Direct and indirect role of Fe doping in NiOOH monolayer for water oxidation catalysis

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Abstract

The oxygen evolution reaction (OER) activity of pristine NiOOH is enhanced by doping with Fe. However, the precise role of Fe is still being debated. Here, we use the first-principles DFT+U approach to study three different types of active sites: one on pristine and the other two on Fe-doped NiOOH monolayers to account for the direct and indirect roles of Fe. To compare the activity of the active sites, we consider two mechanisms of OER based on the source of O-O bond formation. Our results show that the mechanism involving the coupling of lattice oxygen is generally more favorable than water nucleophilic attack on lattice oxygen. On doping with Fe, the overpotential of NiOOH is reduced by 0.33 V in excellent agreement with experimental findings. Introducing Fe at active sites results in different potential determining steps (PDS) in the two mechanisms, whereas Ni sites in pristine and Fe-doped NiOOH have the same PDS regardless of the mechanism. The Fe sites not only have the lowest overpotential but also decrease the overpotential for Ni sites.

Keywords

Density-functional theory, transition metal oxyhydroxides, water oxidation, oxygen evolu-

tion reaction, heterogeneous catalysis, reaction mechanism

1 Introduction

A key obstacle to the success of electrochemical water splitting is the oxygen evolution reaction (OER), a kinetically inefficient but crucial half-reaction.¹ OER is a significant contributor to the overpotential as it involves the exchange of four protons and electrons as well as an O-O bond formation, necessitating the use of catalysts.² Of the transition metal-based catalysts, nickel hydroxide/oxyhydroxides have emerged as the most promising catalysts for OER.³⁻⁷ Nickel hydroxide mainly exists in four different phases⁸ and among them, β -NiOOH and γ -NiOOH are more active than the others for OER.⁹⁻¹² NiOOH, with and without doping, has been extensively studied for OER at both experimental and computational levels.^{3,11,13-15} Compared with other transition metals, the doping of Fe in NiOOH has been shown to increase the OER activity significantly,^{9,16,17} with an optimal doping of 25%.^{17,18}

A direct role of Fe in the OER was proposed given its lower electronegativity compared to Ni and, hence, easier oxidation at OER conditions.¹⁹ However, it has also been argued that Fe can influence the oxidation state of Ni ac-

tive sites and hence improve their OER activity.^{20–22} A cooperative effect between the two metal sites in facilitating the stabilization of key intermediates, has also been proposed.²³ Despite the extensive studies on the active sites and mechanisms of OER,^{12,24–29} the role of Fe doping remains a source of debate.^{30,31} The lattice oxygen coupling (LOC) mechanism in OER^{32,33} is largely ignored for the metal hydroxide/oxyhydroxide materials since it was deemed unfavorable for such systems.^{34,35} More recently, lattice oxygen participation in OER was confirmed for Ni and NiCo LDHs and ruled out for NiFe-LDH and NiFeCo-LDH.³⁶ However, the LOC mechanism for OER has not been investigated for neither undoped nor Fe-doped NiOOH. Interestingly, it is anticipated that, unlike bulk, low-dimensional forms of metal oxyhydroxides can provide structural flexibility for LOC mechanism.^{37,38}

In this work, we investigate the direct and indirect effects of Fe doping in NiOOH monolayer (with the structure of β -NiOOH) on improving the OER activity using density-functional theory (DFT) methods. We compare the activity of an active site on undoped NiOOH (AS-1) with two types of active sites on Fe-doped NiOOH - one that involves the Fe atom (AS-3) and one that does not (AS-2). We assess the activity via two OER mechanisms for both undoped and Fe-doped NiOOH monolayers. The mechanisms differ in the source of O-O bond formation: in one case, the bond is formed between lattice oxygen and an oxygen atom from H₂O, i.e., water nucleophilic attack (WNA) mechanism, while in another case, both oxygen atoms are from the catalyst lattice, i.e., lattice oxygen coupling (LOC) mechanism. We find that the LOC mechanism involves lower thermodynamic overpotentials in Fe-doped NiOOH when Fe is present at the active site. Consequently, OER will proceed through LOC rather than WNA at Fe sites. The Ni sites in Fe-doped NiOOH (AS-2) have a lower overpotential than AS-1 suggesting an indirect role of Fe in this case. However, the Ni sites have the same overpotential along both LOC and WNA mechanisms.

2 Methods and Computational Details

All the calculations were performed using spin-polarized density functional theory implemented in Quantum ESPRESSO.³⁹ The Hubbard U correction was used along with Perdew-Burke-Ernzerhof (PBE) XC functional.⁴⁰ The U value of 6.6 eV and 3.5 eV were used for Ni and Fe, respectively, calculated by Friebel et al.¹⁸ from linear response theory⁴¹ in literature. For pristine NiOOH, the converged plane wave basis cutoff of 65 Ry and charge density cutoff of 500 Ry was used. For Fe-doped NiOOH, the converged plane wave basis and charge density cutoffs of 90 Ry and 800 Ry were used, respectively. In the case of pristine NiOOH, on changing the cutoffs from 65 Ry and 500 Ry to 90 Ry and 800 Ry, the reaction energy of step A changes by only 0.9 meV, confirming the accuracy of NiOOH results obtained using 65 Ry and 500 Ry. The projector-augmented-wave (PAW) pseudopotentials were considered to describe the core regions. The structures were optimized using the BFGS algorithm and assumed optimized when no force component is larger than 10^{-5} Ry/Bohr. The $2 \times 2 \times 1$ supercell was used to study the structural properties of undoped NiOOH and Fe doped NiOOH monolayer. The monolayer was modeled by taking 15 Å in z -direction to minimize the interaction between the periodic images (see Fig. S1 (a)). Monkhorst-pack k-point grid was converged to $6 \times 6 \times 1$ (see Fig. S1 (b)) for 2×2 supercell and $3 \times 3 \times 1$ grid for 4×4 supercell.

The $4 \times 4 \times 1$ supercell was used to study the water oxidation mechanism over the monolayer. All the reaction intermediate were also optimized to the force threshold of 10^{-5} Ry/Bohr. The Gibbs free energies of the reactions were calculated using the formula $\Delta G = \Delta E + \Delta ZPE - T\Delta S$ where ΔE is the difference of energy of reactant and product species in every step of mechanism calculated by DFT+U, ΔZPE is the change in zero-point energy, T is temperature, and ΔS is the change in entropy. The simple harmonic oscillator model was used to calculate the frequency required

to get ΔZPE . The frozen phonon calculations were performed by displacing the Ni, O, and H atoms near the adsorbed intermediate species. In these calculations, it was assumed that the atoms far from the adsorbed species were not having a significant effect. The entropies of gaseous species are adopted from the NIST database.⁴² Only the vibrational contributions to the entropy are taken into account for adsorbed species. We calculate the Gibbs free energy in each elementary step using the computational hydrogen electrode model⁴³ with an electrode potential of 0 V and pH = 0.

3 Results and Discussion

3.1 Structure of Pristine NiOOH Monolayer

As reported earlier,⁴⁴ for OER, the monolayer of NiFe layered double hydroxides deposited on glassy carbon disk electrode is more active than the corresponding bulk due to more accessible active sites and increased electronic conductivity on exfoliation to monolayers. Using DFT calculations, Li and Selloni reported that Fe-doped β -NiOOH is the most active phase among all Ni and Fe-based oxides and hydroxides.⁹ Hence, we choose the monolayer of NiOOH with the structure of β -NiOOH. Bulk β -NiOOH is an H-bonded layered structure. Inter-sheet H-bonding stabilizes arrangements of protons leading to many kinds of octahedral coordination.^{45,46} Unlike bulk, the inter-sheet interactions are absent in the NiOOH monolayer, but the latter can also exhibit multiple octahedral coordination. While the most stable H-arrangements were reported for CoOOH monolayers⁴⁷ they are not known for the NiOOH monolayer.

Therefore, we first determined the most stable H-distribution on the NiOOH monolayer. We considered three unique types of H-arrangements named as H_S , H_C , and H_D for the supercell of NiOOH monolayer with the stoichiometry of β -NiOOH containing four metal atoms per unit cell (see Figure 1 (a)). In H_C , there are two types of octahedral coordination:

i) O_A : four O and two OH, ii) O_B : two O and four OH, arranged alternatively along the x-axis. In H_S and H_D , there is only one type of octahedral coordination sphere O_C composed of three O and three OH. The protons in H_S point in one direction resulting in a polar structure due to non-zero dipole moment, but in H_C and H_D , half of the protons are distributed on each side of the layer yielding zero dipole moment. The octahedra have a center of inversion at Ni atoms in the case of H_C structure, but not in H_S and H_D .

The monolayer in each of the three coordinations was fully optimized in antiferromagnetic (AFM) and ferromagnetic (FM) spin arrangements. The H_C structure emerged as the most stable structure, with the ground state being FM in all the distributions considered.⁴⁶ The calculated energies are compared in Table S1. H_S and H_D structures are 1.78 eV and 0.48 eV per unit cell higher in energy than H_C structure. The preference of centrosymmetric coordination over the non-centrosymmetric coordination of Ni is in agreement with the findings in bulk β -NiOOH⁴⁵ and in contrast with CoOOH.⁴⁷ Therefore, we considered the H_C structure of undoped NiOOH for the further calculations for the OER reaction. Unlike Co in CoOOH,⁴⁷ Ni atoms in all configurations are in a +3 oxidation state irrespective of the type of octahedral coordination, which is consistent with the finding by Conesa.⁴⁵ The analysis of bond lengths in H_C reflects the presence z_{in} and z_{out} types of Jahn-Teller distortion in both types of octahedra (i.e. O_A and O_B), respectively. Table S2 presents the bond lengths.

3.2 Structure of Fe-doped NiOOH Monolayer

25% Fe-doped NiOOH was obtained by replacing one of the four Ni atoms in the $2 \times 2 \times 1$ supercell with Fe. Like undoped NiOOH, there are several possible H-distributions over Fe-doped NiO₂ monolayer as depicted in Figure 1 (b). No two Fe share corner or edge of octahedra. A comparison of the energies of H-distributions shows that the Fe atom prefers to be present in O_A type of octahedra in H_C -

Figure 1: Types of H-distributions over (a) NiO₂ and (b) NiFeO₂ monolayers. Numeric values in the name of distribution represent the number of H in the octahedral coordination of the Fe atom. The numbers in parentheses are the relative energies (in eV) of the corresponding structures. Separate reference energies are used for pristine NiOOH and Fe-doped NiOOH. For pristine NiOOH, the relative energies presented are for FM spin alignment. In the Fe-doped case, the relative energies showed for the spin configuration in which Fe sublattice is in antiferromagnetic alignment with Ni sublattice.

2 structure. In H_C-2, Fe attains Fe⁴⁺ (d⁴) oxidation state in high spin John-Teller configuration. As a result, one Ni³⁺ (d⁷, low spin) in O_B octahedron is reduced to Ni²⁺ (d⁸, low spin) while the other two Ni in the unit cell remains as Ni³⁺ (d⁷, low spin). Our findings are consistent with the study on Fe-doped bulk β -NiOOH by Conesa.⁴⁵

3.3 Active Sites

Since the (0001) surface is the most dominating and stable surface in NiOOH synthesis and at electrochemical conditions, we chose the active sites to be on the terraces of the undoped and Fe-doped NiOOH monolayers.^{29,48–50} For OER, the terrace sites are nearly equally important as the edge sites. For example, the edge sites in bulk NiOOH, i.e., (011 $\bar{2}$) surface, have been reported to be less active for OER ($\eta = 1.16$ V) than the terrace sites, i.e., (0001) surface ($\eta = 0.50$ V).⁴⁷ For pristine monolayer NiOOH,

the overpotential of edge sites (0.55 V) is comparable to that of terrace sites (0.60 V).⁴⁷ After doping the NiOOH monolayer with Fe, the edge sites become less efficient than the terrace sites with the overpotential of the former being higher by 0.61 V.⁴⁷ In another study,¹⁵ the overpotential of bulk edge and terrace sites were found not to differ significantly. Also, it was concluded that the overall OER activity of β -NiOOH is uniform across all various crystallographic surfaces, including the most stable (0001) surface. Furthermore, it has been experimentally shown that only a small amount (10 $\pm$ 3%) of Fe ions are present in tetrahedral coordination (edge sites), and the majority are in octahedral coordination (terrace sites).¹⁸

Among the two types of active sites in NiOOH – hydroxo and oxo (Figure S2 in SI) – hydroxo sites have lower overpotential than oxo sites for OER on (0001) surface of β -NiOOH.¹⁵ Therefore, we considered hydroxo sites to evaluate OER mechanisms on pristine NiOOH mono-

layer (AS-1). On Fe-doped NiOOH, the active sites are further distinguished by their coordination environments. For example, the hydroxo groups on Fe-doped NiOOH monolayer are coordinated with either three Ni (AS-2) or two Ni and one Fe (AS-3). We considered both, AS-2 and AS-3, possibilities in this work. All considered active sites are depicted in Figure 2.

In AS-2, the Fe is not directly available to adsorbate species and presumably plays an indirect role by modifying the electronic structure of Ni on active sites. In contrast, in AS-3, one Fe is adjacent to the active site and can be directly involved in the oxygen evolution reaction.

3.4 Mechanisms for OER

Several OER mechanisms have been previously studied, including single-site and dual-site mechanisms.^{9,12,47} Herein, we simulated and compared two mechanisms for OER based on two different ways of O-O bond formation. The first mechanism (WNA) involves the oxidation of O^{2-} from a water molecule. The second mechanism (LOC) involves the oxidation of lattice oxygen which is later recovered by consuming the water molecules. The mechanisms are depicted in Figure 3 and Figure 4 for undoped and Fe-doped NiOOH, respectively. The A–B–C–D–I–J sequence of reactions in the inner cycle and the A–E–F–G–H–I–J sequence in the outer cycle represent WNA and LOC mechanisms, respectively. The corresponding reaction free energies are presented in Table 1.

In the first step (A), the initial hydroxo group (HO^*) undergoes dehydrogenation by removal of coupled proton and electron in reaction to produce O^* . The first step A is common in both WNA and LOC mechanisms. In the next step O-O bond has to form. The two mechanisms differ in the next step of O-O bond formation. WNA mechanism proceeds by the adsorption of a H_2O molecule with simultaneous removal of coupled proton and electron to form HOO^* in step B. Next, in steps C and D, dehydrogenation and O_2 evolution lead to the creation of a vacancy on the catalyst. Subsequently, adsorption of a H_2O molecule (H_2O^*) in step I, followed by dehydrogenation in step J, regen-

erate the catalyst. On the other hand, LOC mechanism branches off to step E, forming O-O bond by coupling of two lattice oxygen atoms to form $(O-O_L)^*$. After step E, O_2 evolution creates two O vacancies (V_O^*) in the lattice in step F. Then, the vacancies were filled by a H_2O adsorption followed by the removal of pairs of proton and electron in steps G, H, I, and J. Step I and J are also common in both WNA and LOC mechanisms. Steps D, E, F, and I are non-electrochemical. In contrast, all others are electrochemical as they include the exchange of proton and electron.

3.4.1 OER at AS-1

In the active site AS-1, the hydroxo group coordinated to three Ni atoms, out of which one Ni has an O_A octahedron while the other two Ni have O_B octahedra. The abstraction of a pair of proton and electron from HO^* leads to oxidation of Ni^{3+} in O_B to Ni^{4+} ($t_{2g}^6 e_g^0$). The O-O bond formation in step B via nucleophilic attack of water and a simultaneous dehydrogenation is less energy demanding than step A. In step B, Ni^{4+} reduces back to Ni^{3+} . Furthermore, the dehydrogenation of hydroperoxo (HOO^*) intermediate in step C and successive O_2 evolution in step D remains less energy demanding than step A. In the vacancy (*) formation in step D, one Ni atom in O_B is reduced from Ni^{3+} (d^7) to Ni^{2+} (d^8). The reduction of Ni has also been reflected in Löwdin charge analysis as spin polarization changes from 1.19 to 1.68 after vacancy formation. Ni^{2+} remains unchanged during adsorption H_2O in step I. The reduced Ni^{2+} gets oxidized to Ni^{3+} in the last dehydrogenation step J. All steps in WNA mechanism are comparatively less energy-demanding than step A (see Table 1). Therefore, the formation of O^* in step A is the potential determining step (PDS) with an overpotential of 0.68 V via WNA mechanism in the case of pristine NiOOH. The PDS found in the pristine NiOOH monolayer agrees well with the findings of Rajan et al. on (0001) surface of pristine β -NiOOH. The overpotential was predicted to be 0.69 V using PBE+U with $U(Ni)=5.5$ eV.¹⁵ Tripkovic et al. also found the

Figure 2: Three types of active sites. (a) pristine NiOOH, (b), and (c) Fe-doped NiOOH. The numbers in parentheses are the vacancy formation energies in eV.

Figure 3: OER mechanisms on pristine NiOOH at active site AS-1. Outer and inner cycles represent LOC (blue arrows) and WNA (red arrows) mechanisms, respectively. The green box indicates that HO^* is the starting point for OER. LOC branches off after step A by forming O-O bond between two lattice oxygen atoms highlighted with small blue circles. The transition state structure for step G is presented in Figure S3 in SI. Violet and green spheres, respectively, represent adsorbate oxygen and hydrogen atoms.

formation of O^* from HO^* as the PDS with an overpotential (η) of 0.6 eV⁴⁷ although they used the H_D type for the structure of the NiOOH monolayer.

Step A continues to be the PDS even in LOC mechanism since all of the other electrochemical elementary steps in LOC mechanism require less energy to proceed. After step A has oc-

(a) OER mechanisms on AS-2

(b) OER mechanisms on AS-3

Figure 4: OER mechanisms on Fe-doped NiOOH at active sites - (a) AS-2 and (b) AS-3. Other features are same as Figure 3.

curred, there will be competition between steps B and E. Step E is a chemical step, with a potential-independent and negligibly small free energy cost (0.04 eV). In contrast, step B is an electrochemical step, and its free energy demand decreases by applied potential. These findings are in line with the experimental study by Lee et al. that the lattice oxygen atom are involved in OER in pure Ni hydroxides.³⁶

3.4.2 OER at AS-2

On doping with Fe, Fe^{4+} replaces Ni^{3+} in pristine NiOOH which can significantly change the potential of the active site. In the case of AS-2, when Fe is away from the active site all the effects coming from Fe will be by indirect modification of the electronic structure of Ni and O atoms near the active site. A schematic of the OER mechanism on Fe-doped NiOOH is shown in Figure 4.

It is worth noting that the reaction-free energy of step A decreases by an amount of 0.13 eV on changing the active site from AS-1 to AS-2 (see Table 1). As indicated by reaction free energies of steps A and B in Table 1, the presence of Fe^{4+} stabilizes the O^* and the HOO^* by the same amount, which leads to a decrease in the reaction free energy of step A while that of step B remains constant. The Fe remains in +4 oxidation state along WNA mechanism whereas one of the Ni^{3+} (in O_B type octahedron) at active site oxidizes to Ni^{4+} in step A. Similar to AS-1, step A at AS-2 is highest energy demanding step along both WNA and LOC mechanisms and remains as PDS with an overpotential of 0.55 V. It should be noted that when, in step E on AS-2, two oxygen atoms from lattice combine to form an O-O bond then the Fe becomes part of the active site in LOC mechanism (see Figure 4 (a)). Unlike AS-1, the O-O bond formation in step E is exergonic with free energy of -0.09 eV. The oxidation state of Fe remains unaltered in LOC mechanism as well. On comparing WNA and LOC mechanisms on AS-2, OER is equally likely to occur via both mechanisms (see Table 1). The indirect effect of Fe has also been observed experimentally in Fe-doped Ni oxide films by Li et al. where Fe^{3+}

act as Lewis acid in nickel oxide host and facilitates the formation of Ni^{4+} which in turn promotes O-O bond formation and hence, the OER activity.²² In step I at AS-2, it is more challenging to remove proton and electron from the H^* than at AS-1 in the pristine NiOOH . The H is bound to O and bonded more firmly to Fe^{4+} at AS-2 than to Ni^{3+} at AS-1. The O-O bond formation is thermodynamically favorable in the case of AS-2. Therefore, after the step A has occurred OER will follow LOC mechanism (via step E) rather than WNA mechanism (via step B). In addition, the Gibbs free energy change of the water adsorption process in step I is nearly identical in pristine (AS-1) and Fe-doped NiOOH (AS-2 and AS-3).

3.4.3 OER at AS-3

The presence of Fe at the active site leads to the different PDS in WNA mechanism than in AS-2. The stabilization of O^* by Fe is more pronounced at AS-3 where Fe oxidizes from Fe^{4+} to Fe^{5+} whereas at AS-2 Ni oxidizes from Ni^{3+} to Ni^{4+} . Therefore, the strong adsorption of O and high stability of O^* intermediate lead to the lowest free energy of step A on AS-3 among all three active sites. Consequently, step A is no longer a PDS. Notably, the O-O bond formation in step B at AS-3 is the least feasible among all active sites considered in this work. Consequently, step B becomes the PDS when the reaction proceeds through WNA mechanism (see Table 1). In LOC mechanism at AS-3, unlike AS-1 and AS-2, the O-H bond breaking in step H is the PDS with an overpotential of 0.35 V which is much lower than that in WNA mechanism (0.53 V). Hence, OER at the Fe sites will proceed predominantly through the LOC mechanism.

The overpotential of AS-1 in undoped NiOOH (0.68 V) is decreased by 0.33 V by Fe-doping (0.35 V in LOC mechanism). These findings are in good agreement with the experimental study by Klaus et al., where the overpotential of NiOOH decreased by 0.25 V when there were Fe impurities in the system.¹⁶ Liu et al. recently investigated similar kinds of active sites to study the WNA type of mechanism on the

Ir-doped NiOOH monolayer.⁵⁰ They found that the Ni sites near Ir show the lowest overpotential followed by Ni sites on pure NiOOH. For the WNA mechanism case, our results are in good agreement with Liu et al.⁵⁰ In addition, unlike Ir sites on Ir-doped NiOOH,⁵⁰ the Fe sites are the most active sites among three active sites considered in our work.

A recent experimental study presented evidence of the involvement of lattice oxygen in OER in NiFe oxyhydroxide catalysts.⁵¹ In that study, the O-O bond formation is shown to be a rate-limiting step and not the O-H bond breaking. This distinction in the potential determining step in our work and rate-limiting step in the experiments⁵¹ could be due to the kinetics of OER which is omitted here. Furthermore, in the theoretical part of the same study, undercoordinated Fe sites at edges in Fe-doped γ -NiOOH are considered as active sites, whereas in our work, active sites are at the terrace of the NiOOH monolayer (with the structure of β -NiOOH). The key difference is that at edge sites, the intermediates not involving lattice oxygen are solely adsorbed on Fe. In contrast, on the terrace site, adsorbed species are shared by three metal atoms.

For the Fe doping case, the disagreement between our result for AS-3 ($\eta=0.53$ V) and that of Tripcevik et al.⁴⁷ ($\eta=0.43$ V) could be because of the different structural models in the two studies. In our work, Fe has the oxidation state of +4 in the H_C-2 structure, whereas, in the latter study, Fe is in the oxidation state of +3 in the H_D-3 type structure. As mentioned earlier, H_C-2 has a lower formation energy and would hence be the more likely structure.

Overall, in WNA mechanism, Ni sites in both pure and Fe-doped NiOOH show the formation of O* as PDS, while for Fe sites the PDS changes to O-O bond formation. By changing the mechanism from WNA to LOC at the Fe site in Fe-doped NiOOH, the PDS changes from O-O bond formation to O-H breaking. Consequently, the thermodynamic overpotential on AS-3 decreases significantly from 0.53 V to 0.35 V. The free energies for WNA and LOC mechanisms for all three active sites are shown in Table 1.

The thermodynamics of elementary steps suggest that the LOC mechanism is the dominant mechanism. However, this could completely be changed if kinetic barriers are taken into account. We calculated the activation barriers of chemical step G at AS-1, AS-2, and AS-3 using the climbing image nudged elastic method (NEB-CI) and the activation free energies are 1.12 eV, 1.16 eV, and 1.42 eV, respectively. The activation barrier of O-O bond formation via nucleophilic attack of water (step D) is calculated in very few cases. For example, at OER conditions (1.8 V), the activation barrier on IrO₂ and RuO₂ surfaces is 0.5 eV or less.^{52,53} Using metadynamics, another study reported the barrier of 0.96 eV (PBE) and 0.79 eV (B3LYP) for Ru-complex.⁵⁴ Furthermore, the formation of HOO* from O* in step D can also be thought of as a combination of an electrochemical step (O-H bond breaking), and a chemical step (O-O bond formation).²³ At Ni site in γ -NiOOH, Xiao et al. calculated the free energy barrier of exergonic chemical O-O bond formation between an adsorbed O and an O from water as in WNA mechanism to be 0.48 eV at the U=2.28 eV.²³ The activation barrier for the electrochemical O-H bond breaking is clearly less than typical values for the O-O bond formation estimated from these works.⁵³ Since step G has a high barrier, presumably higher than step D, LOC mechanism is likely to be kinetically slow. A more accurate assessment can result from computation of the barrier for step B in our case. However, such a calculation has not been done in the present study.

In this work, we have not taken into account the solvation and the Gibbs free energies are considered pH-independent. Implicit solvation by water does not significantly affect the Gibbs free energies of OER, and the PDS remains unchanged.^{15,25} The inclusion of explicit solvation, however, can change the Gibbs free energy and the PDS of undoped NiOOH and Fe-doped NiOOH.¹⁴ The difficulties in explicit solvation as a large number of water molecules are required for accurate solvation and different configurations of water molecules are possible on the surface, greatly increasing the amount of computational cost.⁵⁵ Furthermore, NiOOH is

Table 1: Reaction Gibbs free energy of OER on all three active sites – AS-1, AS-2, and AS-3. The Gibbs free energies and overpotentials (η) are presented in the units of eV and V, respectively. WNA mechanism: A–**B–C–D**–I–J; LOC mechanism: A–**E–F–G–H**–I–J.

Reaction step		AS-1		AS-2		AS-3	
		ΔG	η	ΔG	η	ΔG	η
A	$\text{HO}^* \rightarrow \text{O}^* + \text{H}^+ + \text{e}^-$	1.91	0.68	1.78	0.55	1.37	
B	$\text{O}^* + \text{H}_2\text{O} \rightarrow \text{HOO}^* + \text{H}^+ + \text{e}^-$	1.52		1.52		1.76	0.53
C	$\text{HOO}^* \rightarrow \text{OO}^* + \text{H}^+ + \text{e}^-$	0.67		0.68		1.01	
D	$\text{OO}^* \rightarrow \text{O}_2 + *$	-0.10		-0.07		-0.42	
E	$\text{O}^* + \text{O}_\text{L} \rightarrow (\text{O}-\text{O}_\text{L})^*$	0.04		-0.09		0.03	
F	$(\text{O}-\text{O}_\text{L})^* \rightarrow \text{O}_2 + \text{V}_\text{O}^*$	0.16		0.05		-0.09	
G	$\text{V}_\text{O}^* + \text{H}_2\text{O} \rightarrow \text{H}^* + \text{H}^+ + \text{e}^-$	0.39		0.58		0.84	
H	$\text{H}^* \rightarrow * + \text{H}^+ + \text{e}^-$	1.49		1.60		1.58	0.35
I	$* + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}^*$	-0.01		-0.09		-0.03	
J	$\text{H}_2\text{O}^* \rightarrow \text{HO}^* + \text{H}^+ + \text{e}^-$	0.93		1.10		1.22	

catalytically active for OER in an alkaline electrolyte and the presence of OH^- anions in the solvent leads to the deprotonation of NiOOH layers which increases the activity of NiOOH .⁵⁶ As long as Fe doping is applied in step A, the effect of Fe doping on Ni oxidation is still expected even in an alkaline medium. Due to the prohibitive computational cost, we have, however, omitted the explicit solvation.

3.5 Electronic Structure of Key Intermediates

Doping of Fe into NiOOH monolayer increases the stability of O^* intermediate by creating extra local positive charge and destabilizes HOO^* . Spin density analysis of the O-O bond in HOO^* indicates a triplet nature of the O-O bond (see Figure S4 in SI). After deprotonation of HOO^* , the triplet like nature of the adsorbed O_2 is retained in the case of AS-1 and AS-2 (see Figure 5 (a,b)). Interestingly, in the case of AS-3, the adsorbed O_2 attains singlet character resembling the $^1\Sigma_g^+$ state of molecular O_2 . It can be clearly seen in Figure 5 (c) that the π_x and π_y orbitals of the adsorbed O_2 have antiparallel spin densities. In step C, the O_2 desorbs from the surface as a triplet oxygen. Note that spin density in adsorbed O_2 is antiferromagnetically

coupled with metal atoms at all active sites. In the case of AS-1 and AS-2, spin density on Ni atoms is antiferromagnetic to that on O_2 adsorbate. In the case of AS-3, the spin density in π_x is antiferromagnetic with spin density on Fe, whereas spin density in π_y is antiferromagnetic with Ni atoms. This configuration is preferred because the metal atoms are antiferromagnetically coupled to each other. To validate our argument, we calculated the spin density with all metal atoms in ferromagnetic configuration (See Figure 5 (d)). This magnetic configuration is 0.33 eV higher in energy than a configuration where Ni atoms and Fe atoms are antiferromagnetically aligned. It is observed that in the higher energy configuration O_2 attains triplet character antiferromagnetically aligned with surrounding metal atoms. Thus, it is the antiferromagnetic coupling between Ni and Fe, that drives the O_2 adsorbate to a singlet state.

The O-O bond formation through the lattice oxygen in LOC mechanism always results in a triplet state for bound oxygen. It is worth noting that, in contrast to Ni atoms, the adsorbed O_2 is weakly bound to adjacent Fe atom. The adsorbed O_2 in the intermediate $(\text{O}-\text{O}_\text{L})^*$ remains as triplet by maintaining antiferromagnetic coupling with adjacent Ni atoms.

Figure 5: Spin density of O_2^* intermediate for undoped and Fe-doped NiOOH. The isosurface value used is $0.02 a_0^{-3}$. The shaded region presents the active region for OER.

4 Conclusions

Considering the lowest energy structures for pristine and Fe-doped NiOOH over several proton distributions, we have investigated the OER activity over three types of active sites – one on NiOOH and two on Fe-doped NiOOH – via the WNA and LOC mechanisms which differ in the source of O to form O-O bond. We find that Fe doping indirectly enhances OER activity at Ni sites by lowering the free energy demand of the potential determining step in the WNA mechanism. On the other hand, the Fe dopants in NiOOH lattice directly enhance the OER efficiency by providing active sites that stabilize the O^* intermediate and involve the lesser energy-demanding oxidation of Fe^{4+} to Fe^{5+} rather than Ni^{3+} to Ni^{4+} . Moreover, at Fe sites, the LOC mechanism has a lower overpotential than the WNA mechanism. As a consequence, reaction at the Fe sites preferentially proceeds through the oxidation of lattice oxygen atoms rather than water. Interestingly, the PDS at the Ni sites is common between the WNA and LOC mechanisms rendering either mechanism likely. This emphasizes the importance of the lattice coupling mechanism in OER in NiOOH, which has thus far been largely ignored.

Conflicts of interest

There are no conflicts to declare.

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Supporting Information Available

The following files are available free of charge.

- supplementary.pdf: This file contains supplementary information, including the tables of energies of various structures in different magnetic states, image highlighting oxo and hydroxo sites on NiOOH, comparison of transition state structure and free energy barriers of step E at all active sites, and spin density plot of HOO^* at AS-3.
- coordinates.zip: This file contains the optimized cartesian coordinates of all the structures of pristine and Fe-doped monolayers, reaction intermediates, transition states.

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