



Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Dischargeable nickel matrix charges iron species for oxygen evolution electrocatalysis

Sinwoo Kang^a, Kahyun Ham^a, Hyung-Kyu Lim^b, Jaeyoung Lee^{a,c,*}^a Electrochemical Reaction & Technology Laboratory (ERTL), School of Earth Sciences and Environmental Engineering, Gwangju Institute of Science and Technology (GIST), Gwangju 61005, Republic of Korea^b Division of Chemical Engineering and Bioengineering, Kangwon National University, Chuncheon 24341, Republic of Korea^c Ertl Center for Electrochemistry and Catalysis, GIST, Gwangju 61005, Republic of Korea

ARTICLE INFO

Article history:

Received 24 December 2020

Revised 13 April 2021

Accepted 13 April 2021

Available online 28 April 2021

Keywords:

Oxygen evolution reaction catalysis

Nickel-iron (oxy)hydroxide

Operando X-ray absorption spectroscopy

Ultraviolet photoelectron spectroscopy

Work function

ABSTRACT

Nickel-iron (oxy)hydroxide (NiFeO_xH_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 NiFeO_xH_y compared to unary metal (oxy)hydroxide. The higher Fermi level of FeO_xH_y compared to NiO_xH_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.

© 2021 Elsevier Ltd. All rights reserved.

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 NiFeO_xH_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 (Fe^{4+}) is regarded as a key intermediate in the NiFeO_xH_y electrocatalyst [18–20]. *Ab initio* molecular dynamics (AIMD) simulations by Zhou et al. showed that Fe in a highly oxidized state (Fe^{4+}) forms Fe clusters on the NiOOH surface [21]. Chen et al. [22] and Goldsmith et al. [23] further detected Fe^{4+} species through operando spectroelectrochemical measurements using Mössbauer and UV-vis spectroscopy, respectively. Hunter et al. detected over-oxidized 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 Fe^{3+} is the maximum oxidation state when NiFeO_xH_y evolves oxygen under OER potential. The proposed oxidation state of Fe during OER ranges from Fe^{3+} to 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 Fe^{3+} in NiFeO_xH_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].

* Corresponding author at: Electrochemical Reaction & Technology Laboratory (ERTL), School of Earth Sciences and Environmental Engineering, Gwangju Institute of Science and Technology (GIST), Gwangju 61005, Republic of Korea.

E-mail address: jaeyoung@gist.ac.kr (J. Lee).