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Article

Highly efficient mixed-metal spinel cobaltite electrocatalysts for the oxygen evolution reaction

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ABSTRACT

Cation substitution in spinel cobaltites (e.g., ACo_2O_4 , in which $A = \text{Mn, Fe, Co, Ni, Cu, or Zn}$) is a promising strategy to precisely modulate their electronic structure/properties and thus improve the corresponding electrochemical performance for water splitting. However, the fundamental principles and mechanisms are not fully understood. This research aims to systematically investigate the effects of cation substitution in spinel cobaltites derived from mixed-metal-organic frameworks on the oxygen evolution reaction (OER). Among the obtained ACo_2O_4 catalysts, FeCo_2O_4 showed excellent OER performance with a current density of $10 \text{ mA} \cdot \text{cm}^{-2}$ at an overpotential of 164 mV in alkaline media. Both theoretical calculations and experimental results demonstrate that the Fe substitution in the crystal lattice of ACo_2O_4 can significantly accelerate charge transfer, thereby achieving enhanced electrochemical properties. The crystal field of spinel ACo_2O_4 , which determines the valence states of cations A, is identified as the key factor to dictate the OER performance of these spinel cobaltites.

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1. Introduction

Solar or wind energy can be converted from electricity into chemical energy, and hydrogen fuel can be generated and stored by means of water splitting. During water splitting, the

reaction kinetics of the oxygen evolution reaction (OER) at the anode are typically much slower than those of the hydrogen evolution reaction at the cathode. [1]. Therefore, it is critical to accelerate the rate of the OER at the anode and improve the overall efficiency of water-splitting. Currently, iridium dioxide

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(IrO₂) and ruthenium dioxide (RuO₂) have been commonly used as OER catalysts. However, the most frequently used electrocatalysts, IrO₂ and RuO₂, are not only expensive but also have unsustainable supply and environmental issues. Hence, it is critical to develop non-noble and abundant metal-based electrocatalysts for the OER, with good catalytic activity and high durability for practical applications in water splitting. To date, huge efforts have been made to develop transition metal oxides/hydroxides [2], phosphate [3], and sulfides [4] for the OER.

Three-dimensional metal-based spinel oxides have recently attracted enormous attention due to the wide range of technological applications in the semiconductor industry, such as high-frequency devices, catalysts, magnetic recordings, biomedical devices, microwave absorbers, gas sensors, and optical materials/devices [5–8]. They possess a stoichiometric AB₂O₄ cubic structure, where A and B stand for tetrahedral and octahedral configurations of transition metals, respectively [9]. Because of highly distributed metal cations A and B between each position with different oxidation states in the spinel structure AB₂O₄, the mixed-transition metal spinel structures exhibit various interesting physical and chemical properties, particularly in the catalytic field. The partially filled nature of the 3d transition metal orbitals enables the electron transfer process, which plays a key role in creating excellent magnetic, electronic, and electrochemical properties. These provide us with an opportunity to tune their electrical structures at the atomic scale to achieve highly efficient water splitting electrocatalysts and further match the demand for electrolyzers and fuel cells, etc. [10]. Recently, there has been an increased interest in using mixed-metal spinel oxides for the OER applications [11–14].

However, the relationship between the electrocatalytic performance of the mixed-metal spinel oxides and their elementary compositions, valence states, and distribution of sites is still not fully understood. Experimental observations and theoretical analyses have been performed [15–18] to identify the exact roles of spinel oxides in the OER. For example, Prabu et al. [19] found that Ni³⁺ ion substitution at the octahedral sites of the NiCo₂O₄ can significantly enhance the OER performance. Hutchings et al. [20] reported that the active sites of Co₃O₄ for the OER are mainly the octahedral sites of Co³⁺. Wei et al. [17] identified that Mn³⁺ ions in the octahedral positions of MnCo₂O₄ are the active sites for the OER. These well-documented studies clearly indicate that electrocatalytic performances of the cobalt-based spinel oxides for the OER strongly depend on the valence states of transition metal cations (A) and their corresponding site distributions in the ACo₂O₄ spinel structure [10]. The substitution of transition metal cations (A) can be a promising strategy for precisely modulating the electronic properties and optimizing the electrochemical OER performance of cobalt-based spinel oxides (e.g., ACo₂O₄, in which A = Mn, Fe, Co, Ni, Cu, or Zn).

In this paper, we report a series of the cobalt-based spinel oxides with well-defined compositions and morphologies, derived from the precursor mixed-metal-organic frameworks (MMOFs). A site substitution by different transition metal cati-

ons in cobalt-based spinel oxides and their corresponding OER behavior have been discussed in detail. Among these ACo₂O₄, FeCo₂O₄ showed an excellent catalytic activity with a current density of 10 mA·cm⁻² at an overpotential of 164 mV in alkaline media. Furthermore, charge transport, electronic structure, and spinel crystal fields of these ACo₂O₄ were systematically investigated based on experimental studies and density functional theory (DFT) calculations. The underlying mechanisms for the enhanced electrocatalytic performance induced by substitutions of cations with different numbers of d-electrons between 5 and 10 have also been clarified.

2. Experimental

2.1. Synthesis of FeCo₂-PTCDA MMOFs.

In a typical synthesis process [21], Fe(OAc)₂·2H₂O (0.133 mmol) and Co(OAc)₃·4H₂O (0.267 mmol) were dissolved in 22.5 mL deionized water, and PTCDA (0.2 mmol) was dissolved in 12.5 mL NaOH solution (0.8 mmol NaOH). The PTCDA solution was added dropwise to the mixed solution of metal acetates under constant stirring. The immediate formation of a precipitate was observed. The reaction mixture was stirred at room temperature for 30 min, and then transferred into a Teflon-lined stainless steel vessel (45 mL) and heated at 100 °C for 8 h. After cooling down to room temperature, the precipitate was collected by centrifugation, washed with water and dried.

The obtained FeCo₂-PTCDA MOFs were annealed at 400 °C in the air for 1 h with a heating ramp of 1 °C·min⁻¹. For the synthesis of other ACo₂-PTCDA (A = Zn, Cu, Ni, Co, and Mn) MMOFs, the processes are similar to those described above for the FeCo₂-PTCDA, except for the choice of metal acetates.

2.2. Catalyst characterization

Morphologies, chemical compositions, and crystalline structures of all the samples were characterized using various methods. The X-ray diffraction (XRD) measurements were performed using an X'pert PRO diffractometer (PANalytical B.V.) with a Cu K_α X-ray source operated at 40 kV and 40 mA. Surface and internal microstructures were investigated using field emission scanning electron microscopy (FE-SEM, Nova NanoSEM 450) and high-resolution transmission electron microscopy (HR-TEM, 300 kV Titan Probe corrected TEM, Titan G2 60-300). Surface chemical states of the samples were analyzed using an X-ray photoelectron spectroscopy (XPS, ThermoFisher-ESCALab 250). The shift of the core-level spectra was calibrated using the C 1s neutral carbon peak at 284.8 eV. The Brunauer-Emmett-Teller (BET) surface area (*S*_{BET}) and pore size distribution were determined using a Micromeritics ASAP 2000 nitrogen adsorption apparatus. All the samples were degassed at 180 °C prior to the BET measurements.

2.3. Electrochemical measurements

The catalytic activity of the prepared ACo₂O₄ loaded onto standard glassy carbon electrodes was evaluated using elec-

trochemical measurements for the OER with a three-electrode electrochemical cell in 1 M KOH aqueous solution as the electrolyte. To prepare the electrode, 2 mg ACo_2O_4 sample was dispersed into a 1 mL mixture of water, ethanol, and Nafion solution (5 wt% in a mixture of lower aliphatic alcohols and water, Aldrich) with a volume ratio of 1:3.85:0.15, under a constant ultra-sonication for 10 min. The final catalyst ink suspension had a concentration $2.0 \text{ mg}\cdot\text{mL}^{-1}$, and its suspension of $19.8 \mu\text{L}$ was then transferred onto a polished glassy-carbon electrode of 5 mm in diameter, resulting in a mass loading of $0.2 \text{ mg}\cdot\text{cm}^{-2}$.

Cyclic voltammetry (CV) and linear sweep voltammetry (LSV) were conducted using an electrochemical station (CHI 750D, CH Instruments). Standard glassy carbon (GC) electrode (5 mm in diameter, Pine Instruments) was used as the working electrode. Hg/HgO was used as the reference electrode, and a graphite electrode was used as the counter electrode. Tafel plots of the samples were obtained similar to those reported in the literature [22,23]. LSV curves and Tafel plots were recorded at two different scan rates of 5 and $0.1 \text{ mV}\cdot\text{s}^{-1}$, respectively. Electrochemical impedance spectroscopy (EIS) was used (Autolab PGSTAT302N) with a frequency range from 0.01 Hz to 1 MHz and a potential amplitude of 10 mV. Impedance value (R) of the 1 M KOH solution was measured to be 6.9Ω at room temperature. Unless stated otherwise, the tests were made without iR compensation in 1 M KOH solution.

Measurements using rotating ring-disk electrodes (RRDEs) were conducted in 1 M KOH electrolyte at room temperature using a three-electrode system (Pine Instruments and WaveDriver Workstation). The measurement was conducted in a solution of N_2 -saturated 1 M KOH for seven times with various rotation speeds (i.e., 400, 620, 900, 1225, 1600, 2025, 2500 rpm). The Tafel slope was calculated using the Koutecký-Levich equation with the RRDE for the OER without iR [24]:

$$\frac{1}{i} = \frac{1}{i_K} + \frac{1}{i_L} = \frac{1}{i_K} + \frac{1}{0.62nFAD_0^{2/3}\omega^{1/2}\nu^{-1/6}C_0^*} \quad (1)$$

The electrochemical surface area (ECSA) of the catalyst plays a crucial role in electrochemical reactions. To study the ECSA of ACo_2O_4 , we conducted cyclic voltammograms at different scan rates (10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 110, and $120 \text{ mV}\cdot\text{s}^{-1}$) in a non-faradaic potential region. The ECSA is the product of $R_F S$, in which R_F stands for the roughness factor, which is obtained from the ratio of C_{dl} of the test sample and the C_s ($= 60 \mu\text{F}\cdot\text{cm}^{-2}$) of a smooth surface [25]. S stands for the real surface area of the smooth metal electrode, which generally equals the geometric area of the carbon electrode [26]. The values of C_{dl} were obtained using cyclic voltammetry, and the results are shown in Fig. S3. As shown in Fig. S3, the C_{dl} were obtained to be 8, 5.4, 5.3, 3.7, 2.6 and $1 \text{ mF}\cdot\text{cm}^{-2}$ for ZnCo_2O_4 , Co_3O_4 , NiCo_2O_4 , MnCo_2O_4 , FeCo_2O_4 , and CuCo_2O_4 , respectively.

The faradaic efficiency (FE) was obtained according to the method reported in the literature [27]. The FE (or current efficiency) is defined as the ratio of the measured amount of produced oxygen and the theoretical amount of produced oxygen, according to Faraday's Law. It can be calculated as follows:

$$\eta = 4(N \times F)/(I \times t) \quad (2)$$

where η is the theoretical yield (current efficiency); N stands for the Molar amount of produced oxygen; I represents the current in ampères; t is the time in seconds (in this work, $t = 1 \text{ min}$); 4 is the oxidation state (number of displaceable electrons per O_2); and F is Faraday's constant, $F = 96487 \text{ C}\cdot\text{mol}^{-1}$.

Chronopotentiometry was applied at a given potential (1.53 V) to maintain constant O_2 generation. N_2 was constantly purged into the cathodic compartment at a flow rate of $5 \text{ cm}^3\cdot\text{min}^{-1}$, and the compartment was connected to the gas-sampling loop of a gas chromatograph (GC2020, Hubei Hengxinshiji Scientific Instrument Co.). A thermal conductivity detector (TCD) was used to detect and quantify the generated O_2 .

All the measured potentials were calibrated using a reversible hydrogen electrode (RHE) based on the following equation:

$$E_{\text{RHE}} = E_{\text{Hg}/\text{HgO}} + 0.098V + 0.059\text{pH} \quad (3)$$

2.4. Density functional theory calculations

All the DFT calculations were performed using the Vienna Ab initio Simulation Package (VASP) [28]. The interaction between core ions and valence electrons was described by the projector augmented wave (PAW) method [29], while the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) function was used for electron exchange-correlation interactions [30]. The energy cut-off for the plane waves was chosen to be 520 eV. To correctly describe the electronic structure of the A-3d states ($A = \text{Mn, Fe, Co, Ni, Cu, and Zn}$), a rotational invariant type GGA+U method, as proposed by Dudarev et al. [31], was employed. The effective on-site Coulomb terms (U values) for the 3d states of Mn, Fe, Co, Ni, Cu, and Zn were selected to be 5.5, 3, 4.5, 10.5, 4.5, and 10 eV, respectively. The Monkhorst-Pack scheme sampling with a $2 \times 2 \times 2$ k-point mesh was adopted for the integration in the irreducible Brillouin zone. The structural parameters of the ACo_2O_4 were obtained based on the XRD analysis. The lattice parameters and atomic positions were fully relaxed and calculated using the hybrid HSE06 functional, and the final forces on the relaxed atoms were less than $0.05 \text{ eV}\cdot\text{\AA}^{-1}$. Spin-polarized calculations and ferromagnetic ordering were employed for all the cases.

3. Results and discussion

To identify the exact role of spinel oxides (Figs. S1 and S2), the ACo_2O_4 with well-defined morphologies and compositions was synthesized under a controlled temperature as low as 350°C [21]. The OER activities of ACo_2O_4 samples were investigated using a standard three-electrode configuration with 1 M KOH aqueous solution at 25°C . Figs. 1(a) and 1(b) show the OER specific activities of ZnCo_2O_4 (curve 1), CuCo_2O_4 (curve 2), NiCo_2O_4 (curve 3), Co_3O_4 (curve 4), FeCo_2O_4 (curve 5), and MnCo_2O_4 (curve 6) at a scan rate of $5 \text{ mV}\cdot\text{s}^{-1}$ after correction by removing the contribution of ECSA (Fig. S3). We compared the Tafel plots and overpotentials at $10 \text{ mA}\cdot\text{cm}^{-2}$ using various OER catalysts (Fig. 1(c)). The catalytic dynamics in terms of the turnover frequency (TOF) were further analyzed for ACo_2O_4

Fig. 1. Electrochemical measurements: (a) linear sweep polarization curves (LSV) of ZnCo₂O₄ (1), CuCo₂O₄ (2), NiCo₂O₄ (3), Co₃O₄ (4), FeCo₂O₄ (5), and MnCo₂O₄ (6) for the OER specific activities (corrected by removing the contribution of ECSA) in 1 M KOH; (b) Tafel slopes; (c) Tafel slope versus overpotential at 10 mA·cm⁻² for reported OER catalysts; (d) Turnover frequency (TOF) of specific activity for ACo₂O₄; (e) FE for the OER, and the average oxygen production of ACo₂O₄; (f) Chronoamperometric response recorded using FeCo₂O₄, initially and after 10000 cycles with a scan rate of 100 mV·s⁻¹, at a constant overpotential to reach a current density of 10 mA·cm⁻² for the OER. The inset shows the chronoamperometric curve of the FeCo₂O₄ for the OER at a static potential of 1.4 V for 20 h.

(Fig. 1(d)). Their OER activities were then compared with those of highly active electrocatalysts recently published in the literature (Table S1). Among them, FeCo₂O₄ MOFs showed an excellent catalytic activity with a current density of 10 mA·cm⁻² at a bias of 1.394 V (vs. RHE) and a small Tafel slope (61 mV·dec⁻¹) in alkaline media. Figure S4 shows gas chromatography (GC) curves of FeCo₂O₄ before and after the OER at the given current density of 10 mA·cm⁻². The GC results clearly confirm that the produced bubbles are O₂. The (FE) and the average oxygen production were measured from the samples ACo₂O₄ for the OER (Fig. 1(e)). The 98.6 % FE of FeCo₂O₄ confirms that the current is mainly related to water oxidation reaction (Fig. 1(e)). After testing with the continuous cyclic voltammetry characterization for 10,000 cycles at a scanning rate of 100 mV·s⁻¹, the FeCo₂O₄ still exhibited a polarization curve with a stable overpotential of 140 mV at 10 mA·cm⁻² (Fig. 1(f)). Fig. 1(f) inset shows that the FeCo₂O₄ electrolyzer can retain a current density of 10 mA·cm⁻² over 20 h of continuous operation without any distinct degradation. After the durability test, the morphology of catalysts was characterized (Fig. S5). The results showed good stability for 20 h. The concentrations of Co and Fe were detected by inductively coupled plasma mass spectrometry (ICP-MS). The levels of Co and Fe in the solution after the durability test were 0.4 and 0.2 µg·L⁻¹, respectively.

Morphology features of the as-obtained FeCo₂O₄ were further characterized using SEM. The image of FeCo₂O₄ shown in Fig. 2(a) reveals that the sample surface is covered with flower-like particulates (with an average size of 2 µm) formed by

dozens of nanoplates with an average thickness of around 60 nm. Energy-dispersive X-ray spectroscopy (EDX) mapping analysis (Fig. 2(b)) reveals that iron, cobalt, and oxygen elements are homogeneously distributed in the FeCo₂O₄ sample with the molar ratio of oxygen (46.92 at%), iron (14.49 at%), cobalt (29.31 at%), and carbon (9.27 at%). The Fe/Co ratio is determined to be 1/2 (inset of Fig. 2(a)).

Further analysis of these nanoplate structures using TEM reveals that they are mesoporous structures (Fig. 2(c)) composed of nanoparticles with an average size of about 12 nm (Fig. 2(d)). Fig. 2(d) displays a representative HRTEM image of the FeCo₂O₄ nanoparticles. The lattice parameter indicated by the arrows in Fig. 2(d) was measured to be 0.22 nm, corresponding to the (311) crystal plane of FeCo₂O₄. The nanoplates were further characterized using the selective area electron diffraction (SAED). The four marked diffraction rings in Fig. 2(e) correspond to the (220), (311), (511), and (440) planes of FeCo₂O₄.

The porosity of the FeCo₂O₄ nanoplates can be determined by N₂ sorption analysis (Fig. 2(f)–(g)). The sample exhibits a typical IV type isotherm with a type H3 hysteresis loop, which confirms that this material has a mesoporous structure with an average pore diameter of 17.4 nm. The BET surface area was around 42 m²·g⁻¹.

Surface chemical composition and element oxidation states of the FeCo₂O₄ MOFs were analyzed using XPS. Fig. 3(a) displays the C 1s spectrum of FeCo₂O₄ MOFs. The peaks at 288.4 and 286 eV are assigned to the O–C=O and C–O–C from the pure

Fig. 2. (a) FESEM images of FeCo_2O_4 , the inset shows EDX analysis; (b) Element mapping images of FeCo_2O_4 for Fe, Co, O, and the RGB images composed of three elemental maps; (c) Transmission electron microscopy (TEM) images; (d) HR-TEM image and the corresponding SAED patterns of FeCo_2O_4 ; N_2 adsorption-desorption isotherms (f) and the pore size distribution (g) of FeCo_2O_4 , respectively.

PTCDA cyclic anhydride, whereas the peak at 284.4 eV is assigned to the C–C. Figure 3(b) shows the O 1s spectrum of

FeCo_2O_4 MMOFs. The peaks at 533.6, 532, and 530.5 eV are assigned to the O–C=O, C=O, and C–O from the PTCDA cyclic anhydride, whereas the peak at 529.1 eV is assigned to the M–O (where M represents the metal). In the Co 2p spectra (Fig. 3(c)), two types of Co species (Co^{2+} and Co^{3+}) are obtained. The binding energies at 782.1 and 797.5 eV are ascribed to Co^{2+} . Another two fitting peaks at 780.1 and 795.4 eV are ascribed to Co^{3+} . These results indicate the co-existence of the Co(II) and Co(III) in FeCo_2O_4 (e.g., $\text{Co}^{3+}/\text{Co}^{2+}$ ratio = 2.0, estimated from the ratio between the corresponding peak areas). In the Fe 2p spectra (Fig. 3(d)), three types of Fe species (Fe^0 , Fe^{2+} , and Fe^{3+}) are detected. The fitted peak at 706.3 eV is ascribed to Fe^0 , the fitted peaks at 709.9 and 726.0 eV are ascribed to Fe^{2+} , and the fitted peaks at 712.3 and 728.7 eV are ascribed to Fe^{3+} . These results indicate that the iron in FeCo_2O_4 has mixed valences ($\text{Fe}^0/\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio = 1/15/10, estimated from the corresponding peak areas). The valence values are identified to change from single to mixed for Fe and Co ions.

When the Fe cations hop through the tetrahedral-trigonal-octahedral paths, the numbers of Fe cations increase, and thus a Bader charge of +1.92 e changes into charges of +2.82 e and +2.83 e at the trigonal transition state (TS) and the tetrahedral saddle-point state (SS), respectively. This suggests that the valence state of Fe increases when the Fe cation diffuses from the octahedron to the tetrahedron position. The Co cations also diffuse by moving through the octahedral–trigonal–tetrahedral path as described above but with an activation energy of 1.3 eV and formation energy into a tetrahedral intermediate of 1.2 eV. The Bader charge of Co changes from +2.92 e to +1.82 e and +1.83 e at the TS and SS states, respectively. This indicates that the valence state of Co is reduced when the Co cation diffuses from the octahedron to the tetrahedron position. The valence values of Fe and Co, which are obtained from the DFT analysis, are consistent with the XPS results (Fig. 3(c) and 3(d)).

Figure 4(a) illustrates the diffusing paths of metal ions from

Fig. 3. XPS analysis of FeCo_2O_4 MMOFs. (a) C 1s; (b) O 1s; (c) Co 2p; (d) Fe 2p.

Fig. 4. (a) Geometries of a migrating cation at unique positions along the reaction path. The five representative figures show the initial position of the cation in the octahedral site (1), the cation in the trigonal transition state (I) geometry (2), the cation in the tetrahedral saddle-point geometry (3), the cation in the trigonal transition state (II) geometry (4) and the final position of the cation in the octahedral site (5). The reaction coordinate labels correspond with those of the diffusion potential energy plot. Color scheme: gold sphere for migrating cation, blue for Co, gray for Fe, and red for O. The dotted squares and green arrows indicate cationic vacancies and the direction of the migrating cation along the reaction path, respectively. (b) Hopping activation energies for octahedral-octahedral migration for Fe, Co, and O ions in FeCo₂O₄ and Co ion in Co₃O₄; (c) Activation energies and relative rates for cations (A = Mn, Fe, Co, Ni, Cu, and Zn) hopping in ACo₂O₄.

the initial octahedral sites to the neighboring octahedral vacancies via a saddle-point plane. As shown in Fig. 4(b), the obtained hopping activation energies of Fe, Co, and O diffusions are 0.5, 1.3, and 1.7 eV, respectively. The obtained hopping activation energies of cationic (Fe and Co) diffusion for octahedral-octahedral migrations are lower than those of anionic (oxygen) diffusion. This can be attributed to the considerably higher equilibrium concentration of cation vacancies than those of oxygen vacancies in the ACo₂O₄ under the OER conditions. Recent studies proved that the crucial step for the OER was the cation diffusion in the spinel catalysts [12,32,33].

The conductivity of catalysts is linked closely with the hopping activation energies, which govern the hopping rate of ion diffusion [12,34,35]. We used DFT-based atomistic modeling to calculate the hopping activation energies of ion diffusion processes. Fig. 4(c) depicts the obtained hopping energies for A (A = Mn, Fe, Co, Ni, Cu, and Zn) ions in ACo₂O₄ crystals at 25 °C. The hopping activation barrier energies of Fe (0.5 eV) are much smaller than those of Cu (0.7 eV), Mn (0.8 eV), Ni (1.0 eV), Co (0.95 eV), and Zn (1.4 eV) in ACo₂O₄. Based on the ratios of the Arrhenius equations for the various migrations and their associated activation energies [12], the relative rates of cationic hopping through the ACo₂O₄ spinels were calculated, and the results are shown in Fig. 4(c). Clearly, the order sequence of the relative rates is as follows: FeCo₂O₄ > CuCo₂O₄ > MnCo₂O₄ > Co₃O₄ > NiCo₂O₄ > ZnCo₂O₄.

Electrical impedance spectroscopy (EIS) characterization (in Fig. S6) was further performed to study the effect of substitution of A on the electrical resistance of the ACo₂O₄ electrodes. The charge transfer between the catalyst and electrolyte was

an important indicator for evaluating the catalytic properties. EIS was utilized to analyze the behavior of charge transfer at the interface or the surface. Huge difference in the charge-transfer resistance (R_{in}) was observed for these ACo₂O₄ electrodes, ranging from the lowest value of FeCo₂O₄ (12.9 $\Omega\cdot\text{cm}^{-2}$) to the highest value of ZnCo₂O₄ (992 $\Omega\cdot\text{cm}^{-2}$). Therefore, the high electrical conductivity and faster charge transport of the FeCo₂O₄ as an electrode can guarantee its excellent OER performance [36].

When the A-site element is substituted with the transition metal elements Mn, Fe, Co, Ni, Cu, to Zn in a sequence, the electron numbers of the corresponding outer d-orbitals change from 5 to 10. The ions of metal elements existed in the form of Zn²⁺, Mn²⁺, and Cu⁺, whereas the elements Ni, Co, and Fe exhibited various oxidation states based on the XPS results (Fig. 5). According to the crystal field (CF) theory [37], the preference of an element to be in octahedral or tetrahedral geometry is mainly determined by the octahedral site preference energy (OSPE), which is defined as the difference between the crystal field splitting energy (CFSE) of the octahedral complex and a tetrahedral complex. To compare the preferences of forming an octahedral field or tetrahedral field, the OSPE can be written as:

$$\text{OSPE} = \text{CFSE}(\text{oct}) - \text{CFSE}(\text{tet}) \quad (4)$$

From Equation 4, the OSPE value as a function of the number of d-electrons can be calculated. The order of OSPE values for all the cations can be ranked as follows: Ni²⁺ > Fe²⁺ > Co³⁺ > Co²⁺ > Fe³⁺ > Mn²⁺ > Cu²⁺ > Zn²⁺.

The elements Mn²⁺, Cu⁺, and Zn²⁺ preferably occupy a tetrahedral position, but the elements of Ni²⁺ and Fe²⁺ prefer an octahedral position. The OSPE values of Ni²⁺ and Fe²⁺ are larger

Fig. 5. XPS analysis for Zn 2p in ZnCo₂O₄ (a), Cu 2p in CuCo₂O₄ (b), Ni 2p in NiCo₂O₄ (c), Co 2p in Co₃O₄ (d), Fe 2p in FeCo₂O₄ (e), and Mn 2p in MnCo₂O₄ (f).

than that of Co³⁺, so these cations in the tetrahedron can be exchanged with the octahedral Co³⁺. The cations A' valence state and distribution can be obtained from the state density of ACo₂O₄ crystal (Fig. S7) and X-ray absorption spectroscopy (XAS) [12,17]. For the Fe²⁺ ions, the results showed that exchange between Fe(Td) ↔ Co(Oh) easily occur. Thus, Fe can occupy both octahedron and tetrahedron positions. This might be the reason why the FeCo₂O₄ can easily form composite hybrid spinel structures. Our findings are supported by previous reports that the cations A' valence values depend on the occupied positions [12,14,17]. As stated above, the dominant factor for the OER performance of electrode materials is the spinel crystal field. According to the crystal field theory, the spinel crystal field was identified as the essential parameter to control cation A valence values and occupied positions.

4. Conclusions

In summary, ACo₂O₄ phases (A = Mn, Fe, Co, Ni, Cu, or Zn) were successfully synthesized in this work. Among these, the FeCo₂O₄ spinel oxide showed excellent OER catalytic activities with a current density of 10 mA·cm⁻² at an overpotential of 164 mV in alkaline media. Based on our experimental results and theoretical analysis, the spinel crystal field is the dominant factor for the OER performance of electrode materials. The spinel crystal field was further identified as the essential parameter for controlling the hopping activation energies, occupied positions, and valence states of cation A.

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Graphical Abstract

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Highly efficient mixed-metal spinel cobaltite electrocatalysts for the oxygen evolution reaction

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Cation substitution of spinel cobaltites is a promising strategy for optimizing the electrochemical performance for water splitting. The FeCo_2O_4 has an overpotential of 164 mV at a current density of $10 \text{ mA}\cdot\text{cm}^{-2}$ in alkaline media. The underlying mechanisms have been clarified by cation substitution with different numbers of d-electrons between 5 and 10. The crystal field of spinel ACo_2O_4 is identified as the key factor in dictating the OER performance of these spinel cobaltites.

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基于尖晶石型混合金属钴矿的高效析氧电催化性能

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摘要: 尖晶石钴矿(例如 ACo_2O_4 , 其中A = Mn, Fe, Co, Ni, Cu或Zn的阳离子取代)是一种精确调控其电子结构/性质, 并因此改善相应的电催化水分解析氧(OER)性能的有前途的策略. 然而, 有关它的基本原理和机制尚未完全理解. 为了确定尖晶石氧化物在OER中的作用, 已有实验和理论报道. 例如, Prabu发现 Ni^{3+} 离子取代 NiCo_2O_4 的八面体位点可以显著提高OER性能; Hutchings报道OER性能提高源自 Co_3O_4 八面体 Co^{3+} 的活性位; Wei研究发现 MnCo_2O_4 八面体位置的 Mn^{3+} 离子是OER

的活性位点。尽管多数研究没有对此给出清晰的解释,但这些研究清楚地表明,尖晶石氧化物对OER的电催化性能在很大程度上取决于过渡金属阳离子(A)的化合价态及其在尖晶石结构中的相应位点分布。本文旨在合成具有同种形貌的尖晶石 ACo_2O_4 混合金属有机骨架(MMOFs)材料,通过A位引入外层 d 电子数从5到10的过渡金属元素,如Mn, Fe, Co, Ni, Cu和Zn,系统研究催化水分解析氧机理。基于实验详细分析了不同阳离子的取代和其OER的催化行为,在获得的六种尖晶石 ACo_2O_4 催化剂中, FeCo_2O_4 催化剂在碱性溶液中具有出色的OER性能和稳定性,其在电流密度 $10\text{ mA}\cdot\text{cm}^{-2}$ 的超电势下 164 mV 。催化剂的电荷传输性能与离子和空位扩散的跳跃率密切相关。我们使用密度泛函理论计算阳离子在 ACo_2O_4 晶体中的扩散以及扩散的活化能,并且计算过程考虑自旋的激发能。使用VASP的搜索过渡态方法(NEB-DMTS)确定离子扩散的最小能量反应路径。结果表明,尖晶石钴矿 ACo_2O_4 晶格中的Fe取代可以显著加速电荷转移,从而获得增强的电催化性能。由第一性原理计算Fe阳离子通过四面体-三角平面-八面体路径扩散,具有 0.4 eV 的活化能和 0.5 eV 的能量以形成八面体中间体。当它跳跃时,阳离子(Fe)分别在过渡态和四面体鞍点(亚稳态)下从 $+1.82$ 的Bader电荷增加到 $+2.82$ 和 $+2.83$ 的电荷,这表明扩散的Fe在不同的位置具有的相应的价态。根据晶体场理论,通过八面体位置偏好能量(OSPE)是用于判断阳离子占据八面体或四面体的位置,其被定义为占据八面体和四面体的晶体场能量(CFSE)差。OSPE的顺序依次是 $\text{Ni}^{2+} > \text{Ni}^{3+} > \text{Mn}^{3+} > \text{Fe}^{2+} > \text{Co}^{3+} > \text{Co}^{2+} > \text{Fe}^{3+} > \text{Mn}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+}$,由于Fe(II)、Co(II)和Ni(II)的OSPE值大于Co(III)的OSPE值,这三种阳离子在四面体可以与八面体Co(III)发生交换。对Fe(II)离子,研究发现 $\text{Fe}(\text{Td}) \leftrightarrow \text{Co}(\text{Oh})$ 交换很容易进行,Fe既可以占据八面体又可以占据四面体,所以 FeCo_2O_4 为复合尖晶石结构,可以从 ACo_2O_4 晶体的X射线吸收光谱法获得阳离子A的价态和分布证实。更深入研究发现尖晶石 ACo_2O_4 的晶体场,不仅决定A位阳离子的价态,同时影响这些尖晶石钴矿OER性能的关键因素。
关键词: 阳离子取代的尖晶石钴矿; 晶体场; 氧还原反应; 水分解; 电催化

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