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A core-shell structured CoMoO₄•nH₂O@Co_{1-x}Fe_xOOH nanocatalyst for electrochemical evolution of oxygen



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ABSTRACT

Nickel-iron oxyhydroxide (Ni_{1-x} Fe_xOOH) is well recognized as the best-performing oxygen evolution reaction (OER) catalyst in alkaline electrolytes, however its analogue cobalt-iron oxyhydroxide (Co1-_xFe_xOOH) is surprisingly less explored despite their structural similarity. Inspired by our recent study on high-performance HER catalyst using the nanostructured CoMoO₄ • nH₂O precursor, herein, we report a facile synthesis of Co1-xFexOOH catalyst derived from the same precursor and its excellent electrocatalytic properties towards the OER in alkaline electrolytes. A core-shell structured nanocatalyst consisting of disordered Co1-xFexOOH layer over the surface of crystalline CoMoO4 nH2O nanosheets was synthesized using a simple hydrothermal method followed by anodic electrooxidation. Thus-prepared catalyst exhibited extraordinarily high and stable activity towards the OER in alkaline electrolyte, which outperformed most Co-based OER catalysts. Combined with the HER catalyst derived from the same CoMoO₄•nH₂O precursor as the cathode, we further developed and tested a simple water-splitting cell, which significantly surpasses the benchmarking IrO2-Pt/C couple (1.63 V) and requires a voltage of only 1.517 V to afford 10 mA cm⁻² in 1.0 M KOH solution. Density functional theory calculations were conducted to gain insight into the Fe-doping induced improvement of OER activity.

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1. Introduction

Electrochemical splitting of water, when coupled with renewable energy, provides a sustainable way to produce H₂, a clean and efficient energy carrier. This conversion of renewable but intermittent energy into storable chemical fuel is a highly desirable approach to solving the energy challenges [1-3]. Crucial to enabling this scheme is the development of active and robust electrocatalysts for both the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER). In contrast to the two-electron HER with one intermediate (H*), OER involves four-electron transfer and multiple catalytic intermediates (OOH*, OH*, O*) with strongly correlated binding energies [4-6]. As a consequence, OER typically requires a much larger overpotential than the HER, thus imposing a bottleneck for water splitting.

In the past decades, a number of noble and non-noble metal

Corresponding author. E-mail address: mspwang@scut.edu.cn (P. Wang). catalysts had been examined in terms of electrocatalytic activity towards the OER [4-8]. It was found that IrO_2 and RuO_2 performed best in acid conditions [5,9,10], while in basic electrolytes, these benchmark catalysts were outperformed by some non-noble metal catalysts, such as transition metal oxides/hydroxides [11-13], nitrides [14–16], sulfides [17–19], an selenides [20–22]. The identification of these active and low-cost OER electrocatalysts clearly represents an important progress in developing alkaline water electrolysis technology. From the studies of these non-noble metal catalysts, judicious combination of operando characterization and theoretical calculations has provided valuable insights into the local structure and surface chemistry of the catalysts at OER conditions [4,6,23-25]. This has led to a consensus that, regardless of precursor type, VIII group transition metal (Ni, Co, Fe) oxyhydroxides would form on the catalyst surface at high anodic potentials, and function as active phases for the OER [26-29]. In an indepth study of Ni-Fe oxyhydroxide, Bell and coworkers elucidated that the substituted Fe^{3+} cations in the NiOOH lattice were the active sites for the OER and the dramatically improve activity (500-



fold higher OER current density at an overpotential of 0.3 V) compared to those in FeOOH should stem from the alteration of Fe³⁺ electronic property upon incorporation into NiOOH, which in turn optimize the binding energies of OER intermediates [23]. Another study of Ni–Fe layered double hydroxides (LDH) by Stahl and coworkers, however, provided evidence supporting the formation of Fe^{4+} at OER conditions [30]. In addition, a recent theoretical investigation by Goddard and coworkers suggested that the synergy between Fe^{4+} and Ni^{4+} should be responsible for the favorable electrocatalytic performance of (Ni,Fe)OOH [31]. Although the nature of catalytic active site is still in debate, the coexistence of Ni and Fe as prerequisite for achieving high activity and their high valence states under oxidative conditions have been firmly established. In a latest study by Li and coworkers, similar improvement of OER activity in response to Fe³⁺ cation substitution was experimentally observed and theoretically validated in Co-Fe oxyhydroxide [32]. However, Co–Fe (oxy)hydroxide catalysts were significantly inferior to their Ni-Fe counterparts in terms of OER activity [33-36]. This was manifested by the larger OER overpotentials (60–100 mV at a current density of 10 mA cm⁻²) or lower turnover frequencies of Co-Fe catalysts as compared to the Ni–Fe catalysts [34–36]. Given the structural similarities of these two types of catalysts, such a significant difference in OER activity is fascinating. Currently, Co-Fe (oxy)hydroxides are still less explored particularly in comparison with the Ni-Fe (oxy)hydroxide catalysts, and the limited works mainly focused on the Co-Fe LDH [29,37–39]. In this regard, advanced synthetic methods for engineering of the composition and structure of Co–Fe catalyst surface are still required to explore its full potential for the OER.

Herein, we report a facile synthesis of Co_{1-x}Fe_xOOH catalyst and its excellent electrocatalytic properties towards the OER in alkaline electrolytes. A core-shell structured nanocatalyst consisting of the disordered Co_{1-x}Fe_xOOH layer over the surface of crystalline CoMoO₄•nH₂O nanosheets was synthesized using a simple hydrothermal method followed by anodic electrooxidation in a FeSO₄ solution. The thus-prepared catalyst exhibits extraordinarily high and stable activity towards the OER in alkaline electrolyte, which outperforms most Co-based OER catalysts reported up to date.

2. Experiment section

2.1. Chemicals and materials

Cobaltous nitrate hexahydrate (Co(NO₃)₂·6H₂O, 99%), sodium molybdate dihydrate (Na₂MoO₄·2H₂O, 99%), ferrous sulfate (FeS-O₄·7H₂O, 99%), hydrochloric acid (HCl, ca. 36–38% solution in water), potassium hydroxide (KOH, 95%), iridium dioxide (IrO₂, 99.9%), Nafion solution (5 wt% in mixture of lower aliphatic alcohols and water) and other reagents of analytical reagent grade were purchased from commercial sources and used as received. The cobalt foam (CF, \geq 99%) with a thickness of 1.5 mm, an area density of about 480 g m⁻² and an average pore size of 0.3 mm was purchased from Kunshan Jiayisheng Electronics Co., LTD. Deionized (DI) water was used throughout the experimental processes.

2.2. Preparation of electrode materials

A CF-supported cobalt molybdenum oxide-derived electrocatalyst was prepared using a hydrothermal method followed by anodic oxidation in FeSO₄ solution. Prior to use, CF was successively cleaned by ultrasonication in ethanol, HCl aqueous solution (1.0 M) and DI water. The cleaned CF ($1 \times 4 \text{ cm}^2$) together with 30 mL of the aqueous solution containing Co(NO₃)₂·6H₂O (0.02 M) and Na₂MoO₄·2H₂O (0.01 M) was then transferred into a 50 mL Teflonlined stainless autoclave. The autoclave was sealed and maintained at 150 °C for 6 h, then naturally cooled down to ambient temperature. The collected sample was thoroughly washed with DI water and ethanol and then dried in vacuum. The anodic electrooxidation of the catalyst sample was conducted in a CHI 660 E electrochemical workstation using a standard three-electrode setup. The hydrothermal sample was used as working electrode, and a Ag/AgCl electrode and a graphite plate as the reference and counter electrodes, respectively. The electrooxidation operation was performed in 0.01 M FeSO₄·7H₂O solution at a current density of 10 mA cm⁻² for 1 h. It was observed that the electrolyte gradually changed its color from light green to yellow during the electrooxidation process. For comparison, a Fe-free reference catalyst was prepared by anodic electrooxidation of the hydrothermal sample in 1.0 M KOH solution at 10 mA cm⁻² for 1 h. The IrO₂/CF sample was prepared using a universal approach for fabricating commercial noble-metalbased catalysts. Typically, 5 mg of IrO₂ catalyst powder was dispersed in a mixture solution of DI water (400 µL) and ethanol (400 μ L) containing 60 μ L 5 wt% of Nafion solution (Sigma-Aldrich) by sonicating for 1 h to form a homogeneous ink. Then, 450 µL of the homogeneous ink was loaded onto the CF $(1 \times 1 \text{ cm}^2)$ and then dried at 60 °C. According to the weight change of samples before and after catalyst loading, the IrO2 loading amount on CF was about 2.5 mg cm⁻². In preparation of the HER catalyst, the hydrothermal sample was annealed at 450 °C under a flowing H₂/Ar (1:10) atmosphere for 2 h. The ramping rate was $10 \circ C \cdot min^{-1}$.

2.3. Characterization

The morphology and microstructure of the catalyst samples were examined using field-emission scanning electron microscope (FE-SEM, ZEISS MERLIN) and high-resolution transmission electron microscope (HRTEM, JEOL-2100 F), both of which were equipped with an energy dispersive X-ray spectroscopy (EDS) analysis unit. Phase structure of the catalyst samples was analyzed by X-ray diffraction (XRD, Rigaku RINT 2000, Cu K α radiation). X-ray photoelectron spectroscopy (XPS) analyses of the catalyst samples were performed in a Thermo Scientific K-ALPHA⁺ spectrometer with binding energies referenced to adventitious carbon at 284.8 eV. The curve fitting was performed by XPS PEAK 4.1 software. Raman spectra were measured by Thermo Fisher Micro DXR microscope with a He–Ne laser (532 nm) excitation source at a resolution of 2 cm⁻¹.

2.4. Electrochemical measurements

Electrochemical measurements were performed in a CHI 660 E electrochemical workstation using a standard three-electrode setup, which consists of the as-prepared catalysts as working electrodes, a graphite plate and Hg/HgO (with 1.0 M KOH) as the counter electrode and reference electrode, respectively. All the measured potentials were referenced to the reversible hydrogen electrode (RHE) by adding a value of $(0.059 \times pH + 0.098)$ V. The polarization curves were measured by linear sweep voltammetry (LSV) in O₂-saturated 1.0 M KOH solution at a scan rate of 1 mV s^{-1} with iR compensation. According to the control experiments, an optimal compensation level of 85% was applied to achieve best curve shape and meanwhile to avoid curve distortion by overcompensation (Fig. S2, Supplementary Materials). The electrochemical impedance spectroscopy (EIS) measurements were carried out at open circuit potential in a frequency range of 100 kHz to 10 mHz with an amplitude of 5 mV. The Zview2 software was used for curve fitting. Electrochemical active surface areas (ECSA) of the catalysts were calculated based on the electrical double-layer capacitance (C_{DL}), which were determined from the scan-rate dependence of capacitive current in cyclic voltammetry (CV) measurements. The Faradaic efficiency (FE) was evaluated by comparing the theoretical value with the experimentally measured gas volume using a classic water-displacement method. All of the experiments were carried out at ambient temperature.

2.5. Theoretical calculations

All calculations were performed with the projector-augmented wave (PAW)[40] method using Vienna ab initio simulation packages (VASP) [41,42]. An energy cutoff of 450 eV was applied for the plan-wave basis set with Perdew-Burke-Ernzerhof (PBE) exchangecorrelation functional [43]. Spin-polarized density functional theory plus Hubbard-U framework (DFT + U) method [44,45] was employed with the value of U - J = 3.52 eV for both Co and Fe [46]. The (104) surface of β -CoOOH, the energetically most stable facet in a potential range of 1–1.9 V [46], was modelled by a five-layer 2×2 supercell with a vacuum layer of 15 Å. One of the top layer Co atoms was substituted by a Fe atom to present Fe-doped β -CoOOH. A $3 \times 5 \times 1$ Monkhorst-Pack k-point sampling was used for all surface properties. The adsorbed species and the top two layers of the surfaces were allowed to relax till all residual forces declined below 0.02 eV/Å, while the remaining layers were fixed. The free energy (ΔG) with the zero point energy and entropy corrections was computed following the procedure detailed in Ref.46. The theoretical overpotential was obtained from $\eta = \max [\Delta G1, \Delta G2, \Delta G3,$ $\Delta G4$]/e - 1.23 [V], in which $\Delta G1 \sim \Delta G4$ are the corresponding free energies of each elementary reaction step of OER.

3. Results and discussion

As illustrated in Scheme 1, the targeted $CoMoO_4 \cdot nH_2O@Co_1_xFe_xOOH$ catalyst was prepared by a two-step procedure. First, nanostructured cobalt molybdenum oxide was grown on a piece of cobalt foam (CF) via hydrothermal reaction. The resulting sample was then subjected to anodic electrooxidation in FeSO₄ solution. Interestingly, as demonstrated in our previous study, varying the second step from anodic electrooxidation to reductive annealing resulted in the formation of a high-performance HER catalyst [47]. A combination of these two catalysts derived from the same oxide precursor exhibited outstanding catalytic performance towards full water splitting, as stated below.

Morphology observation by FE-SEM (Fig. 1a and b) in

combination with XRD analysis (Fig. 2a and Fig. S1, Supplementary Materials) clearly showed that large amounts of crystalline $CoMoO_4 \cdot nH_2O$ nanosheets with a lateral size of several hundred nanometers were grown on the CF surface in the hydrothermal process, which self-assembled into 3D flower-like nanostructure [47]. This was further corroborated by selected area electron diffraction (SAED) analysis and HRTEM observation (Fig. 1c and d).

After the anodic electrooxidation in a FeSO₄ solution, the nanosheet morphology was well preserved (Fig. 1e). An EDS mapping analysis (Fig. S3, Supplementary Materials) clearly evidenced the incorporation of Fe element into the sample. According to the XPS (Fig. 2b) analysis, the Co/Fe molar ratio on the catalyst surface was about 1.25 and all the incorporated Fe existed in the form of Fe(III) cations. Meanwhile a fraction of Co(II) showed increased oxidation state from +2 to +3. These results, together with the pourbaix diagrams of Fe-H₂O and Co-H₂O systems [48,49], suggested the formation of a single-phase Co_{1-x}Fe_xOOH or CoOOH/ FeOOH composite under the applied anodic oxidation condition (1.7 V vs. RHE). In an effort to ascertain the nature of the oxyhydroxide, we conducted control experiments using in situ Raman spectroscopy technique. It was observed that the Co-O bands of CoOOH at 464 cm⁻¹ and 546 cm⁻¹ appeared with proceeding the anodic electrooxidation of CoMoO₄ • nH₂O in an alkaline solution (Fig. S4, Supplementary Materials). Similarly, the characteristic Fe-O vibrations of FeOOH were identified at 515 cm⁻¹ and 660 cm⁻¹ in the anodic electrooxidation of Fe foam in a Fe^{2+} aqueous solution [50]. When the anodic electrooxidation of the $CoMoO_4 \cdot nH_2O/CF$ sample was performed in a FeSO₄ solution, the Raman bands of the electrooxidation product appear to center at approximately 474 and 563 cm⁻¹, close to those observed in CoOOH, indicating the formation of oxyhydroxides. The slight blue shift of the Raman modes compared to those of CoOOH is probably due to the partial doping of Fe into CoOOH (Fig. 2c). Prolongation of electrooxidation duration caused intensity increase of Raman bands, but exerted no influence on the Raman wavenumbers. These results clearly suggested the possible formation of Fe-doped Co₁₋ _xFe_xOOH in the anodic electrooxidation of CoMoO₄•nH₂O in FeSO₄ solution. In the parallel XRD (Fig. 2a), SAED (Fig. 1f) and HRTEM (Fig. 1g) characterizations, no newly formed crystalline phase was detected. Rather, a close examination of the HRTEM image found that some tiny disordered domains with sizes typically below 5 nm appeared at the edge of nanosheets, forming an uneven



Scheme 1. Schematic illustration of the synthetic routes for CoMoO₄•nH₂O@Co_{1-x}Fe_xOOH/CF (OER) and Co/Co₂Mo₃O₈/CF (HER) catalysts.



Fig. 1. (a,b) FE-SEM images, (c) TEM image with the inset showing the corresponding SAED pattern and (d) HRTEM image of CoMoO₄•nH₂O/CF sample. (e) FE-SEM images, (f) TEM image and the corresponding SAED pattern (inset), (g) HRTEM image of the selected area in (h) as marked by white frame, (h) HAADF-STEM image and the corresponding EDS line scan profile along the red line as indicated and (i) EDS elemental mapping results of CoMoO₄•nH₂O@Co_{1-x}Fe_xOOH/CF sample. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

and semicontinuous amorphous layer covering the CoMoO₄•nH₂O nanocrystallites. Importantly, the parallel EDS line scanning profile (Fig. 1h) and elemental mapping (Fig. 1i) analyses revealed that this amorphous surface layer was supplemented by Fe. In an attempt to discern the role of Fe(III) in the amorphous surface layer, a control CoOOH sample over the surface of CoMoO₄•nH₂O was prepared using the similar anodic electrooxidation treatment, and the resulting sample was denoted as CoMoO₄•nH₂O@CoOOH/CF.

Property measurements were performed on the CoMoO₄•n-H₂O@Co_{1-x}Fe_xOOH/CF catalyst activity towards the OER in alkaline electrolyte, particularly in comparison with the benchmark IrO₂ and other relevant catalysts. As shown in Fig. 3a, it required an overpotential of only 230 mV to reach a current density of 10 mA cm⁻² in 1.0 M KOH, which was significantly lower than those required for IrO₂ (277 mV) and CoMoO₄•nH₂O@CoOOH/CF (285 mV) catalysts. Here, the small oxidation peaks at 1.35 V vs. RHE might be attributed to the oxidation of cobalt ions [51,52]. This

activity advantage was further manifested by the Tafel plots. As seen in Fig. 3b, the Tafel slope of the CoMoO₄•nH₂O@Co_{1-x}Fe_xOOH/ CF (42 mV·dec⁻¹) catalyst was much lower than those of CF (88 mV·dec⁻¹) and CoMoO₄·nH₂O@CoOOH/CF (87 mV·dec⁻¹) catalysts. The activity of CoMoO₄ • nH₂O@Co_{1-x}Fe_xOOH/CF catalyst is among the top level for the reported Co-based OER electrocatalysts, as tabulated in Table S1 in the Supplementary Materials. To better understand its outstanding activity and in particular its advantage over the Fe-free counterpart, we measured charge transfer resistance (R_{ct}) and C_{DL} using EIS technique and CV method, respectively. As seen in Fig. 3c and d, the two catalysts had similar R_{ct} and C_{DL}. This was quite understandable in view of their similarity in morphology, microstructural features and phase structure. Here, it was noticed that the R_{ct} values of the two catalysts were surprisingly low for the oxide materials. Presumably, the improved electrical conductivity should be attributed to the in situ growth of oxyhydroxides in the anodic electrooxidation process, which



Fig. 2. (a) XRD patterns. (b) XPS spectra of CoMoO₄•nH₂O@Co_{1-x}Fe_xOOH/CF and CoMoO₄•nH₂O/CF samples. (c) *In situ* Raman spectra of the CoMoO₄•nH₂O/CF sample in the process of anodic electrooxidation in FeSO₄ solution.



Fig. 3. (a) OER polarization curves with 85% iR compensation and the inset shows an enlarged view of OER polarization curves at 10 mA cm⁻². (b) The corresponding Tafel plots for the various electrocatalysts. (c) EIS Nyquist plots and fitting curves at onset potentials for $CoMoO_4 \cdot nH_2O@Co_{1-x}Fe_xOOH/CF$ and $CoMoO_4 \cdot nH_2O@CoOH/CF$ catalysts. (d) The capacitive current densities at open circuit potential (OCP) as a function of scan rate. (e) A comparison of the polarization curves of the $CoMoO_4 \cdot nH_2O@Co_{1-x}Fe_xOOH/CF$ before and after 6000 CV cycles in 1.0 M KOH. (f) Chronopotentiometry curves of $CoMoO_4 \cdot nH_2O@Co_{1-x}Fe_xOOH/CF$ with a manual 85% iR compensation, where electrolyte resistance was obtained from EIS analysis.

converts the Co(II) in the CoMoO₄ • nH₂O to the Co(III) in the oxyhydroxides and would likely generate Co vacancies in the CoMoO₄•nH₂O matrix simultaneously to maintain the overall charge neutrality and the mass balance of the metal species. This process seemingly also helps produce a low-resistance electrical contact between the oxyhydroxides and the Co-Mo-O matrix, as evidenced by a remarkable decrease of R_{ct} , from 22.73 Ω to 3.46 Ω in the CoMoO₄•nH₂O/CF sample (Fig. S5, Supplementary Materials). Additionally, in line with this speculation, the Co $2p_{1/2}$ signal showed subtle but significant shift to higher binding energy after the anodic electrooxidation (Fig. 2b). From these preliminary analyses, it was evident that the dramatically different OER activities between the two catalysts with and without Fe-doping should originate from the variation of intrinsic activity, instead of the differing electrical conductivity and electrochemically active surface area. This was further validated by our DFT calculations.

Fig. 4 illustrates the elementary steps of the OER on the (104) surface of pristine and Fe-doped CoOOH (a) as well as the corresponding free energy change profiles (b). Here, owing to the amorphous nature of CoOOH with and without Fe dopant, we selected the energetically most stable (104) facet as modelled surface. Our calculation results showed that the potential-limiting step of OER on pristine CoOOH surface is the formation of OOH on the Co site with a free energy change of 1.72 eV, and the resulting overpotential of 490 mV agrees well with the literature results [46,53]. After Fe doping in CoOOH, the rate-limiting step remains the same but the computed overpotential (400 mV) on the Fe site was remarkably lower than that on the Co site of CoOOH. These calculation results rationalized the experimental observation. highlighting the pronounced effect of Fe doping in improving the OER activity in alkaline conditions. Besides the high intrinsic activity of Co_{1-x}Fe_xOOH surface layer, the CoMoO₄•nH₂O substrate also play an important role in improving the electrocatalytic properties of the catalyst. This might be understood from two aspects: one is the hierarchical nanostructure of CoMoO₄•nH₂O offers opportunity for generating abundant accessible active sites. The other is the improved electrical conductivity presumably due to the presence of abundant Co-vacancies in the oxide lattice.

Besides the exceptionally high activity, the CoMoO₄•nH₂O@Co₁₋ _xFe_xOOH/CF catalyst also exhibited excellent durability. As shown in Fig. 3e and f, the catalyst showed negligible activity decay after 6000 CV cycles. And in the 24 h of constant-current measurements, it showed a potential fluctuation of only ± 1 mV at 10 mA cm⁻² and ± 10 mV at 100 mA cm⁻². Examination of the post-used catalyst by SEM, TEM, SAED and XPS (Fig. S6, Supplementary Materials) found that the morphology, phase structure and microstructural features of the catalyst sample were well preserved after long-term operations, further highlighting its superior stability towards the OER in alkaline conditions.

The present study demonstrated that anodic electrooxidation of CoMoO₄•nH₂O in FeSO₄ solution resulted in the formation of a highly active and robust catalyst towards the OER in alkaline electrolyte. Interestingly, our previous study found that the resulting catalyst from reductive annealing of the same precursor exhibited outstanding catalytic performance towards the HER in alkaline conditions [47]. For instance, the post-annealed Co/ Co₂Mo₃O₈ catalyst required an overpotential of 25 mV to afford a current density of 10 mA cm⁻² in alkaline solution, which is comparable to the performance of Pt/C catalyst. Inspired by these encouraging results, we further conducted overall water splitting test using these two catalysts derived from the same precursor as the anode and cathode, respectively. As seen in Fig. 5a, the twoelectrode water electrolysis cell required a voltage of only 1.517 V to afford 10 mA cm⁻² in 1.0 M KOH solution, which significantly outperformed the benchmarking IrO_2-Pt/C couple (1.63 V). Furthermore, the cell voltage showed only a negligible potential fluctuation in a 24 h of constant-current measurement at 10 mA cm⁻² (Fig. 5b). The FE of overall water splitting was measured at a current density of 10 mA cm⁻². It was observed that the collected O₂ and H₂ amounts match well with the theoretical values and the O₂/H₂ molar ratio is very close to 1:2, indicating a near-unity FE (Fig. 5c). Owing to the high electrocatalytic activities of the OER and HER catalysts, water electrolysis process could be driven by a single-cell AA battery with a nominal voltage of 1.5 V (Fig. 5d), as visually observed in the movie S1 in the Supplementary Materials.

Supplementary data related to this article can be found at https://doi.org/10.1016/j.electacta.2020.136125.



Fig. 4. (a) Schematic illustrations of the elementary steps of the OER on the (104) surface of pristine or Fe doped β-CoOOH. Red, pink and dark green spheres represent O, H, and Co atoms, respectively. Gold sphere represents active Co in pristine β-CoOOH or Fe atom in doped β-CoOOH. (b) Corresponding free energy landscape of the OER at Co site of pristine β-CoOOH and at Fe site of doped β-CoOOH. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)



Fig. 5. (a) LSV polarization curves for overall water splitting at a scan rate 1 mV s⁻¹. (b) Long-term durability of overall water splitting at a current density of 10 mA cm⁻². (c) Theoretically calculated and experimentally measured gas amount as a function of the overall water splitting time. (d) Photograph of the water-splitting cell powered by a single-cell AA battery.

4. Conclusions

A core-shell structured nanocatalyst consisting of disordered Co_{1-x}Fe_xOOH layer over the surface of crystalline CoMoO₄•nH₂O nanosheets was synthesized using a simple hydrothermal method followed by anodic eletrooxidation in a FeSO₄ solution. The thusprepared catalyst exhibited extraordinarily high and stable activity towards the OER in alkaline electrolyte. For example, it required an overpotential of only 230 mV to reach a current density of 10 mA cm⁻² in 1.0 M KOH, and showed a ± 1 mV potential fluctuation in a 24 h of constant-current durability test. According to our DFT calculations, such outstanding catalytic performance should originate from the presence of the Fe^{3+} doping in CoOOH lattice, which results in the optimization of the binding energies of OER intermediates. Since multicomponent transition metal oxides with novel nanostructures can be readily synthesized by solvothermal method, our work may open a new avenue to the development of high-performance electrocatalysts for the OER.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Jiajun Wang: Conceptualization, Methodology, Validation, Writing - original draft. **Hui Yin:** Investigation, Software. **Zhengjun Chen:** Formal analysis. **Guoxuan Cao:** Software, Data curation. **Ning Xu:** Visualization. **Hui Wu:** Writing - review & editing. **Ping Wang:** Writing - review & editing, Supervision, Project administration, Funding acquisition.

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Appendix A. Supplementary data

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