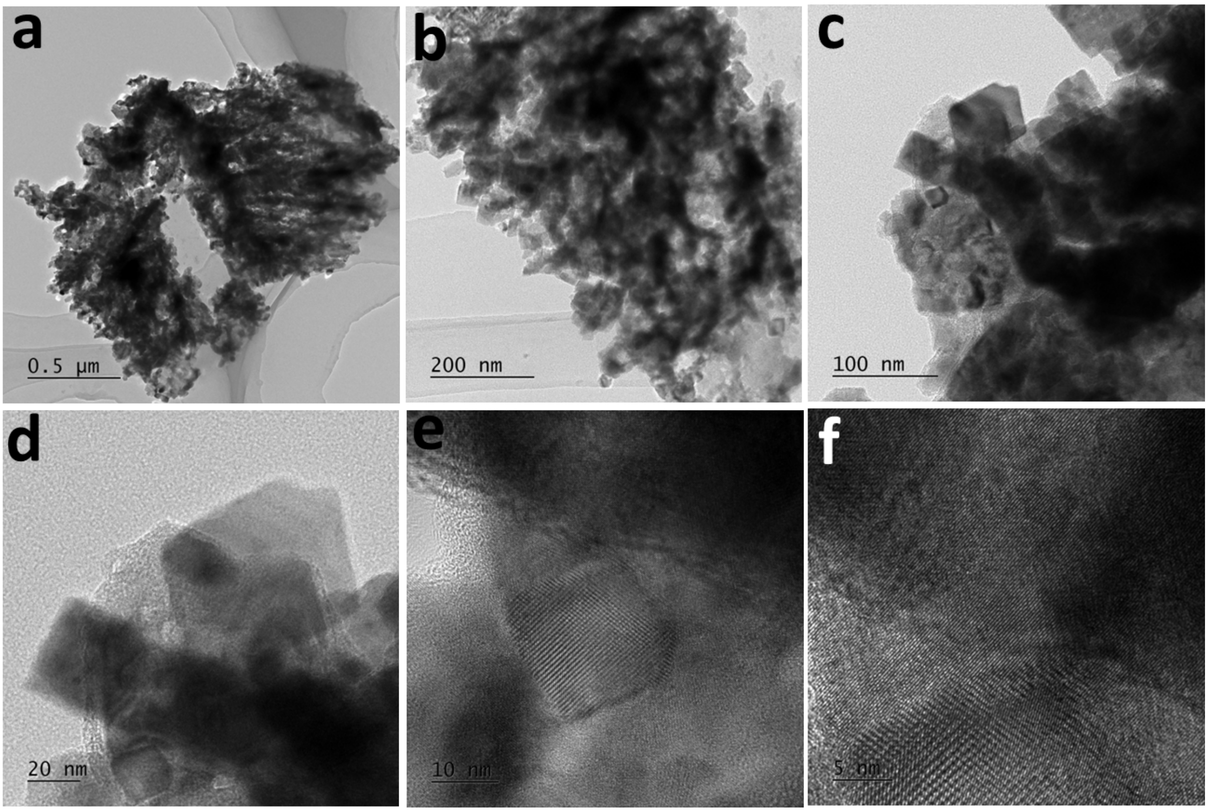

Figure S5. TEM and HRTEM images of LPSFCNO after OER

Table S1. Summary of reported OER various perovskite electrocatalysts in 1.0 M KOH alkaline condition.

Catalyst	Overpotential (mV)	Tafel Slope (mV dec^{-1})	References
LPSFCNO	304	59.4	This work
LSCFO-0.50	310	107	ACS Catal., 2024, 15, 1, 477-486
$La_{0.5}Pr_{0.5}CoO_3$	312	80.6	Nano Energy, 2020, 74, 104948.
$LaCr_{0.5}FeO_3$	390	114	Small, 2024, 20, 10, 2305662.
$LaCo_{0.75}Fe_{0.25}O_3$	310	58	Chem. Mater., 217, 29, 24, 10534-10541
$LaCoO_{3-x-\delta}F_x$	390	114	Small, 2023, 19, 10, 2206367
$LaCoO_{3-x-\delta}S_x$	364	127	Chem. Mater., 2020, 32, 8, 3439-3446
$La_{0.6}Sr_{0.4}Co_{0.9}Fe_{0.1}O_{3-\delta}$	330	71.56	Chem. Eng. J. 2023, 478, 147415
$La_{0.85}Ce_{0.15}NiO$	340	45	Adv. Energy Mater. 2021, 11, 12, 2003755
$La_{0.7}Sr_{0.3}Co_{0.25}Mn_{0.75}O_3$	340	111	Electrochim. Acta 2018, 279, 301-310.
SNCF-NRS	350	61	Adv. Energy Mater. 2017, 7, 8, 1602122.
$LaCo_{0.9}Fe_{0.1}O_3$	360		Chem. Mater. 2017, 29, 24, 10534-10541
La_2NiMnO_6	370	58	J. Am. Chem. Soc. 2018, 140, 36, 11165-11169
(111)-$SrFeO_{2.5}$	390	70.5	ACS Catal. 2023, 13, 4, 2751-2760.
$LaMn_{0.4}Co_{0.6}O_3$	400	95	J. Alloys Compd. 2021, 878, 160433.
$LaNi_{1-x}Fe_{0.5x}Co_{0.5x}O_3$	410	65	ACS Appl. Energy Mater. 2022, 5, 1, 343-354.
$Sr_{0.95}Nb_{0.1}Co_{0.9-x}Ni_xO_{3-\delta}$	438	64	J. Mater. Chem. A 2019, 7, 33, 19453-19464.