Degree of Geometric Tilting Determines the Activity of FeO₆ Octahedra for Water Oxidation

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ABSTRACT: Fe oxides and (oxy)hydroxides are promising cost-effective catalysts for the scalable water electrolysis. To improve the understanding of the structural factors required by the most active Fe sites, the role of geometric tilting in determining the activity of FeO₆ octahedron for water oxidation was investigated. The catalytic performance of FeO₆ octahedron in a series of crystalline structure, i.e., perovskites AFeO₃, spinel ZnFe₂O₄, and β-FeOOH, were found to be negatively correlated with their octahedral tilting degree. This correlation was rationalized through the Fe-O covalency, which is reflected by the O 2p-band center as well as the charge-transfer energy obtained from ab initio calculations. Thus, it was disclosed that FeO₆ octahedral tilting alters the activity for water oxidation through changing the covalency degree of Fe-O bonds.

INTRODUCTION

The oxygen evolution reaction (OER) is a critical reaction of several renewable energy technologies, such as water splitting^{1,2} and rechargeable metal-air batteries.^{3,4} However, the sluggish kinetics of the OER greatly impedes the efficiency of these technologies.^{5,6} To raise the reaction rate of OER, great effort has been made to explore superior OER electrocatalysts.⁶⁻¹⁶ Currently, oxides based on noble metals, such as RuO₂ and IrO₂, are benchmark catalysts for OER.^{17,18} Yet, their scalable application is restricted by the preciousness of these noble metals. Instead, oxides and (oxy)hydroxides based earth-abundant transition metals, such as Mn,^{19,20} Fe,¹³ Co,^{6,8,9,14} and Ni,^{9,21} are found more hopeful recently, because of their low cost and promising performance.

For a long time, Fe oxides and (oxy)hydroxides have been recognized to be slow at catalyzing OER, of which the performance is inferior to those with Co or Ni.²²⁻²⁴ Nonetheless, the addition of Fe into Co- or Ni-based oxide or (oxy)hydroxide catalysts significantly enhances their OER activity,²⁵⁻²⁸ and notably Ni_{1-x}Fe_xOOH are among the most active catalysts in alkaline solution.²¹ Recent relevant research undermines the previous conclusions about Fe-based catalysts and sheds new light on the role played by Fe in OER catalysis. Trotochaud et al. discovered that the incorporation of iron impurities in electrolyte was critical for the

high OER activity of NiOOH, which were intrinsically poor catalysts.²⁸ The similar phenomenon was also observed in Co-Fe (oxy)hydroxides.²⁵ Friebe et al. identified that the octahedrally-coordinated Fe³⁺ in Ni_{1-x}Fe_xOOH, with unusually short Fe-O bond lengths, acted as active sites for catalyzing OER.²⁹ Burke et al. revised the OER activity trends for first-row transition metal oxyhydroxides and demonstrated that FeOOH had the highest intrinsic activity.³⁰ Enman et al. analyzed the effects of metal dopants (Ti, Mn, La, Ce and Fe) on the OER activity and the Ni²⁺/Ni³⁺ oxidation potential of NiO_xH_y and concluded that Fe was the active site in Ni(Fe)O_xH_y.³¹ Besides the above findings about Fe (oxy)hydroxides, Fe-based oxides are reported to be capable of efficiently catalyzing OER. For example, Yagi et al. found that CaCu₃Fe₄O₁₂, CaFeO₃ and SrFeO₃ have high activities comparable to that of Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-δ}, a state-of-the-art OER catalyst in alkaline.¹³

As the above latest findings collectively indicate, Fe sites are capable of playing as an active site in OER catalysis. And in view of the rich resources of ferrite in the Earth, Fe-based OER catalysts may be a possible selection for large-scale water electrolysis.³² To facilitate the development of Fe-based catalysts, a good understanding of the local chemical structure required by the most active Fe sites is vital. Although a few reports have tried to correlate the activity of Fe sites with their Fe-O bond length,²⁹ coordination number²⁶ or

oxidation state,³³ the active Fe sites in these reports were detected on Ni/Co (oxy)hydroxides matrix, and thus the synergetic effect between Fe and Ni/Co may have an influence on the results. Therefore, a further study purely based on pristine Fe sites for OER catalysis is necessary.

Here, we set the ferrite polyhedra into a series of crystal-line phases, i.e., perovskites AFeO_3 ($\text{A} = \text{La, Pr, Gd, and Y}$), spinel ZnFe_2O_4 and $\beta\text{-FeOOH}$, to modulate the frame of FeO_6 octahedra. Perovskite and spinel (marked as ABO_3 and AB_2O_4 , respectively), are two most widely studied oxide families owing to their adjustability in physicochemical properties. In perovskites ABO_3 , A-site cations, usually occupied by rare earth, alkaline, and alkaline earth metals, are regarded to be catalytically inactive, while B-site transition metals are known as active sites.³⁴ Yet, varying the size of A-site cations may lead to the rotation and distortion of BO_6 octahedra.³⁴ For spinel oxides AB_2O_4 , the octahedrally-coordinated B-site cations are reported to play a key role in catalyzing OER.¹¹ And when occupied by Zn^{2+} cations with d^{10} electronic configuration, the tetrahedrally-coordinated A sites (Zn^{2+}) in spinel are considered as catalytically inactive.^{11,35} In this work, the OER activities of FeO_6 octahedra in AFeO_3 ($\text{A} = \text{La, Pr, Gd, and Y}$), ZnFe_2O_4 and $\beta\text{-FeOOH}$ were examined. And with the help of density functional theory (DFT) calculations, two electronic parameters related to Fe-O covalency, the O 2p-band center⁸ and the charge-transfer energy,³⁶ were computed to reveal how the geometric tilting of FeO_6 octahedron influences the OER catalytic performance. This investigation contributes to a better understanding of the factors that affect the intrinsic OER activity of Fe-based catalysts, and aids in the further development of highly cost-effective OER catalysts.

EXPERIMENTAL SECTION

Material synthesis. Perovskites AFeO_3 ($\text{A} = \text{La, Pr, Gd, and Y}$) were synthesized with a sol-gel method reported in literature.³⁷ Briefly, stoichiometric quantities of A-site metal nitrate ($\text{A} = \text{La, Pr, Gd, and Y}$) and iron nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) were dissolved into a solution containing Ethylenediaminetetraacetic acid (EDTA), ammonium hydroxide (NH_4OH), and citric acid ($\text{C}_6\text{H}_8\text{O}_7$). Then, the mixture was heated and continuously stirred at 260°C until the solution became a homogeneous gel. After it, the gel was heated at 200°C in an oven to form precursor. Finally, the precursor underwent calcination at 1000°C for 5 hours in air. For the synthesis of spinel ZnFe_2O_4 , 10 mmol $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 20 mmol $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 60 mmol $\text{C}_6\text{H}_8\text{O}_7$ and 30 mmol urea were dissolved in 200 ml deionized water. Added with 20 mL nitrite acid, the solution was heated and continuously stirred at 90°C until a homogeneous gel formed. Then the gel was heated at 170°C for 12 hours to form precursor, followed by annealing at 800°C in air for 6 hours. $\beta\text{-FeOOH}$ was synthesized by a hydrolysis method previously reported.³⁸ 10 mL of 0.5 mol/L aqueous FeCl_3 was added into 70 mL deionized water. After dried in an oven at 100°C for 24 hours, the solution became precipitates. Then the formed precipitates were washed with deionized water and ethanol several times and dried at 80°C for 12 hours.

Physical characterization. The crystal structures of as-synthesized materials were characterized with a Bruker D8 Advance XRD with Cu $\text{K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) at a scan rate of 2° min^{-1} . The field emission scanning electron microscope (FESEM) images of samples were recorded on a JEOL FESEM 7600F at 5kV. The Brunauer-Emmett-Teller (BET) specific surface areas of samples were measured with ASAP Tristar II 3020. X-ray Absorption Spectroscopy (XAS) characterization was carried out at Singapore Synchrotron Light Source, XAFCA beamline.

Electrode preparation. Electrodes for electrochemical characterization were prepared by drop-casting the ink of catalysts onto glassy carbon rotating-disk electrodes (RDEs) with the geometric surface area of 0.196 cm^2 . The ink of catalysts is $5 \text{ mg}_{\text{oxide}} \text{ mL}^{-1}$ mixture, composed of 5 mg sample, 2 mg acetylene black (AB), 750 μL water, 225 μL isopropanol (IPA) and 25 μL Nafion® perfluorinated resin solution (5 wt% in water). Before drop-casting, RDEs were polished with alumina slurry and then repeatedly ultrasonicated in a solution consisting of ethanol and DI water. After being cleaned, electrodes dried at room temperature in air. Then the ink of catalysts underwent ultrasonication for 30 minutes to make oxides and AB homogenously dispersed in the suspension. Finally, 10 μL ink was drop-casted on an electrode and dried at ambient condition for the evaporation of water and IPA.

Electrochemical characterization. Electrochemical measurements were conducted in a three-electrode cell on a PINE WaveDriver 20 bipotentiostat. A RDE electrode, a platinum wire and a saturated calomel reference electrode (SCE) were used as the working electrode, the counter electrode, and the reference electrode, respectively. All electrochemical measurements were performed in O_2 -saturated 0.1 M KOH electrolyte. Cyclic voltammetry (CV) measurements were conducted from 0.2 V to 0.8 V (vs. SCE) at a scan rate of 10 mV s^{-1} and a rotation speed of 1600 rpm. For the correction of capacitive currents, the currents used for comparison is the average of the forward and backward scan of a CV scan. And the measured potentials were corrected by solution resistance. The solution resistance was determined by electrochemical impedance spectra (EIS) tests. All EIS were recorded at 0.6 V (vs. SCE) with frequencies ranging from 10^5 to 10^{-1} Hz and an AC voltage amplitude of 10 mV. In this study, all potentials were referenced to the reversible hydrogen electrode (RHE) scale ($\text{RHE} = \text{SCE} + 1.0134 \text{ V}$).

Density functional theory (DFT) calculations. DFT calculations were performed using the Vienna Ab Initio Simulation Package (VASP) software^{39,40} with the projector-augmented plane-wave (PAW) method.⁴¹ And the exchange-correlation interactions of valence electrons are treated by the generalized gradient approximation (GGA) method with a Perdew-Burk-Ernzerhof (PBE) functional.⁴² The effective Hubbard U parameter for describing the on-site Coulomb interaction of the d-electrons of Fe was set to be 4.0 eV.³² The magnetic configurations of AFeO_3 ($\text{A} = \text{La and Gd}$) at room temperature were found to be G-type antiferromagnetic (GAFM).^{43,44} For consistency, the magnetic structures of all samples were set to be GAFM. A γ -centered $7 \times 7 \times 5$ k-point mesh was used for AFeO_3 , a $5 \times 5 \times 5$ k-point mesh

for ZnFe_2O_4 and a $4 \times 4 \times 14$ k-point mesh for $\beta\text{-FeOOH}$. In all calculations, the energy cutoff was set to be 520 eV, and the energy tolerance was set to be 10^{-6} eV. After structural relaxation with a force tolerance of 0.02 eV/Å, the density of states (DOS) was calculated using the tetrahedron method with Blöchl corrections.⁴⁵

RESULTS AND DISCUSSION

Chemical environmental variables for FeO_6 octahedra. To modify the frame of FeO_6 octahedra, perovskite AFeO_3 (A = La, Pr, Gd, and Y), spinel ZnFe_2O_4 and $\beta\text{-FeOOH}$ were synthesized (Figure S1), and their phase purity is verified by the Rietveld refined XRD patterns in Figure 1. The reliability factors of these Rietveld refinements are quite small (Table S1). In crystal structure, FeO_6 octahedra in perovskites are totally corner-shared, in contrast with $\beta\text{-FeOOH}$. In cubic perovskite structure (Figure 2a), FeO_6 are regular octahedra, and Fe-O-Fe bond angles are 180° . Driven by the mismatch of A-site cation size, GdFeO_3 -type perovskites (Figure 2b) deviate from the ideal cubic phase to stabilize crystal structure, resulting in the adjustability of FeO_6 octahedra frame. In GdFeO_3 -type distortion, essentially rigid FeO_6 octahedra are tilted, and Fe-O-Fe bonds are bent.⁴⁶ In this study, all the as-synthesized AFeO_3 are GdFeO_3 -type perovskites, crystalizing in orthorhombic structure with Pnma space group (Figure 1a-d and Table S1). Identically with trivalent valence state, A-site cations in AFeO_3 are with ionic radii in decreasing order: $\text{La}^{3+} > \text{Pr}^{3+} > \text{Gd}^{3+} > \text{Y}^{3+}$ (Table S2). And the smaller the A-site ionic radius is, the more distorted the corresponding AFeO_3 is, bringing about the modulation of the FeO_6 octahedra frame. In the normal spinel ZnFe_2O_4 (Figure 2c), iron cations occupy octahedral sites while zinc cations reside in tetrahedral sites. The FeO_6 octahedra in the normal spinel ZnFe_2O_4 are purely edge-linked, and the way of connection is different from that in $\beta\text{-FeOOH}$ (Figure 2d).

Figure 1. XRD patterns and Rietveld refinement results of as-synthesized (a) LaFeO_3 , (b) PrFeO_3 , (c) GdFeO_3 , (d) YFeO_3 , (e) ZnFe_2O_4 , and (f) $\beta\text{-FeOOH}$.

Figure 2. Illustration of FeO_6 octahedra frames in perovskite AFeO_3 , spinel ZnFe_2O_4 , and $\beta\text{-FeOOH}$. In an ideal cubic perovskite (a), corner-sharing FeO_6 are regular polyhedra, and Fe-O-

Fe bond angles are 180°. In GdFeO₃-type perovskites (b), essentially rigid FeO₆ octahedra are tilted. In the normal spinel ZnFe₂O₄ (c), FeO₆ octahedra are edge-connected, and Fe-O-Fe bond angles are close to 90°. In β-FeOOH (d), double chains of edge-sharing FeO₆ are linked by corners, and thus there are several values of Fe-O-Fe bond angles.

To evaluate the distortion degree of FeO₆ octahedra in AFeO₃, ZnFe₂O₄, and β-FeOOH, two variables were employed, i.e., the deformation index δ and the average Fe-O-Fe angle $\langle\text{Fe-O-Fe}\rangle$. Specifically, δ is used to describe the deformation of FeO₆ from regular octahedra and is calculated by the equation

$$\delta = \frac{1}{n} \sum_i \left[\frac{(r_i - r)}{r} \right]^2$$

where r_i , r and n represent the Fe-O bond length, average Fe-O bond length and the number of Fe-O bonds in a FeO₆ octahedron, respectively. With less deformation, the index is smaller; and if the octahedron is regular, δ approaches to 0. Another variable $\langle\text{Fe-O-Fe}\rangle$, the mean value of Fe-O-Fe bond angles, is used to indicate the tilting degree of FeO₆ octahedra. The more tilted the FeO₆ octahedra are, the smaller $\langle\text{Fe-O-Fe}\rangle$ is; when the FeO₆ octahedra are orthogonal, $\langle\text{Fe-O-Fe}\rangle$ is 180°. The Fe-O bond lengths and Fe-O-Fe bond angles of AFeO₃ and ZnFe₂O₄ used for above calculation are obtained from the results of Rietveld refinement (summarized in Table S3 and Table S4). In β-FeOOH, the FeO₆ octahedra are not only edge-shared but also corner-shared, resulting in the variety of Fe-O lengths and Fe-O-Fe angles, and thus the Rietveld refinement is incapable to give reliable results. Hence, the crystal parameters for β-FeOOH⁴⁷ is taken from Inorganic Crystal Structure Database (ICSD) and summarized in Table S5.

Figure 3. (a) Internal deformation index δ and average Fe-O bond length of AFeO₃, ZnFe₂O₄, and β-FeOOH. (b) Average Fe-O-Fe angle $\langle\text{Fe-O-Fe}\rangle$ of AFeO₃, ZnFe₂O₄, and β-FeOOH, which is an indicator of the FeO₆ octahedral tilting degree.

As shown in Figure 3a, the deformation index δ of AFeO₃ and ZnFe₂O₄ are near to zero, indicating that their FeO₆ octahedra remain essentially undeformed ($\delta \approx 0$). The δ of β-FeOOH is as small as 0.00251, and hence the internal deformation of FeO₆ octahedra in β-FeOOH is insignificant. Besides, the average Fe-O bond length of every sample is around 2.0 Å, despite that of β-FeOOH (2.0835 Å) is a little longer. In contrast, the values of $\langle\text{Fe-O-Fe}\rangle$ follow the trend, AFeO₃ > β-FeOOH > ZnFe₂O₄, as displayed in Figure 3b. Notably, the average Fe-O-Fe angle of AFeO₃ increases at the same pace with the increment of A-site ionic radii, which

agrees well with previous reports.^{48,49} In addition, it is necessary to mention that the only value of the Fe-O-Fe angle in ZnFe₂O₄ (94.854°) is sharply larger than the smallest one in β-FeOOH (86.619°). According to the above analysis, the main distortion in AFeO₃, ZnFe₂O₄, and β-FeOOH is FeO₆ octahedral tilting.

Figure 4. (a) Normalized Fe K-edge XANES spectra of AFeO₃, ZnFe₂O₄, β-FeOOH, and standard materials. (b) Fe valence states in AFeO₃, ZnFe₂O₄, and β-FeOOH.

To confirm the oxidation states of Fe in the ferrites tested in this study, Fe K-edge X-ray absorption near edge spectroscopy (XANES) was employed. In the normalized Fe K-edge XANES spectra (Figure 4a), the shift of the absorption edge reflects the variation of Fe valence states. The position of the absorption edge is set to be the energy at the highest peak of the first derivative of the absorbance. Since the oxidation states of Fe in the standard reference (Fe₃O₄ and Fe₂O₃) are known, the valence states of Fe in other ferrites can be quantified by comparing the edge positions. It can be drawn from Figure 4b that Fe in AFeO₃, ZnFe₂O₄, and β-FeOOH is uniformly in trivalent state, which is in agreement with our expectation. Moreover, Zn K-edge, as well as Fe K-edge, extended X-ray absorption fine-structure spectroscopy (EXAFS) was used to verify the occupation of Fe on the octahedral sites in the ZnFe₂O₄ (Figure S2).

Integrating the results of above characterizations, the primary environmental variable for FeO₆ octahedra in AFeO₃, ZnFe₂O₄ and β-FeOOH is the octahedral tilting indicated by $\langle\text{Fe-O-Fe}\rangle$, in view of the little difference in the average Fe-O bond length, internal deformation of FeO₆ octahedra, and the valence state of Fe.

Electrochemical performance. The OER catalytic performance of AFeO₃, ZnFe₂O₄, and β-FeOOH were evaluated by CV in 0.1 M KOH at a scan rate of 10 mV s⁻¹ and a rotation speed of 1600 rpm. To obtain the intrinsic activity of these materials, their current densities are normalized by their surface area determined by nitrogen BET analysis (Figure S3 and Table S6). As shown in Figure 5a, the intrinsic OER activities of AFeO₃ surpass those of ZnFe₂O₄ and β-FeOOH and enhance along with the increase of A-site cation size: LaFeO₃ > PrFeO₃ > GdFeO₃ > YFeO₃. In Figure 5b, the specific activity of the best performance rutile IrO₂ is taken from the landmark report.¹⁷ The performance of LaFeO₃ tested here (~ 1.59 V at 50 μA cm⁻²_{oxide}) is consistent with that reported by Suntivich et al.⁶ It is noteworthy that the intrinsic activ-

ity of LaFeO_3 in alkali is approaching to that of the benchmark IrO_2 , and this further demonstrates that Fe-based materials are promising cost-effective OER catalysts.

Figure 5. (a) The iR-corrected and capacitance-corrected OER currents of AFeO_3 , ZnFe_2O_4 , and $\beta\text{-FeOOH}$ measured in O_2 -saturated 0.1 M KOH at 10 mV s^{-1} scan rate and 1600 rpm. (b) OER specific activities of Fe-based catalysts and benchmark rutile IrO_2 .¹⁷ The error bars represent at least three independent measurements.

In Figure 6, the OER catalytic performance of Fe-based materials can be directly correlated with their average Fe-O-Fe bond angles, $\langle\text{Fe-O-Fe}\rangle$. The specific activities at 1.7 V vs. RHE and the iR-corrected potential at 0.04 mA cm^{-2} (Table S7) are used as the figures of merit. As indicated by the trend line, the closer to 180° the $\langle\text{Fe-O-Fe}\rangle$ is, the higher the OER activity is. Yet, there is a small discrepancy that the activity of $\beta\text{-FeOOH}$ is lower but the $\langle\text{Fe-O-Fe}\rangle$ of $\beta\text{-FeOOH}$ is larger than that of ZnFe_2O_4 . This seemingly divergency may be due to a couple of reasons. First, the more deformed FeO_6 octahedra and stretched Fe-O bonds in $\beta\text{-FeOOH}$ (Figure 3a) may lower the activity of $\beta\text{-FeOOH}$. Second, Fe-O-Fe angles in $\beta\text{-FeOOH}$ are widely ranged, and the smallest one may be heavily weighted against OER catalysis. In view of the justifiability of this minor discrepancy, it still can be inferred that the OER activity of ferrites is negatively related to the FeO_6 octahedral tilting. Uncovering the origin of this correlation is necessary for the further understanding of the activity difference observed among these Fe-based catalysts.

Figure 6. Evolution of (a) the specific activity at 1.7 V vs. RHE and (b) the iR-corrected potential at 0.04 mA cm^{-2} versus the average Fe-O-Fe angle of AFeO_3 , ZnFe_2O_4 , and $\beta\text{-FeOOH}$. The dashed gray lines are displayed for guidance. The error bars represent at least three independent measurements.

Density of states analysis. Recently, the importance of the metal-oxygen covalency is highlighted by the studies on transition metal oxides with high OER activity.^{6,7,13,50,51} The metal-oxygen covalency is linked to the interfacial charge-transfer kinetics during the OER.⁶ The enhanced covalency can lead to increased intrinsic activity.⁶ As ever reported, the electronic properties of perovskites are highly sensitive to the small changes of structural distortion, e.g., the variation of metal-oxygen-metal bond angles.⁵²⁻⁵⁴ Hence, the Fe-O covalency in AFeO_3 probably is influenced by the average Fe-O-Fe bond angle varying with A-site ionic radii. Accordingly, the Fe-O covalency affected by FeO_6 octahedral tilting may be the cause of the difference in the OER activities of AFeO_3 , ZnFe_2O_4 , and $\beta\text{-FeOOH}$.

To verify this conjecture, DFT calculations were performed on fully relaxed structures of AFeO_3 , ZnFe_2O_4 , and $\beta\text{-FeOOH}$ to study their electronic properties. The calculated partial density of states (PDOS) of Fe 3d and O 2p orbitals are displayed in Figure 7. It can be observed that their density of states (DOS) at the Fermi energy is 0 and their band gaps (summarized in Table S8) are smaller than 3 eV, indicating that they are semiconductors.⁵⁵ It is also observable that the valence band near the Fermi level is dominated by O 2p states, with a small contribution from Fe 3d states. As for the conduction band (unoccupied states above E_F), it is primarily attributed to Fe 3d states, with a small amount of O 2p character. The above observations reasonably agree with existing theoretical^{32,43} and experimental^{48,56-58} studies.

Figure 7. PDOS plots of O 2p-band and Fe 3d-band for (a) LaFeO₃, (b) PrFeO₃, (c) GdFeO₃, (d) YFeO₃, (e) ZnFe₂O₄, and (f) β-FeOOH. The black dashed lines are displayed to indicate the position of the Fermi energy level E_F , which is at $E = 0$ eV.

To reflect the degree of covalency, two electronic parameters are calculated, i.e., the O 2p-band center ($\bar{\epsilon}_{O\ 2p}$) and the charge-transfer energy (Δ). As illustrated in Figure 8a, the O 2p-band center is the first moment of occupied O 2p states. It has been shown that the DFT calculated O 2p-band center relative to the Fermi level is a good descriptor for the OER activity of perovskite oxides and a higher O 2p-band center indicates better activity.^{8,9} This is justified by that the shift of the O 2p-band center reflects the variation of metal-oxygen hybridization⁸, which alters the degree of covalency.⁵⁰ Yet, the recent report by Shao-Horn et al. experimentally demonstrates that the charge-transfer energy is a more universal OER activity descriptor in view of the difference in the OER mechanisms on semimetallic and semiconducting oxides.³⁶ For semiconducting oxides, the experimentally determined charge-transfer energy tracks the DFT calculated energy difference between the unoccupied metal 3d and occupied O 2p-band centers (Figure 8a), i.e., the metal-oxygen covalency.³⁶ The lower the charge-transfer energy is, the greater the covalency is, and thus the higher the OER activity is. To make a reliable assessment of the Fe-O covalency, both the two parameters, $\bar{\epsilon}_{O\ 2p}$ and Δ (summarized in Table S9), are extracted from the PDOS plots in Figure 7 and shown in Figure 8a. In General, the O 2p-band center and

the OER activity follow the same trend, $\text{AFeO}_3 > \text{ZnFe}_2\text{O}_4 > \beta\text{-FeOOH}$, which is opposite to that of the charge-transfer energy, i.e., the DFT calculated center gap between the unoccupied Fe 3d-band and the occupied O 2p-band.

Figure 8. (a) Relationships between the Fe 3d and O 2p-band positions, the O 2p-band center ($\bar{\epsilon}_{O\ 2p}$) and the charge-transfer energy (Δ); the trends in the unoccupied Fe 3d and occupied O 2p-band centers of Fe-based catalysts are shown on the right. (b) Relationship between the DFT calculated O 2p-band center relative to E_F (eV) and the average Fe-O-Fe angle. (c) Relationship between the DFT calculated charge-transfer energy (eV) and the average Fe-O-Fe angle. The dashed gray lines are shown for guidance.

In Figure 8b-c, the O 2p-band center relative to the Fermi level and the DFT calculated charge-transfer energy are associated with the average Fe-O-Fe angles of AFeO₃, ZnFe₂O₄, and β-FeOOH. The general trend is that not only the O 2p-band center is uplifted but also the charge-transfer energy is decreased with the increase of $\langle \text{Fe-O-Fe} \rangle$. This is consistent with our conjecture that Fe-O covalency is affected by the FeO₆ octahedral tilting. The higher dependence of the O 2p-band center vs. E_F on $\langle \text{Fe-O-Fe} \rangle$ suggests that the position of the Fermi level is more sensitive to the octahedral tilting than the Fe 3d-band position. Moreover, it is noteworthy that both the O 2p-band center and the charge-transfer energy reflect that ZnFe₂O₄ has a greater Fe-O covalency than β-FeOOH. As mentioned earlier, the electronic properties are strongly related with structural distortion, and thus the small deformation of FeO₆ octahedra and the slight elongation of Fe-O length probably decrease the Fe-O covalency in β-FeOOH to be weaker than that in ZnFe₂O₄. This explanation is also reasonable for the inferior activity of β-FeOOH to that of ZnFe₂O₄.

Figure 9. Evolution of the iR-corrected potential at 0.04 mA cm⁻² versus (a) the O 2p-band center relative to E_F (eV) and (b) the DFT calculated charge-transfer energy (eV) of AFeO₃, ZnFe₂O₄, and β-FeOOH. The error bars represent at least three independent measurements. The dashed gray lines are obtained from linear fitting.

In Figure 9 and Figure S4, both the O 2p-band center and the DFT calculated charge-transfer energy are well correlated with the OER activity, demonstrating the effectiveness of the two parameters as descriptors in these Fe-based materials. Besides, the DFT charge-transfer energy exhibits a better correlation versus the OER activity than the O 2p-band center. This agrees with the conclusion of Shao-Horn et al. that the charge-transfer energy is a better OER activity descriptor than the O 2p-band center.³⁶

In view of the above analysis, the role played by the FeO₆ octahedral tilting in water oxidation can be disclosed. With less tilted FeO₆ octahedra, the Fe-O covalency is augmented, which can be reflected by the O 2p-band center closer to the Fermi level as well as the lower charge-transfer energy, and thus the intrinsic OER activity over Fe sites is enhanced.

CONCLUSIONS

In this study, FeO₆ octahedra were set in a series of crystalline ordered environments, i.e., perovskites AFeO₃, spinel ZnFe₂O₄, and β-FeOOH, to investigate the role of FeO₆ octahedral tilting in catalyzing OER. The average Fe-O-Fe angle, <Fe-O-Fe>, was used as the indicator for the octahedral tilting degree. It was observed that <Fe-O-Fe> is positively related to the OER activity and 180° is expected to be the optimal value. With the aid of DFT calculation, two electronic parameters relevant with Fe-O covalency, the O 2p-band center and the charge-transfer energy, were found to be correlated with <Fe-O-Fe> and the OER activity of ferrites. In view of the above, it was revealed that the FeO₆ octahedral tilting alters the degree of Fe-O covalency and thus affects the OER activity.

ASSOCIATED CONTENT

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