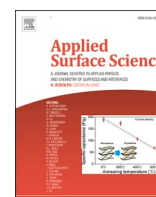




Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: [www.elsevier.com/locate/apsusc](http://www.elsevier.com/locate/apsusc)

## Full Length Article

## Sulfur-incorporated nickel-iron layered double hydroxides for effective oxygen evolution reaction in seawater

Sun Young Jung<sup>a,1</sup>, Sukhyun Kang<sup>b,1</sup>, Kang Min Kim<sup>b</sup>, Sungwook Mhin<sup>c</sup>, Jong Cheol Kim<sup>d</sup>, So Jung Kim<sup>a</sup>, Enkhbayar Enkhtuvshin<sup>a</sup>, Seunggun Choi<sup>e</sup>, HyukSu Han<sup>a,\*</sup><sup>a</sup> Department of Energy Engineering, Konkuk University, 120 Neungdong-ro, Gwangjin-gu, Seoul 05029, Republic of Korea<sup>b</sup> Korea Institute of Industrial Technology, 137-41 Gwahakdanji-ro, Gangneung-si, Gangwon 25440, Republic of Korea<sup>c</sup> Department of Advanced Materials Engineering, Kyonggi University, Suwon 16227, Republic of Korea<sup>d</sup> Daegu Mechatronics & Materials Institute, 11 Seongseogongdan-ro, Daegu 42714, Republic of Korea<sup>e</sup> Department of Energy Engineering, Hanyang University, 222 Wangsimni-ro, Seoul 133-791, Republic of Korea

## ARTICLE INFO

## Keywords:

Seawater splitting  
Oxygen evolution reaction  
Electrocatalyst  
Layered double hydroxide  
Sulfidation

## ABSTRACT

Given the abundance of water on the surface of the Earth, water splitting using seawater may be an effective solution to the future energy crisis. However, oxygen evolution reaction (OER) electrocatalysts require several specific characteristics to be used in seawater electrolysis, such as high catalytic activity, selectivity, and resistivity against chlorine corrosion. This paper reports that sulfur incorporation into nickel-iron layered double hydroxide (NiFe-LDH-S) can fulfill the abovementioned requirements for seawater oxidation. Sulfidation was performed on NiFe-LDH nanosheets homogeneously grown on a porous carbon scaffold via a facile chemical vapor deposition (CVD) process. The best NiFe-LDH-S sample demonstrated excellent catalytic activity with a high corrosion resistance for seawater oxidation.

## 1. Introduction

Water splitting is one of the most promising methods for the production of value-added chemicals (e.g., hydrogen) while utilizing sustainable energies [1–5]. Currently, commercial water electrolyzers require highly purified water under KOH conditions [6–7]. Given that oceans hold > 95% of the total water on Earth, it is suitable to directly produce hydrogen using seawater as a starting feedstock via electrochemical water splitting. However, this is challenging to achieve, mainly due to the cutting-edge requirements with respect to the anode material properties [8–15]. Specifically, a high catalytic activity, high catalytic selectivity for oxygen evolution reactions (OERs), and high resistance against chloride corrosion are required in the anode material for seawater splitting. Although the catalyst has a high activity toward OERs, highly active chloride anions can destroy numerous catalysts or

substrates via the formation of metal chloride-hydroxides [9].

Dai et al. recently reported a novel strategy for the design of a high-performance anode electrocatalyst for seawater oxidation. In particular, a polyanion sulfate/carbonate-passivated NiFe-layered double hydroxide (LDH) was developed through an anodization process, where negatively charged  $S^{2-}$  ions can effectively repel  $Cl^-$  anions in seawater, and therefore, enhance the resistance for chlorine corrosion [9]. In addition to the inherently high selectivity for OERs of NiFe-LDH, sulfur plays two important roles in enhancing electrocatalytic seawater oxidation. In particular, it improves electrical conductivity and generates a negatively charged anion-rich surface. Hence, the atomic-scale incorporation of sulfur into the NiFe-LDH matrix is a suitable method for the development of high-performance electrocatalysts for seawater oxidation.

Sulfidation has been widely applied to functional nanomaterials for improving their physicochemical properties using several methods such

**Abbreviations:** OER, oxygen evolution reaction; LDH, layered double hydroxide; CVD, chemical vapor deposition; CC, carbon cloth; TOF, turn over frequency;  $E_a$ , activation energy; DI, deionized; LSV, linear sweep voltammetry; RHE, reversible hydrogen electrode; EIS, electrochemical impedance spectroscopy; OC, open circuit; GC, glassy carbon; RDE, rotating disk electrode; SEM, scanning electron microscopy; TEM, transmission electron microscopy; EDS, energy-dispersive X-ray spectroscopy; XRD, X-ray diffraction; XPS, X-ray photoelectron spectroscopy; SAEM, selective area diffraction pattern; CV, cycling voltammetry;  $R_{ct}$ , charge transfer resistance; ECSA, electrochemical surface area;  $C_{dl}$ , double layer capacitance; CP, chronopotentiometry.

\* Corresponding author.

E-mail address: [hhan@konkuk.ac.kr](mailto:hhan@konkuk.ac.kr) (H. Han).

<sup>1</sup> The authors contributed equally to this work.

<https://doi.org/10.1016/j.apsusc.2021.150965>

Received 5 July 2021; Received in revised form 12 August 2021; Accepted 13 August 2021

Available online 16 August 2021

0169-4332/© 2021 Elsevier B.V. All rights reserved.