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# Dischargeable nickel matrix charges iron species for oxygen evolution electrocatalysis

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## ABSTRACT

Nickel-iron (oxy)hydroxide ( $\text{NiFeO}_x\text{H}_y$ ) is a state-of-the-art non-precious electrocatalyst for oxygen evolution reaction (OER) in alkaline media. However, the origin of the synergy between Ni and Fe remains unclear. Here, operando X-ray absorption and ultraviolet photoelectron spectroscopy were used to prove the charging-discharging behavior of Ni and Fe when they are adjacent. Fe oxidation and Ni reduction were simultaneously observed during electrocatalytic OER in  $\text{NiFeO}_x\text{H}_y$  compared to unary metal (oxy)hydroxide. The higher Fermi level of  $\text{FeO}_x\text{H}_y$  compared to  $\text{NiO}_x\text{H}_y$  enables charge transfer from Fe to Ni domain near the boundaries. From the experimental results, the combination of Ni and Fe results in superior oxygen-evolving activity by exposing high valent Fe coupled with a dischargeable Ni matrix.

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## 1. Introduction

Water splitting powered by wind and solar energy is the core technology for realizing the hydrogen economy [1]. However, the efficiency in the full configuration of water splitting is limited by the sluggish oxygen evolution reaction (OER) [2,3]. Thus, there has been significant interest in developing highly efficient oxygen-evolving electrocatalysts and electrodes using inexpensive earth-abundant materials [4–13].

Nickel has the best oxygen-evolving capability among the period 4 transition metals due to its appropriate oxophilicity [2]. Incorporating Fe into the Ni matrix dramatically enhances the OER performance [14,15], leading to the development of  $\text{NiFeO}_x\text{H}_y$  as a state-of-the-art OER electrocatalyst [3]. However, the origin of the synergy between Ni and Fe is poorly understood because of the multivariate heterogeneous catalysis. Using differential electrochemical mass spectrometry (DEMS), X-ray absorption spectroscopy (XAS) and UV-vis spectroscopy, Görlin et al. claimed that Ni is the active site based on its reduced oxidation number in the

presence of oxidizing hydroxyl ion during OER [16,17]. However, recent density functional theory (DFT) calculation predicted the active site to be Fe. Especially, high valent Fe ( $\text{Fe}^{4+}$ ) is regarded as a key intermediate in the  $\text{NiFeO}_x\text{H}_y$  electrocatalyst [18–20]. *Ab initio* molecular dynamics (AIMD) simulations by Zhou et al. showed that Fe in a highly oxidized state ( $\text{Fe}^{4+}$ ) forms Fe clusters on the  $\text{NiOOH}$  surface [21]. Chen et al. [22] and Goldsmith et al. [23] further detected  $\text{Fe}^{4+}$  species through operando spectroelectrochemical measurements using Mössbauer and UV-vis spectroscopy, respectively. Hunter et al. detected over-oxidized  $\text{Fe}^{6+}$  in non-aqueous media by Fourier transform infrared (FT-IR) spectroscopy [24]. In contrast, XAS studies by Görlin et al. [16,17] and Friebel et al. [25] showed that  $\text{Fe}^{3+}$  is the maximum oxidation state when  $\text{NiFeO}_x\text{H}_y$  evolves oxygen under OER potential. The proposed oxidation state of Fe during OER ranges from  $\text{Fe}^{3+}$  to  $\text{Fe}^{6+}$ , besides the driving force of Fe oxidation still remains undetermined.

In this operando XAS study, we found clear evidence for Fe oxidation to beyond  $\text{Fe}^{3+}$  in  $\text{NiFeO}_x\text{H}_y$ , especially when there is an adjacent Ni matrix. This agrees with the hypothesis that highly oxidized Fe species are key intermediate supporting Fe as active site in OER catalysis [18–20,26]. By observing Ni oxidation state at OER, we also uncovered the driving force of Fe oxidation is Ni reduction ( $\text{Ni}^{3+}/\text{Ni}^{2+}$ ) of adjacent Ni matrix, which supports recent computational studies [20,23].

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