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Mechanistic understanding on oxygen evolution reaction on γ -FeOOH (010) under alkaline condition based on DFT computational study

Miru Tang, Qingfeng Ge*

Department of Chemistry and Biochemistry, Southern Illinois University, Carbondale, IL 62901, USA

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ABSTRACT

An efficient and economical oxygen evolution reaction (OER) catalyst is critical to the widespread application of solar energy to fuel conversion. Among many potential OER catalysts, the metal oxyhydroxides, especially FeOOH, show promising OER reactivity. In the present work, we performed a DFT + U study of the OER mechanism on the γ -FeOOH (010) surface. In particular, we established the chemical potential of the OH^- and hole pair and included the OH^- anion in the reaction pathway, accounting to the alkaline conditions of anodic OER process. We then analyzed the OER pathways on the surface with OH^- , O- and Fe-terminations. On the surface with OH^- and O- terminations, the O_2 molecule could form from either OH reacting with the surface oxygen species ($-\text{OH}^*$ and $-\text{O}^*$) or the combination of two surface oxygen species. On the Fe-terminated surface, O_2 can only form by adsorbing OH on the Fe sites first. The potential-limiting step of the oxygen evolution with different surface terminations was determined by following the free-energy change of the elementary steps along each pathway. Our results show that oxygen formation requires recreating the surface Fe sites, and consequently, the condition that favors the partially exposed Fe sites will promote oxygen formation.

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1. Introduction

The oxygen evolution reaction (OER) is involved in a number of energy conversion and storage technologies, including solar driven water splitting for hydrogen production and rechargeable metal-air batteries [1–4]. The OER, a four-electron oxidation reaction, is the limiting step of the entire water splitting process due to its slow kinetics [5,6]. Therefore, catalysts are needed to improve the kinetics of OER. The oxidative nature of the anode under the oxygen evolution conditions makes metal oxides the natural choices of the catalysts for OER. The

anode catalysts based on RuO_2 and IrO_2 have been demonstrated to be effective for OER, showing low overpotentials at the high current density in the acidic electrolyte water electrolyzer [7–9]. However, the practical application of these materials has been hindered due to their high costs and low natural abundance.

Recently experimental studies demonstrated that the $\text{BiVO}_4/\text{MOOH}$ (with $\text{M} = \text{Fe}, \text{Ni}, \text{Co}$) co-catalyst shows outstanding performance matching the traditional noble metal oxides-based photocatalyst (IrO_2 , RuO_2 , etc.) for solar water splitting [10–13]. Those studies stimulated great interests in ex-

* Corresponding author. E-mail: qge@chem.siu.edu

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ploring the oxides/oxyhydroxides of the 3d transition metals as catalysts for OER [14–24]. Man et al. [25] measured the overpotential for the OER of oxyhydroxides of several 3d elements on Pt(111) as catalysts and reported an activity trend as $\text{Ni} > \text{Co} > \text{Fe} > \text{Mn}$. Boettcher and coworkers [22,26,27] concluded that the most active structures are those where Fe is supported in a Ni or Co oxyhydroxide host. In such structures, Fe provides the active sites while the host provides the needed electrical conductance and surface area. Hybrid structures including nanotube arrays exhibit high electrocatalytic performance for OER [16].

Matsumoto and Sato [28] summarized various OER mechanisms in both acidic and alkaline conditions. Under acidic condition, the oxidation steps are characterized by the release of $\text{H}^+ + \text{e}^-$ pairs. Most theoretical studies of OER deal with the reaction under acidic condition by treating the oxidation steps as the release of the proton-electron pairs following the example of Rossmeisl et al. [29]. As such, the OER process on the metal oxides has been separated into four elementary steps, the water molecule first adsorbs on the surface of the catalyst, forming three oxygen-containing intermediates, including OH^* , O^* and OOH^* , in a stepwise process. For example, Man et al. [25] showed that the potential-limiting step of OER on LaMnO_3 is the formation of the OOH^* species on the catalytic site. Chen et al. [30] showed that the first proton-coupled electron transfer of water oxidation on anatase TiO_2 occurs sequentially with electron transfer following the proton transfer. Under the alkaline condition, on the other hand, the surface is expected to react with OH^- to create a surface OH species, which will then undergo further reactions to form oxygen. Experimentally, the oxyhydroxides (MOOH) of Fe, Ni and Co all show catalytic activity toward OER [11,17,26] and FeOOH only shows significant OER activity under alkaline condition [31]. These oxyhydroxides contain intrinsically surface hydroxyl groups, which may play important roles in OER.

In the present study, we performed a comprehensive study of the possible OER intermediates on the three surface terminations of $\gamma\text{-FeOOH}$ (010). This selection is based on previous experimental studies that demonstrated $\gamma\text{-FeOOH}$ exhibiting higher water oxidation activity than $\alpha\text{-FeOOH}$ [32,33]. In order to account for the alkaline condition of the anode in a typical alkaline water electrolyzer, we first established the chemical potential of the $(\text{OH}^- + \text{h}^+)$ pair and then treated OH as a reactant in the elementary steps leading to oxygen formation.

2. Computational method

All calculations were performed using the Vienna Ab-Initio Simulation Package (VASP) code, an implementation of the first principles density functional theory (DFT) method with plane wave basis set and spin-polarized generalized gradient approximation [34,35]. In particular, we used the Perdew-Burke-Ernzerhof (PBE) functional [36] with an on-site Coulomb correction ($U_{\text{eff}} = 5.0 \text{ eV}$) [37]. The semicore 3d state of Fe was treated as the valence state within the Projector-Augmented Wave (PAW) method [38].

The crystal structure of $\gamma\text{-FeOOH}$ was built based on the

electron diffractometry data reported by Zhukhlistov [39]. The $\gamma\text{-FeOOH}$ crystal is arranged into a layered structure and each layer consists of a double layer of Fe octahedra with the hydroxyl groups binding the layers through hydrogen bonding, as shown in Fig. 1. The (010) surface was modeled using a slab with a $p(2 \times 2)$ cell in the surface direction and 10 Å vacuum space between the slabs. Thus, the supercell has a dimension of $7.98 \text{ Å} \times 6.06 \text{ Å} \times 15.81 \text{ Å}$. A $4 \times 3 \times 1$ K-point grid was used to sample the surface Brillion zone. Three terminations, including OH-, O-, and Fe-terminated surfaces (Fig. 1), were examined in turn in the present study.

3. Results and discussion

3.1. Determination of the chemical potential of the $(\text{OH}^- + \text{h}^+)$ pair

Before presenting the DFT results of the elementary steps of OER, we first defined and determined the chemical potential of the $(\text{OH}^- + \text{h}^+)$. In the previous theoretical study of electrochemical hydrogen evolution and oxygen reduction reactions, Nørskov and coworkers defined the computational hydrogen electrode (CHE) as $1/2\text{H}_2(\text{g}) = \text{H}^+ + \text{e}^-$ [29,40]. As such, the chemical potential of the proton-electron pair equals half of the chemical potential of hydrogen molecule at the standard state. Such a standard electrode works well under acidic condition where proton coupled electron transfer dominates the rate processes, as demonstrated in many previous studies [29,41–45]. On the other hand, the OER process on the metal oxyhydroxide-based catalysts is typically operated under basic conditions, sometimes very high alkaline concentrations. Under such a condition, using $(\text{H}^+ + \text{e}^-)$ is not likely to reflect the oxidative environment due to abundant OH^- . Therefore, we developed a $(\text{OH}^- + \text{h}^+)$ pair as the reactive species participating in the reaction. The chemical potential of the $(\text{OH}^- + \text{h}^+)$ pair is defined on the basis of CHE by introducing $\text{H}^+(\text{aq}) + \text{OH}^-(\text{aq}) \leftrightarrow$

Fig. 1. Schematic structures of bulk FeOOH and the (010) surface with different terminations. Blue spheres represent the Fe atoms, red the O atoms and white the H atoms.

Fig. 2. The thermodynamics cycle used to determine the chemical potential of the ($\text{OH}^- + \text{h}^+$) pair.

$\text{H}_2\text{O}(\text{l})$ and constructing the thermodynamic cycle shown in Fig. 2. The reaction free energies of each step under the standard condition can be calculated based on the available thermodynamic data. The calculation yielded a reaction free energy of 1.98 eV for $\text{OH}^- + \text{h}^+ \leftrightarrow \text{OH}(\text{g})$. Consequently, we used this value in combination with the DFT calculated energy of OH, i.e. correcting the DFT calculated free energy change for all the steps involving the ($\text{OH}^- + \text{h}^+$) pair by adding 1.98 eV. We note that the value would be 2.32 eV if DFT calculated free energies were used in calculation. In fact, the chemical potential of the ($\text{OH}^- + \text{h}^+$) pair will not only be applicable to the study of OER but also provide us to a tool to study other reactions under alkaline conditions.

3.2. Relative stability of FeOOH (010) with different terminations

The slab with OH-termination maintaining the stoichiometric ratio of FeOOH can be constructed from bulk FeOOH. The most relevant surface is expected to be the O-termination of FeOOH(010), especially in the aqueous environment. Previous DFT study indicated that the Fe-termination could dominate under water-poor conditions [46,47]. The free energy differences between the OH- and O- or Fe- terminated surface can be calculated based on the following reactions:

$$\Delta G = \Sigma G_{\text{product}} - \Sigma G_{\text{reactant}} = -1.36 \text{ eV} + \text{eU} \quad (\text{i})$$

$$\Delta G = \Sigma G_{\text{product}} - \Sigma G_{\text{reactant}} = -0.23 \text{ eV} + \text{eU} \quad (\text{ii})$$

where $-\text{O}^*$ represents the O-termination, $-\text{OH}^*$ represents the OH-termination and $-\text{Fe}^*$ is the Fe-termination. In these equations, the Fe-termination is the reactant and is therefore considered as the reference in the calculation of reaction free energies. Here, the reaction free energy ΔG is calculated as $\Delta G = \Sigma G_{\text{product}} - \Sigma G_{\text{reactant}}$, with the free energies of reactants and products $G = G_0 + G_{\text{U}} + G_{\text{pH}}$, and $G_0 = 1.98 \text{ eV} + E_{\text{i}} + \text{ZPE}_{\text{i}} - \text{TS}_{\text{i}}$, E_{i} is the electronic energy directly from the DFT calculation, $G_{\text{U}} = \text{eU}$ and therefore depends on the applied potentials, and G_{pH} is the pH correction to the free energy. As shown by the free energy differences in (i) and (ii), the oxidation of the Fe-terminated surface under the alkaline conditions is spontaneous, making the OH-termination the most stable without applying an external potential. Of course, an applied external potential could alter the relative stability of different terminations [48].

The above reactions can also be used to include the effect of excessive OH^- . Similar to treating the effect of proton concen-

tration, a correction of $2.303k_{\text{B}}T(14 - \text{pH})$ can be derived based on the Nernst equation. At $\text{pH} = 14$, this correction would be zero.

3.3. The OER Mechanism

Oxygen formation on different surface terminations of FeOOH (010) may undergo different pathways. On OH-termination, the reaction could occur through two different pathways, i.e. involving one or two surface OH groups, as shown below:

Pathway 1 (one $-\text{OH}^*$):

Pathway 2 (two $-\text{OH}^*$ s):

on the O-termination, oxygen formation will occur through the following steps:

Pathway 1 (one $-\text{O}^*$):

Pathway 2 (two $-\text{O}^*$ s):

on the Fe-termination of FeOOH (010), no exposed surface oxygen could participate in the formation of the oxygen molecule. Consequently, oxygen-containing species can only form from reacting with OH^- through the following steps:

Pathway:

In our calculation, we use neutral OH as a reactant instead of the ($\text{OH}^- + \text{h}^+$) pair directly. The neutral OH can be considered as OH^- being oxidized by a hole (h^+). In the free energy calculations, we used a correction of 1.98 eV determined in the previous section for steps involving OH to account for its formation from $\text{OH}^- + \text{h}^+$. Consequently, the reaction Gibbs free energy for each OER step is calculated by following the same procedures of determining the reaction Gibbs energy of reaction (1) and (2), i.e. $\Delta G = \Delta G_0 + \Delta G_{\text{U}} + \Delta G_{\text{pH}}$, with $\Delta G_0 = 1.98 \text{ eV} + \Delta E_{\text{i}} + \Delta \text{ZPE}_{\text{i}} - T\Delta S_{\text{i}}$, where $\Delta \text{ZPE}_{\text{i}}$ and ΔS_{i} are calculated from frequencies of

the system. We note that the steps without involving the ($\text{OH}^- + \text{h}^+$) pair, including reactions (6), (10), (15), (18) and (27), will not be affected by the applied electrode potentials. The theoretical overpotential η for the steps involving $\text{OH}^- + \text{h}^+$ is defined as $[\Delta G/e - 1.23 \text{ V}]$. The largest value of η corresponds to the thermodynamic potential-limiting step in the OER process.

3.4. OER on FeOOH (010)

Based on the OER mechanism on each surface termination discussed above, we optimized the structures of the intermediates and determined the reaction free energies and overpotentials of all the pathways and listed the results in Table 1 and plotted in Fig. 3(a). On the OH-termination of FeOOH (010), we considered two possible OER pathways, as shown in Fig. 3(a). Pathway 1 involves only one surface OH group. Along this pathway, OH from ($\text{OH}^- + \text{h}^+$) reacts with the surface $-\text{OH}^*$ group, forming one water molecule and leaving a surface $-\text{O}^*$. This step, i.e. extraction of the first surface proton by ($\text{OH}^- + \text{h}^+$)

to form water, is the potential-limiting step, with an overpotential of 2.54 V. The resulting surface $-\text{O}^*$ can react further with additional ($\text{OH}^- + \text{h}^+$), forming the surface $-\text{OOH}^*$ species. The $-\text{OOH}^*$ species continues to react with ($\text{OH}^- + \text{h}^+$), leading to the $-\text{OO}^*$ species and releasing a second water molecule. The $-\text{OO}^*$ species would desorb as oxygen molecule, leaving a surface oxygen vacancy and exposing an Fe site. The oxygen vacancy can be replenished by reacting with ($\text{OH}^- + \text{h}^+$), returning the surface to its original state. The intermediates involved in this pathway are depicted in Fig. 3(a). The reaction energies and overpotential for each step of pathway 1 are summarized in Table 1 and plotted in Fig. 3(d).

Pathway 2 of Fig. 3(a) on the OH-termination of FeOOH (010) involves two surface $-\text{OH}^*$ groups. Following this pathway, the ($\text{OH}^- + \text{h}^+$) reacts with the surface $-\text{OH}^*$ groups to form a water molecule and leaves $-\text{O}^*$ on the surface. The $-\text{O}^*$ can then combine with the neighboring $-\text{OH}^*$ to form $-\text{OOH}^*$. Similar to the pathway involving one $-\text{OH}^*$, the surface $-\text{OOH}^*$ continues to react with ($\text{OH}^- + \text{h}^+$), forming $-\text{OO}^*$ and releasing

Table 1

The calculated free energies of the OER intermediates and overpotential of the elementary step on the OH-, O- and Fe-termination of FeOOH (010). Also listed are the net charges of the Fe atoms involved in OER.

N	Surface group	Reaction	$\Delta G_e(\text{eV})$	η (V)	Net charge of Fe1 (e^-)	Net charge of Fe2 (e^-)
OH-termination with one surface OH^*						
	$-\text{OH}^*$		—	—	1.78	1.78
3	$-\text{O}^*$	$-\text{OH}^* + \text{OH}^- + \text{h}^+ \rightarrow \text{H}_2\text{O} + -\text{O}^*$	3.77	2.54	1.46	1.58
4	$-\text{OOH}^*$	$-\text{O}^* + \text{OH}^- + \text{h}^+ \rightarrow -\text{OOH}^*$	-0.92	-2.15	1.44	1.77
5	$-\text{OO}^*$	$-\text{OOH}^* + \text{OH}^- + \text{h}^+ \rightarrow -\text{OO}^* + \text{H}_2\text{O}$	-1.39	-2.62	1.74	1.76
6	Ov	$-\text{OO}^* \rightarrow \text{Ov} + \text{O}_2(\text{g})$	0.26	—	1.35	1.67
7		$\text{Ov} + \text{OH}^- + \text{h}^+ \rightarrow -\text{OH}^*$	-1.24	-2.47	—	—
OH-termination with two surface OH^* s						
	$2-\text{OH}^*$		—	—	1.78	1.78
8	$-\text{OOH}^*$	$2-\text{OH}^* + \text{OH}^- + \text{h}^+ \rightarrow -\text{OOH}^* + \text{H}_2\text{O}$	2.56	1.33	1.35	1.67
9	$-\text{OO}^*$	$-\text{OOH}^* + \text{OH}^- + \text{h}^+ \rightarrow -\text{OO}^* + \text{H}_2\text{O}$	-0.36	-1.59	1.36	1.62
10	2Ov	$-\text{OO}^* \rightarrow 2\text{Ov} + \text{O}_2(\text{g})$	0.71	—	1.23	1.23
11	$-\text{OH}^* + \text{Ov}$	$2\text{Ov} + \text{OH}^- + \text{h}^+ \rightarrow (-\text{OH}^* + \text{Ov})$	-1.19	-2.42	1.35	1.67
12		$(-\text{OH}^* + \text{Ov}) + \text{OH}^- + \text{h}^+ \rightarrow 2-\text{OH}^*$	-1.24	-2.47	—	—
O-termination with one surface O^*						
	$-\text{O}^*$		—	—	1.76	1.74
13	$-\text{OOH}^*$	$-\text{O}^* + \text{OH}^- + \text{h}^+ \rightarrow -\text{OOH}^*$	-0.12	-1.35	1.77	1.72
14	$-\text{OO}^*$	$-\text{OOH}^* + \text{OH}^- + \text{h}^+ \rightarrow -\text{OO}^* + \text{H}_2\text{O}$	-0.36	-1.59	1.71	1.69
15	Ov	$-\text{OO}^* \rightarrow \text{O}_2(\text{g}) + \text{Ov}$	-0.12	—	1.69	1.67
16	$-\text{H}^*$	$\text{Ov} + \text{OH}^- + \text{h}^+ \rightarrow -\text{H}^*$	-0.36	-1.59	1.78	1.76
17		$-\text{H}^* + \text{OH}^- + \text{h}^+ \rightarrow -\text{O}^* + \text{H}_2\text{O}$	1.40	0.17	—	—
O-termination with two surface O^* s						
	$2-\text{O}^*$		—	—	1.76	1.74
18	2Ov	$2-\text{O}^* \rightarrow \text{O}_2(\text{g}) + 2\text{Ov}$	-0.16	—	1.29	1.53
19	$(-\text{H}^* + \text{Ov})$	$2\text{Ov} + \text{OH}^- + \text{h}^+ \rightarrow (-\text{H}^* + \text{Ov})$	-0.97	-2.20	1.47	1.68
20	$(-\text{O}^* + \text{Ov})$	$(\text{Ov} + -\text{H}^*) + \text{HO}^- + \text{h}^+ \rightarrow (-\text{O}^* + \text{Ov}) + \text{H}_2\text{O}$	0.57	-0.66	1.69	1.67
21	$(-\text{O}^* + -\text{H}^*)$	$(-\text{O}^* + \text{Ov}) + \text{OH}^- + \text{h}^+ \rightarrow (-\text{O}^* + -\text{H}^*)$	-0.36	-1.59	1.78	1.76
22		$(-\text{O}^* + -\text{H}^*) + \text{OH}^- + \text{h}^+ \rightarrow 2-\text{O}^* + \text{H}_2\text{O}$	1.40	0.17	—	—
Fe-termination						
	*		—	—	1.39	1.39
23	OH^*	$* + \text{OH}^- + \text{h}^+ \rightarrow \text{OH}^*$	-0.03	-1.26	1.36	1.66
24	O^*	$\text{OH}^* + \text{OH}^- + \text{h}^+ \rightarrow \text{H}_2\text{O} + \text{O}^*$	-0.81	-2.04	1.66	1.68
25	OOH^*	$\text{O}^* + \text{OH}^- + \text{h}^+ \rightarrow \text{OOH}^*$	0.95	-0.28	1.36	1.38
26	OO^*	$\text{OOH}^* + \text{OH}^- + \text{h}^+ \rightarrow \text{H}_2\text{O} + \text{OO}^*$	-0.46	-1.69	1.36	1.65
27		$\text{OO}^* \rightarrow \text{O}_2(\text{g}) + *$	0.83	—	—	—

Fig. 3. Possible pathways for oxygen formation on the (a) OH-, (b) O-, and (c) Fe-termination of the FeOOH (010) surface and the corresponding energy diagrams (d, e, f). Blue spheres represent the Fe atoms, red the O atoms and white the H atoms.

a second water molecule. The -OO^* species desorbs as an oxygen molecule and leaves two surface oxygen vacancies, which can be healed by reacting with two $(\text{OH}^- + \text{h}^+)$ in a sequential order. The first step, with an overpotential of 1.33 V, is the potential-limiting step for this pathway. Clearly, this step also involves the bond breaking process of the surface OH group. The O_2 desorption step has the second highest reaction free energy of 0.71 eV, and the following steps are all spontaneous under an electrode potential of 1.23 V. These results show that breaking the surface O–H bond of the surface OH^* on the FeOOH(010) surface is the potential-limiting step on the OH-terminated surface for both pathways, and pathway 2 required a lower overpotential compared with pathway 1, as shown in Fig. 3(d).

Two possible OER pathways, i.e. involving either one or two surface O atoms, on the O-terminated FeOOH (010) surface are also examined, as shown in Fig. 3(b). For the pathway involving one surface -O^* (pathway 1 in Fig. 3(b)), the $(\text{OH}^- + \text{h}^+)$ first

reacts with the surface -O^* to form -OOH^* . This is followed by -OOH^* reacting with a second $(\text{OH}^- + \text{h}^+)$ pair, forming a water molecule and leaving -OO^* on the surface. The -OO^* species desorbs from the surface in the form of an oxygen molecule, resulting in an oxygen vacancy on the surface, which exposes a Fe site. A new $(\text{OH}^- + \text{h}^+)$ pair binds the exposed Fe site and forms a surface OH^* species, and this OH^* species can further react with $(\text{OH}^- + \text{h}^+)$ to form one water molecule by breaking the H–O bond. This is the potential-limiting step along this pathway with a small overpotential of 0.17 V. As shown in Table 1, the overpotentials η of other elementary steps are all negative. The free energy changes and the overpotentials of each step were plotted in Fig. 3(e).

For the pathway involving two surface oxygen atoms on the O-terminated surface (Fig. 3(b), pathway 2), two surface oxygen atoms first combine to form an O_2 molecule, leaving two oxygen vacancies, and in the meantime, exposing two Fe sites. The two Fe sites can react with two $(\text{OH}^- + \text{h}^+)$ pairs to heal the

surface by forming two surface -OH^* s. This will bring the surface back to the -OH^* terminated surface. The η value for breaking one of the O–H bond of the newly formed -OH^* s under the standard OER potential is negative (-0.66 V), while for breaking the second O–H, the overpotential is only 0.17 V, same as pathway 1. The difference in the overpotentials for the two O–H bond breaking steps can be attributed to the existence of the oxygen vacancy. The oxygen vacancy promotes the breaking of the O–H bond of the first OH group. For O-termination, the overpotentials of the limit step for both mechanisms are the same and are much lower than that on OH-termination. The results indicate that the O-termination has a higher OER activity than the OH-termination. We note that the breaking the O–H bond is also the potential-limiting step of OER on the O-terminated surface, as shown in Fig. 3(e).

On the Fe-terminated surface, the $(\text{OH}^- + \text{h}^+)$ pairs adsorb first on the surface Fe sites before the oxygen formation steps could take place. The reaction with the $(\text{OH}^- + \text{h}^+)$ pairs forms -OH^* , which then transforms to -O^* , -OOH^* and -OO^* following a stepwise process as shown in Fig. 3(c). The -OO^* would desorb from the surface in the form of O_2 . All the elementary steps are energetically favorable under the standard OER potential except for the O_2 desorption step, which has a reaction free energy of 0.83 eV, as shown in Table 1 and Fig. 3(f).

In summary, the (010) surface of FeOOH favors the OH-termination thermodynamically without applied potentials. To activate the surface for OER, an overpotential of 2.54 V has to be applied to break the first O–H bond, resulting in -O^* , which will continue to react under such a potential, finally forming the O_2 molecule. Desorption of the OO^* species to form gas phase O_2 molecule is not spontaneous under the standard condition. Under operating condition of the electrolyzer, the electrode surface would be under a constant transformation due to OH adsorption and oxygen formation. A clearer picture developed from the above analysis of the elementary steps is that an external potential is needed for the OH- and O- terminated surfaces to become activated for OER. The formation and turn-over of the surface oxygen species are the integral steps of the reaction mechanism, in analogue to the Mars-van Krevelen mechanism in heterogeneous catalysis [49,50]. The results also point to the dynamical nature of the surface structure in the reaction process. The structural flexibility allowed by the oxyhydroxides and perovskite oxides made them highly active for catalyzing OER.

In addition to the free energy variations along each reaction pathway, the charge transfer/redistribution would help to shed light on the redox process. Therefore, we performed Bader charge analysis along each reaction pathway on all three surface terminations with the possible intermediates. For convenience, we used bulk hydroxides as the reference. As shown in

Table 2, the Bader charges of the Fe atom in bulk $\text{Fe}(\text{OH})_2$ and FeOOH phases are 1.36 e^- and 1.82 e^- , respectively. Clearly, the Bader charge values reflect qualitatively the relative level of oxidation of Fe in these oxides. We note these values differ from the corresponding formal charge values significantly. As a reference, we also listed the Bader charges of the surface Fe atom directly involved in the reaction on each surface termination in Table 2. Clearly, the surface Fe atoms in OH- and O- terminated surfaces are reduced slightly compared with the Fe atoms in bulk FeOOH . The Fe atom in the Fe-terminated surface is significantly reduced and its net charge is very close to Fe in bulk $\text{Fe}(\text{OH})_2$.

Details of the Bader charge variations of Fe in all three terminations along each OER pathway are shown in Table 1. We focused on the two Fe atoms directly binding the adsorbed surface intermediates (Fe in the dashed box in Fig. 3), which are the active sites for OER. Generally, the Fe atoms are oxidized by reacting with OH, either in the form of H removal or OO^* formation, and reduced by releasing O_2 . Along pathway of left cycle on the OH-terminated surface, the process starts with Fe reduction by losing one H. The Bader charges on the two Fe atoms indicate that the two Fe atoms were not reduced equally. The formation of -OOH^* by further reacting the O^* site with another OH results in one Fe being reduced while another oxidized. This is consistent with the adsorption structure that the -OOH^* is tilted toward the oxidized Fe atom. Losing H from OOH^* further oxidizes the binding Fe site while leaving the other unchanged. Desorption of O_2 causes reduction of both Fe atoms, with the Fe atom binding OO^* having a larger net charge change. Similar redox processes but with different order of appearance could be identified in other cycles.

4. Conclusions

In this work, we studied OER mechanism on the three terminations of the FeOOH (010) surface based on the results of the DFT + U calculations. We first established chemical potential of the $(\text{OH}^- + \text{h}^+)$ pair to include the OH^- anion in the reaction pathway. The inclusion of the $(\text{OH}^- + \text{h}^+)$ pair allows us to account for the anodic OER process under the alkaline conditions. We then analyzed the possible reaction pathways on each surface termination individually. On the surface with OH- and O- terminations, the O_2 molecule may form from either OH reacting with the surface oxygen species or combination of the two surface oxygen species. The potential-limiting steps of the oxygen evolution with different surface terminations were determined by following the free-energy change of each elementary step along each pathway. The Fe-terminated surface is intrinsically active for OER but is thermodynamically unfavorable. External potential helps the turn-over of OH^- under alka-

Table 2

The net Bader charge of Fe (a) in bulk FeOOH and $\text{Fe}(\text{OH})_2$, (b) the first layer of the clean OH-, O- and Fe- termination of FeOOH (010).

Item	FeOOH^a	$\text{Fe}(\text{OH})_2^a$	FeOOH (010) with different terminations		
			OH- ^b	O- ^b	Fe- ^b
Net charge of Fe in bulk (e^-)	1.82	1.36	—	—	—
Net charge of the 1st layer Fe (e^-)	—	—	1.78	1.76	1.39

line conditions and refreshes the surface Fe sites. Our results show that oxygen formation requires recreating the surface Fe sites, and consequently, the condition that favors partially exposed Fe sites will promote formation of oxygen.

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Graphical Abstract

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Mechanistic understanding on oxygen evolution reaction on γ -FeOOH (010) under alkaline condition based on DFT computational study

Miru Tang, Qingfeng Ge*
Southern Illinois University, USA

Oxygen evolution mechanism on FeOOH (010) catalyst under the alkaline condition. The circled OH^- represent hydroxide ions in solution. Blue sphere is Fe, red O and white H.

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DFT计算研究碱性条件下 γ -FeOOH (010)上氧析出反应机理

Miru Tang, Qingfeng Ge*

南伊利诺伊大学化学与生物化学系, 卡本代尔 IL 62901, 美国

摘要: 一个高效经济的氧析出反应(OER)催化剂是大范围应用太阳能转化能源的关键. 在众多有潜力的OER催化剂中, 金属氢氧化物, 尤其是FeOOH表现出很高的OER活性. 我们采用DFT+U研究了 γ -FeOOH (010)表面上OER反应机理; 得到了OH⁻和空穴对的化学势, 并将OH⁻阴离子包含在反应机理中, 以此来说明碱性条件下阳极的OER过程. 随后分析了催化剂中OH⁻, O-和Fe-终止的表面上OER反应路径. 含有OH⁻, O-终止的表面上, O₂分子是通过OH与表面氧化物(-OH*和-O*)反应, 或二个表面氧化物相结合而形成的. 在Fe-终止的表面上, O₂只能通过首先在Fe位上吸附OH而形成. 不同形式表面上O₂析出的化学势决定步骤取决于每个路径中基元步骤自由能的变化. 结果表明, O₂的形成需要重建表面Fe位, 因此, 有利于部分暴露Fe位的条件也将促进O₂的形成.

关键词: 水分解; 氧析出反应; DFT+U; 氢氧化铁

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*通讯联系人. 电子信箱: qge@chem.siu.edu

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