

Study of Fe-Ni based oxyhydroxide catalysts for electrochemical oxygen evolution reaction by first-principles calculations

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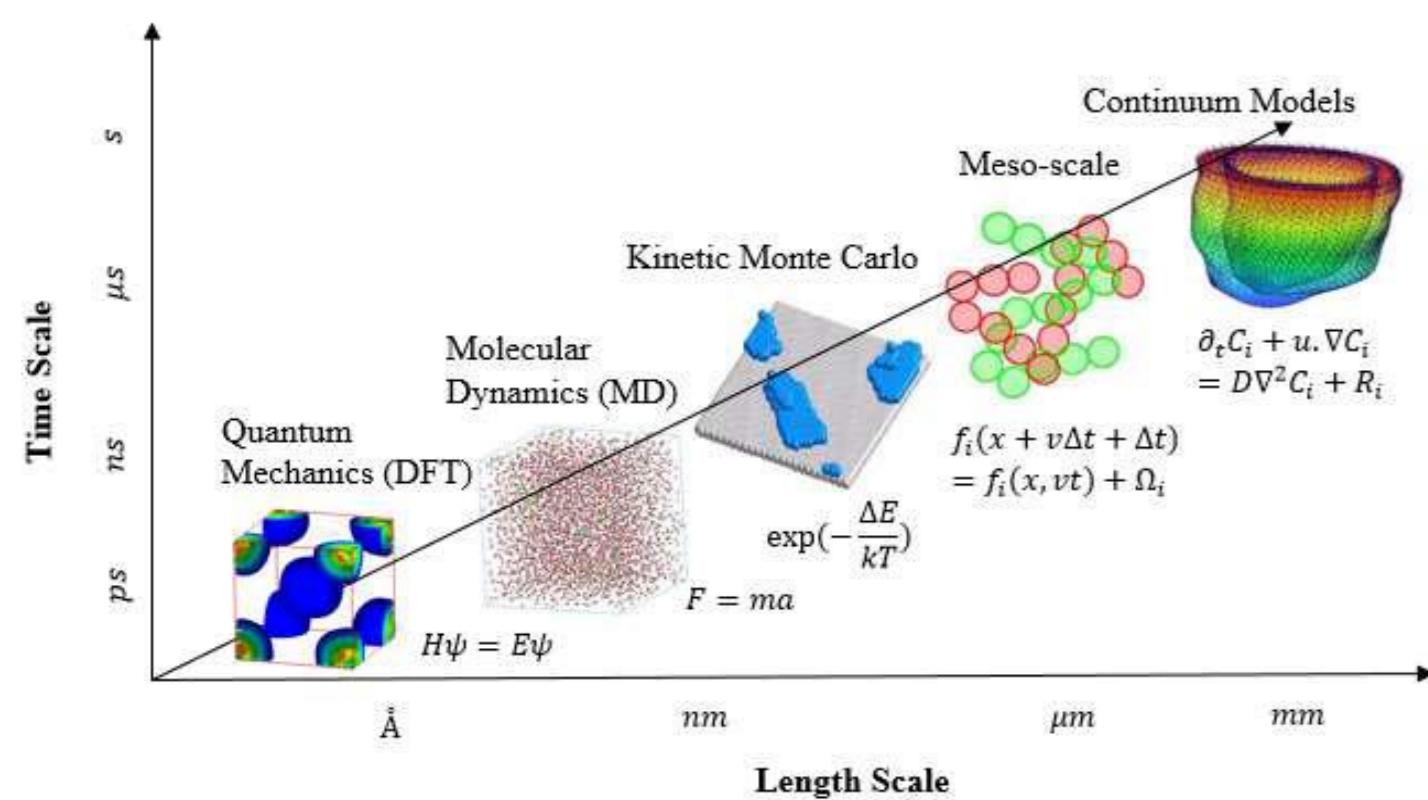
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Abstract

Water-splitting reaction can generate hydrogen and oxygen eco-friendly. Research on oxygen evolution(OER) catalysts, which have complex mechanisms and require more voltage, is essential for efficient and economical production. In this research, we study catalysts based on NiOOH that has high efficiency. We show that oxygen vacancies of Fe-free/Fe-doped NiOOH have higher OER activity than hydroxyl vacancies and active bulk site activity is similar to the experimentally measured onset potential.

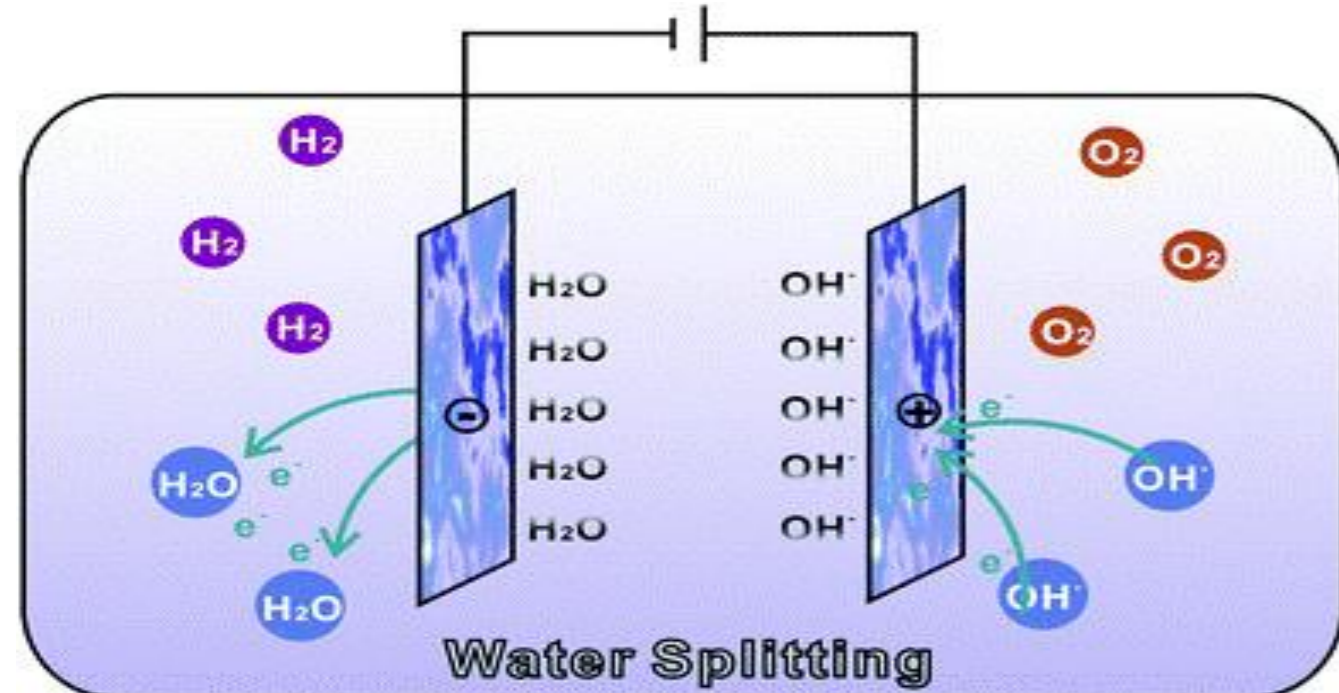
Introduction

- The method of computational chemistry depending on the time and length scales

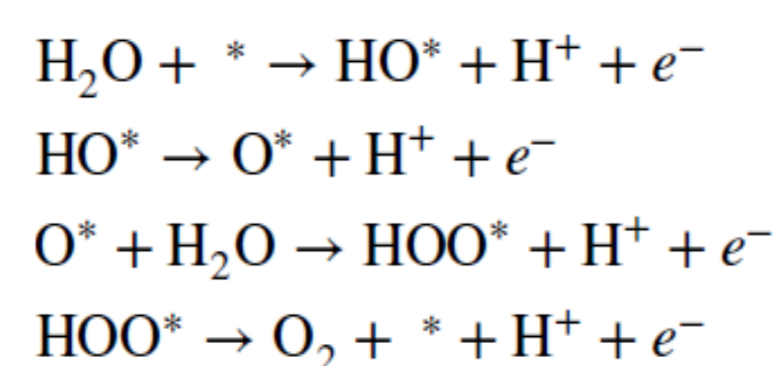


DFT(Density Functional Theory) is a method to solve the quantum mechanics problem of a many-body system by expressing electrons as electron density rather than analyzing the wave function of each electron.

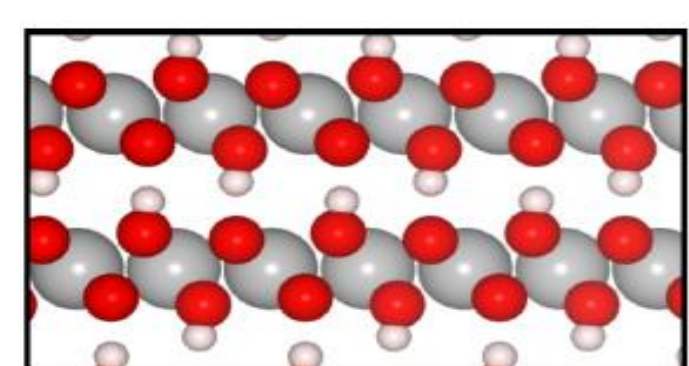
- Scheme of water splitting and OER mechanism



OER Mechanism

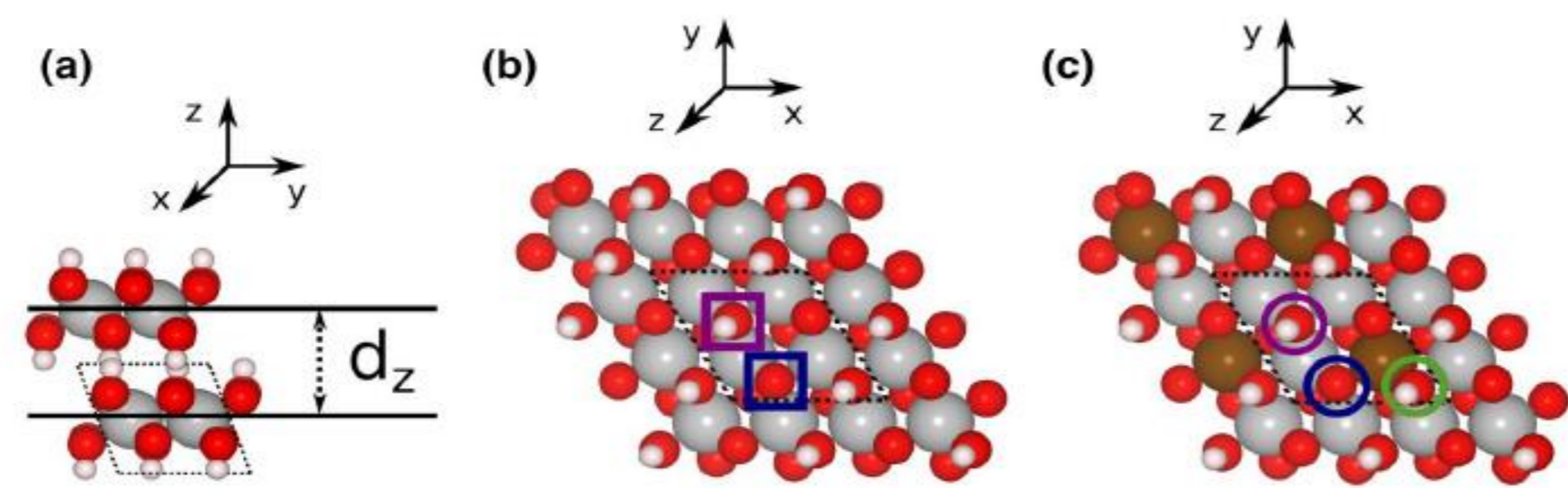


- Structure of the model system



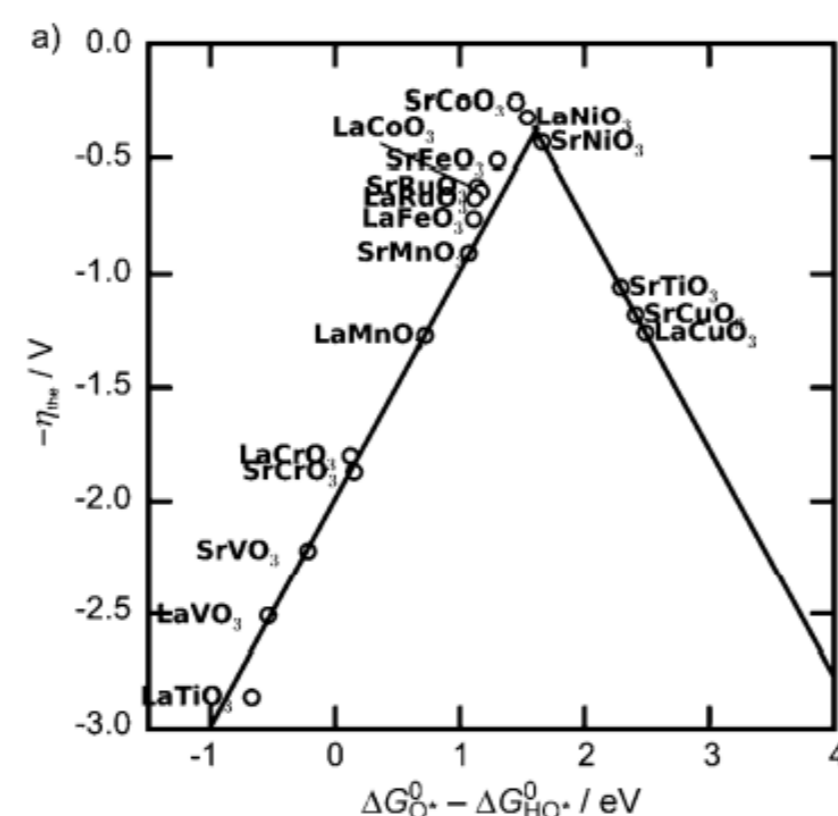
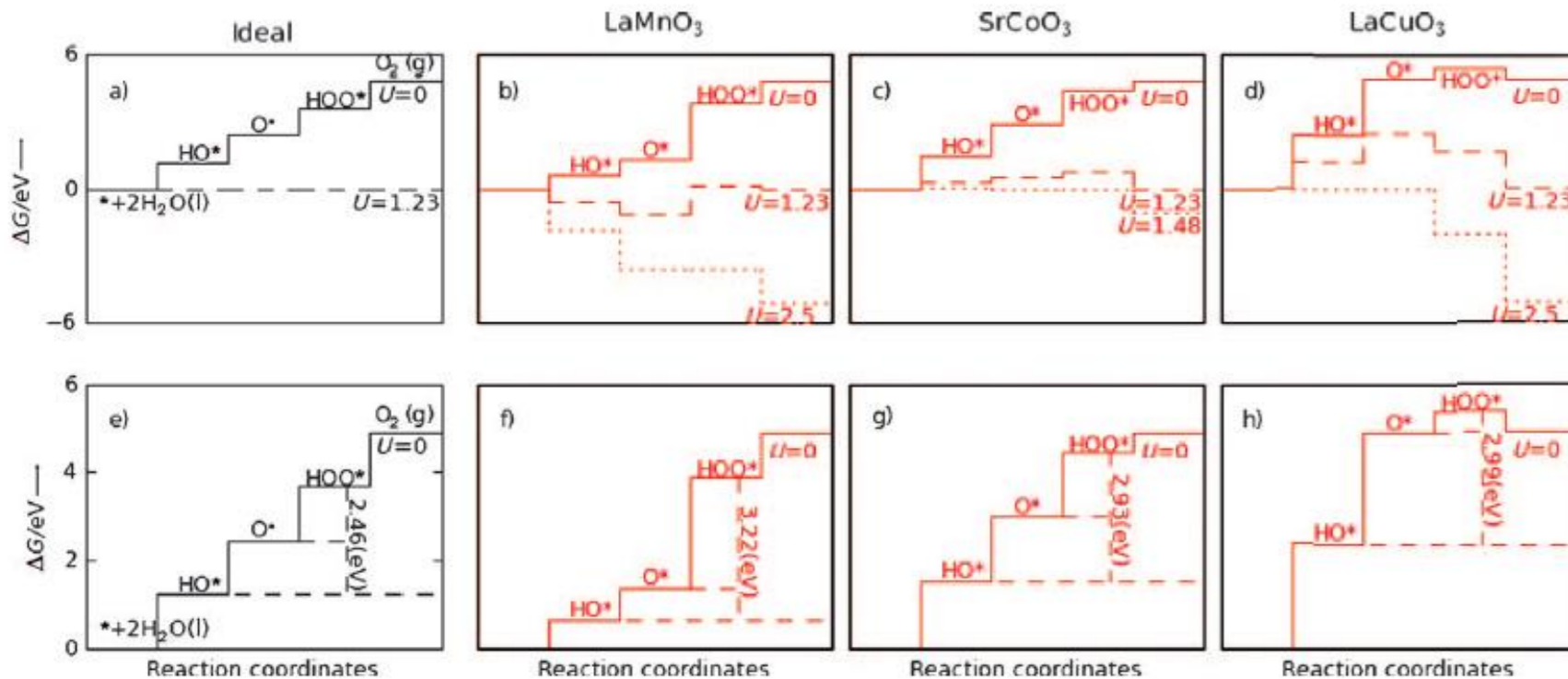
β -NiOOH

The different reactivities of each active site can be get by adjusting the distance interlayer spacing d_z .



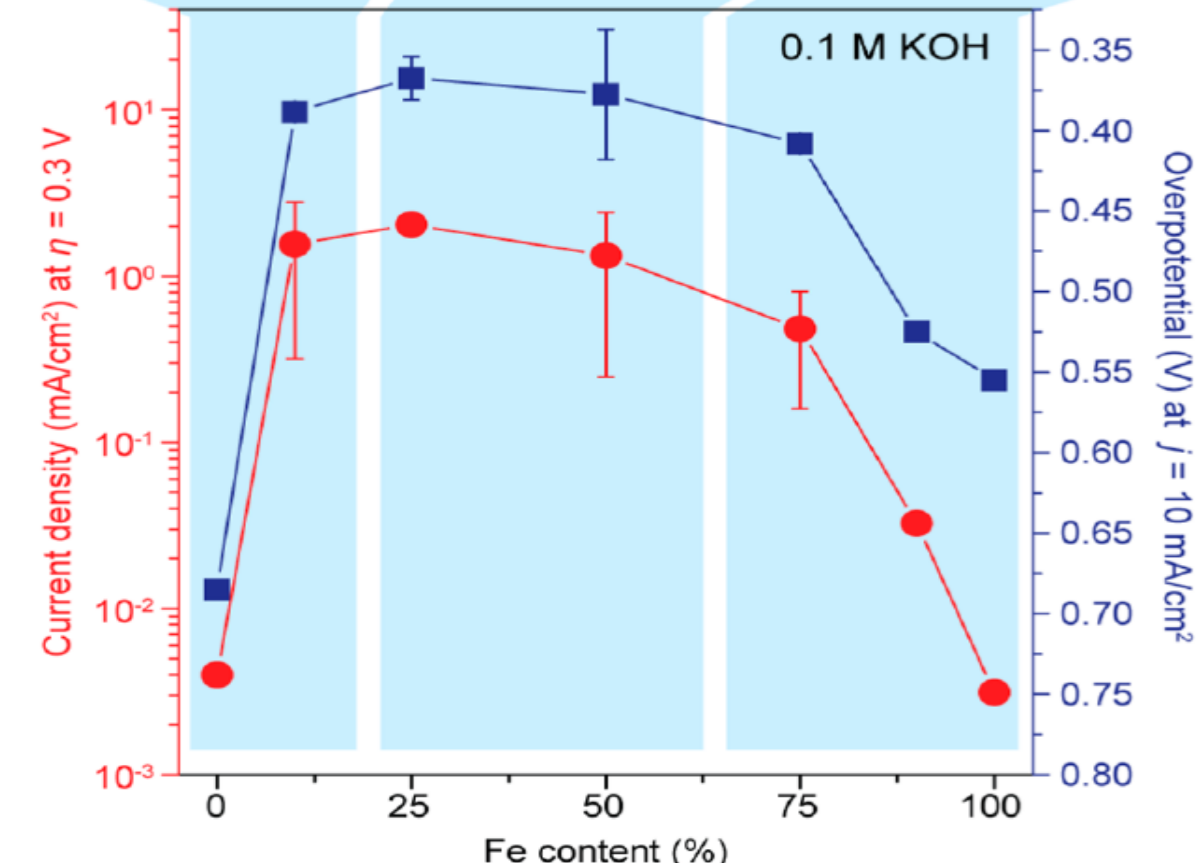
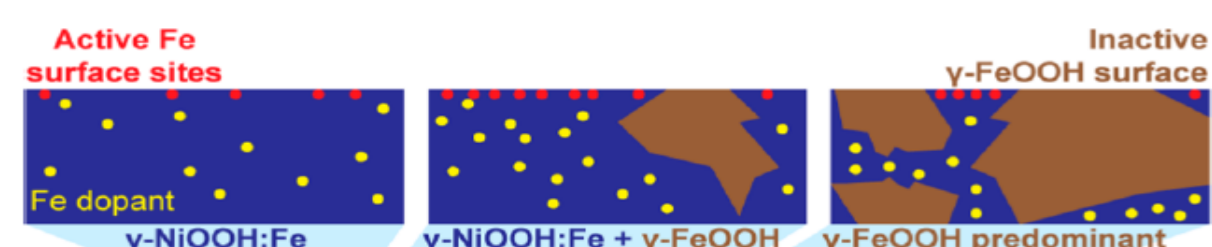
Previous Studies

- Perovskite-type catalysts



$$\eta^{Theory} = [\text{Max}(\Delta G_1^0, \Delta G_2^0, \Delta G_3^0, \Delta G_4^0)]/e - 1.23\text{V}$$

- Fe doped γ -NiOOH catalysts



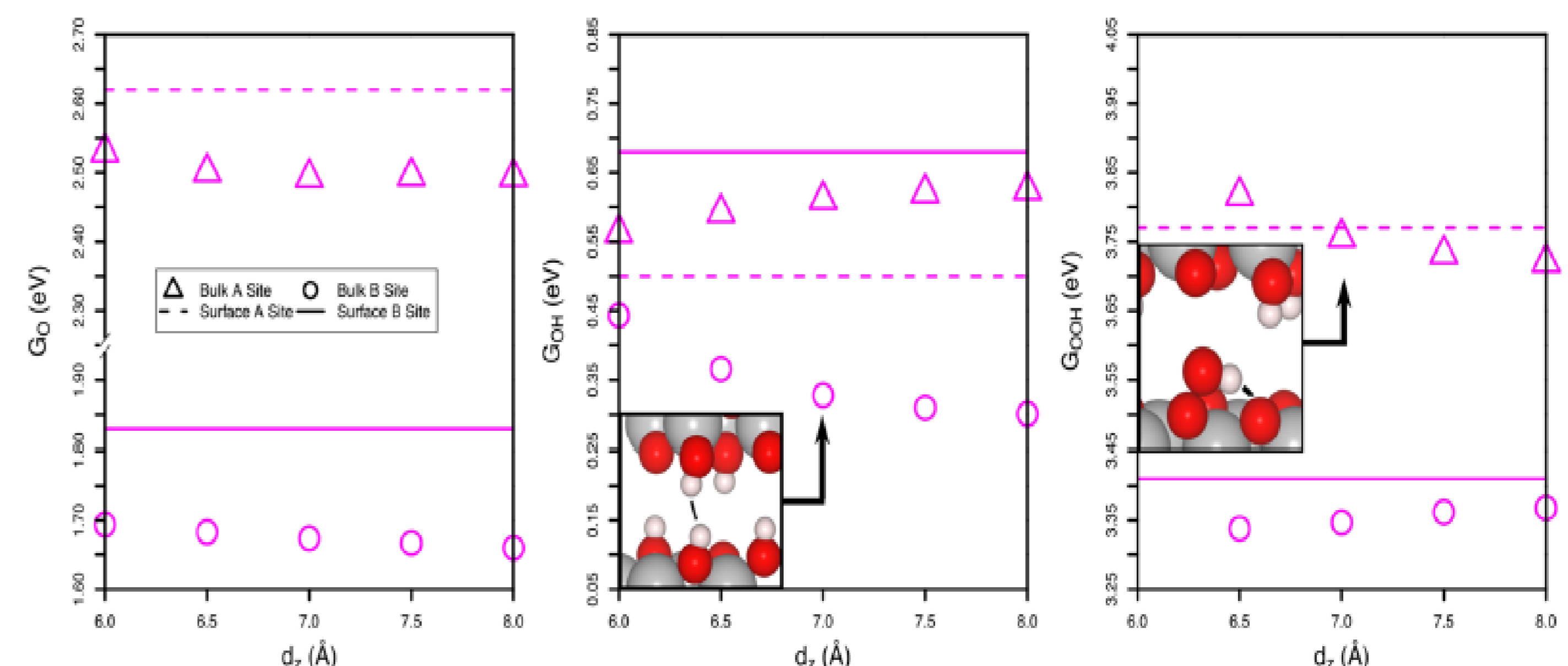
Fe impurities increase the OER activity, and it is maximum at 25%

Results and Discussion

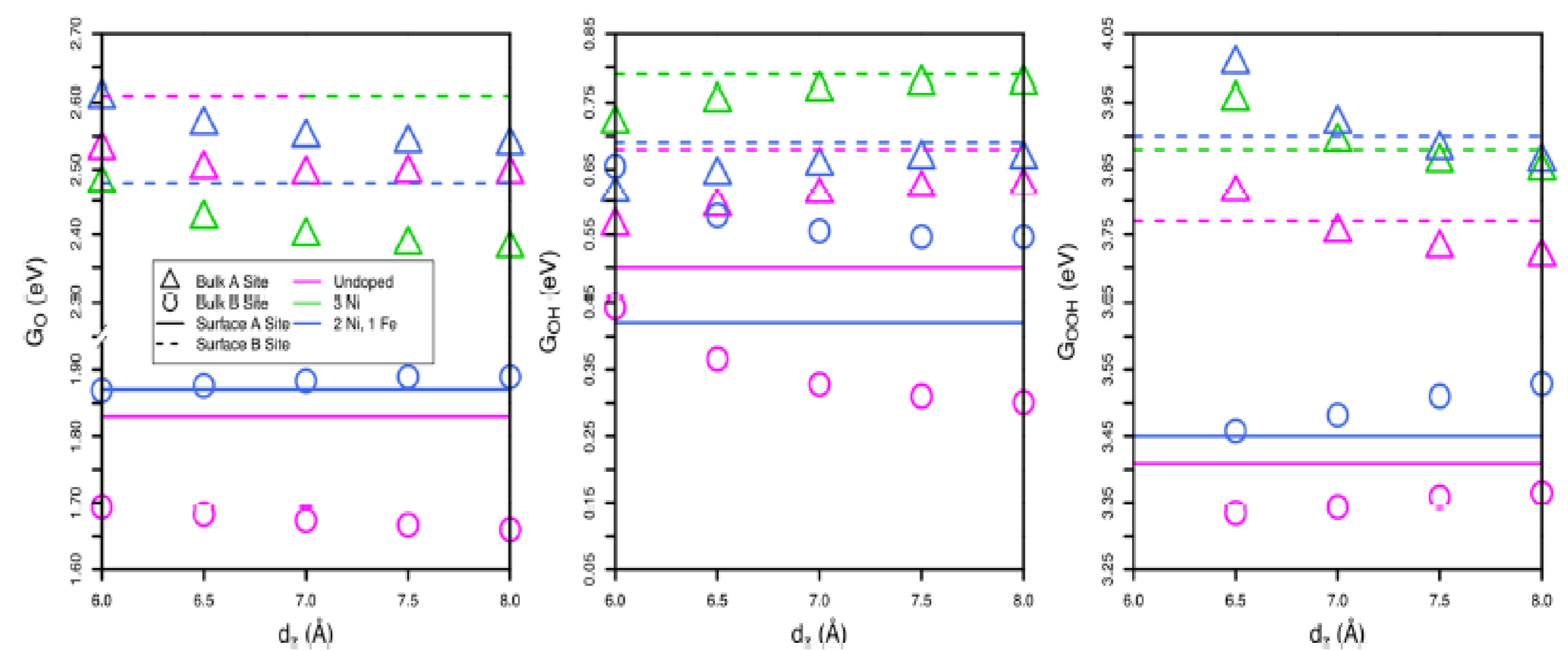
- Required potential in pure NiOOH ($d_z = 6.5 \text{ \AA}$)

Reaction Step	Required Potential (Type A site) [V]	Required Potential (Type B site) [V]
$\text{H}_2\text{O} + * \rightarrow \text{HO}^* + \text{H}^+ + e^-$	0.59	0.37
$\text{HO}^* \rightarrow \text{O}^* + \text{H}^+ + e^-$	<u>1.91</u>	1.32
$\text{H}_2\text{O} + \text{O}^* \rightarrow \text{HOO}^* + \text{H}^+ + e^-$	1.32	<u>1.65</u>
$\text{HOO}^* \rightarrow \text{O}_2 + * + \text{H}^+ + e^-$	1.10	1.58

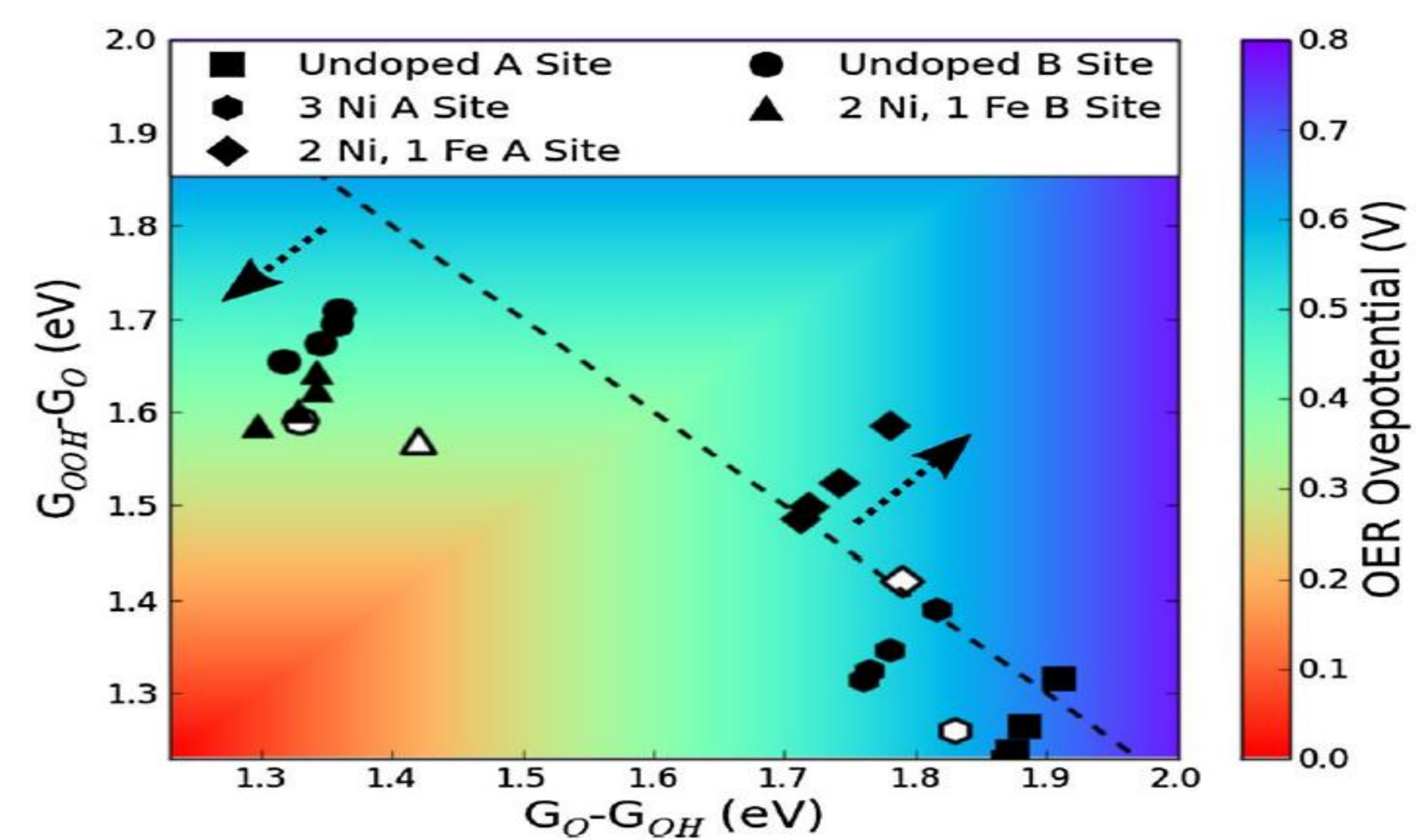
- Adsorption energies of each active site of Fe-free NiOOH



- Comparison of adsorption energies in Fe-doped NiOOH



- Change in activity depending on interlayer spacing and Fe doping



Conclusions

- Since α -Ni(OH)₂ and γ -NiOOH have a complex structure based on β phase, the study of Fe free/doped β -NiOOH should be preceded.
- The research of Ni (oxy)hydroxide on surface are actively in progress, but studies on bulk site are insufficient.
- It was found that oxygen vacancies of Fe-free/Fe-doped NiOOH have higher OER activity than hydroxyl vacancies.
- Active bulk site activity is similar to the experimentally measured onset potential.

Computational methods

- VASP software package
- spin-polarized PBE exchange-correlation functional
- Projector augmented wave (PAW) pseudopotential
- Energy cutoff of 400.0 eV
- 4 × 4 × 6 Monkhorst-Pack k -point mesh