Optimized Co²⁺_(Td)-O-Fe³⁺_(Oh) Electronic State in a Spinel Electrocatalyst for Highly Efficient Oxygen Evolution Reaction Performance

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COMPUTATIONAL DETAILS

First principles calculations based on density functional theory (DFT) were performed with the Vienna ab initio simulation package (VASP).¹⁻⁴ The exchange-correlation energy of the projector augmented wave (PAW) potentials⁵⁻⁶ and the generalized gradient approximation was described by Perdew, Burke, and Ernzerhof.⁷

 Co_3O_4 (311) ($Co_{24}O_{32}$) is obtained by cutting the crystal structure of Co_3O_4 along (311) direction, and the Fe-doped Co_3O_4 is prepared by replacing one Co on octahedron or tetrahedron site with an atomic Fe. During the optimization process the last layer is fixed and the other atoms are allowed to relax. For the investigated systems, a sufficiently large vacuum of 15.0 Å is taken along the z-axis to avoid the image interactions. To investigate the stability of Fe-doped Co_3O_4 , The formation energy (E_f) was evaluated as follows,

$$E_f = E_{total} - E_{Co3o4} - E_{Fe}$$

where E_{total} is the total energy of Fe-doped Co₃O₄; E_{Co3o4} and E_{Fe} are the energy of Co₃O₄ and atomic Fe, respectively. The more negative the value of E_{f_2} the greater the thermodynamic stability of the system. A kinetic energy cutoff of 400 eV is used with a plane-wave basis set. The integration of the Brillouin zone is conducted using a $1 \times 1 \times 1$ Monkhorst–Pack grid.⁸ The convergence criteria of the total energy and the force are 1.0×10^{-5} eV/atom and 0.05 eV/Å, respectively.

The Gibbs free energy was calculated as follows, and the Fe-doped Co_3O_4 is prepared by replacing two Co on octahedron site with two atomic Fe. $\text{Co}^{3+}_{(\text{Oh})}$ and $\text{Fe}^{3+}_{(\text{Oh})}$ as active site for Gibbs energy at each reaction step are calculated, respectively. $\Delta G = \Delta E + \Delta ZPE - T\Delta S$, where ΔG , ΔE , ΔZPE and $T\Delta S$ are the Gibbs free energy, total energy, zero point energy and entropic contributions from DFT calculations, respectively. The plane-wave kinetic energy cutoff was set to 520 eV. For structural relaxations and electronic structure calculations, $2 \times 2 \times 1$ and $12 \times 12 \times 1$ Monkhorst-Pack k-point mesh were used, and the convergence criterion of 10^{-4} eV and 0.05 eV/Å were chosen. A vacuum layer of 18 Å is applied to avoid the interaction between the neighboring slabs.

EXPERIMENTAL SECTION

Materials

Co(NO₃)₂•6H₂O and Fe(NO₃)₃•9H₂O were purchased from Sinopharm Chemical Reagent Co., Ltd. Ethanol (analytical reagent) and isopropyl alcohol (analytical reagent) were purchased from Beijing chemical works. Nafion was purchased from Sigma-Aldrich. SBA-15 was purchased from Nanjing jicang nano technology co., Ltd.

 Co_3O_4 synthesis: ordered mesoporous cobalt oxide (meso- Co_3O_4) was prepared by nanocasting method, 3mmol of $Co(NO_3)_2 \cdot 6H_2O$ (0.87g) was added into 25mL ethanol to produce a clear solution. Then, 0.3g SBA-15 was dispersed in the solution and stirring for 24h. After that, the solution was dried by heating jacket. The dried powder was grounded and repeated preceding process to get Co-precursor/sio₂ composites. The dry powder was sintered at 550°C for 3h and the template was removed by stirring with 2mol hot NaOH solution. The product was collected and washed with deionized water and ethanol for several times.

Iron-Doped Cobalt Oxides Synthesis: Suitable $Co(NO_3)_2 \cdot 6H_2O$ and $Fe(NO_3)_3 \cdot 9H_2O$ were dissolved in 25ml ethanol to produce a clear solution. (The amount of $Co(NO_3)_2 \cdot 6H_2O$ and $Fe(NO_3)_3 \cdot 9H_2O$ are listed in Table S1) The later process was the same as the method of synthesis Co_3O_4 . The yields of the materials are about 66.5%.

Material Characterization: X-ray diffraction (XRD) was obtained by using a Rigaku D/Max 2550 diffractometer with Cu-K α radiation testing at 40 KV and 200 mA by step scanning in the angel range of 15 to 70° with increments of 2°/min. The morphology, structure of the prepared materials were investigated by transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM, FEI TecnaiG2 S-Twin) with a field emission gun operating at 200KV. X-ray photoelectron spectroscopy (XPS, ESCALAB-250) was carried out at constant power mode. Extended X-ray absorption fine structure (EXAFS) and X-ray absorption near edge structure (XANES) spectra of Co K-edge and Fe K-edge were collected at the Beamline BL14W1 (Shanghai Synchrotron Radiation Facility) at 3.5 GeV at room temperature. The synchrotron radiation was monochromatized by a Si (111) double-crystal monochromator. To obtain the best signal-to-noise ratio, the samples diluted by LiF were pressed into the pallets (ϕ 13mm) at 6 MPa.

Electrochemical Measurement: All electrochemical measurements were carried out using an electrochemical workstation (CHI 660E) in a conventional three-electrode configuration, with a platinum wire as counter electrode, a Hg/HgO electrode was used as reference electrode and the modified GCE (5mm in diameter) as working electrode. The working electrode was prepared by drop-casting and drying the as-fabricated material ink on the prepolished GCE. An aqueous solution of potassium hydroxide (1M KOH) was used as the supporting electrolyte. Cyclic voltammetry (CV) was run at least three times before electrochemical test in order to remove the bubbles and activate the electrode. The material ink was prepared by mixing the sample and Ketjenblack (KB) in a ratio of 4:1 and dispersing the mixture in 1mL of isopropanol and 1mL of deionized water and 20µL of Nafion solution by ultrasonic method. The total is 5mg. Finally, 20µL of the ink was added dropwise to a glassy carbon electrode (diameter 5mm) and natural drying.

Material	Co(NO ₃) ₂ . 6H ₂ O(g)	Fe(NO ₃) ₃ . 9H ₂ O (g)	Co Concentration (mmol.L ⁻¹)	Fe Concentration (mmol.L ⁻¹)	Chemical formula
Co ₃ O ₄	0.8706	0	0.3433	0.003612	Co ₃ O ₄
CoFe-5	0.8293	0.0611	0.3798	0.023300	Co _{2.85} Fe _{0.15} O ₄
CoFe-7.5	0.8078	0.0916	0.3056	0.029640	Co _{2.77} Fe _{0.23} O ₄
CoFe-10	0.7858	0.1219	0.2863	0.040300	$Co_{2.70}Fe_{0.30}O_4$

 Table S1. Concentration of Co and Fe calculated by ICP

Table S2. Co/Fe molar ratio, BET surface areas and electrochemical surface areas (ECSAs)

 of as-prepared samples

	Co : Fe molar ratio	ECSA (cm ²)	BET (m ² /g)
Co ₃ O ₄	3.00:0	22.1	61.92
CoFe-5	2.85:0.15	24.7	33.79
CoFe-7.5	2.77:0.23	33.6	22.27
CoFe-10	2.70:0.30	50.7	26.03

Table S3. A comparison with recent and relevant literature data

Material	Overpotential η[mV]at 10mA cm ⁻²	Tafel slope (mV decade ⁻¹)	Reference
Fe-Co ₃ O ₄	380	60	27
Co ₃ O ₄	420	72	27
Co ₃ O ₄ /graphene	346	47	35
Urchin-like Co ₃ O ₄	308	72	36
Co ₃ O ₄ nanosheets	342	80	36
Co ₃ O ₄ nanoparticles	350	84	36
Co ₃ O ₄ nanoshpres	448	99	36
CoFe oxide	340	72	37
Co ₃ O ₄	394	66	37
Co ₃ O ₄	526	-	38
Co ₃ O ₄	411	78	This work
CoFe-5	364	76	This work
CoFe-7.5	317	58	This work
CoFe-10	356	79	This work



Figure S1 XRD of the as-prepared samples.



Figure S2 TEM images of the as-prepared samples.



Figure S3 XPS profiles of Fe2p spectrum and its simulations of the as-prepared samples.



Figure S4 Calculated of partial density of states (PDOS) of Co₃O₄ and Fe_(Oh) - Co₃O₄.



Figure S5 Nitrogen adsorption-desorption isotherm curves of the as-prepared samples.



Figure S6 Cyclic voltammograms at different scan rates of the as-prepared samples to

estimate electrochemical surface areas (ECSA_S).



Figure S7 The charging currents measured at 0.28V vs Hg/HgO plotted as a function of scan rate. The value of double-layer capacitance is gotten by the slope of the linear fits to the data.



Figure S8 LSV curves normalized by the material surface area of the as-prepared samples.



Figure S9 LSV curves normalized by the material electrochemical surface areas (ECSAs) of

the as-prepared samples.

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