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Activation of a Ni electrocatalyst through spontaneous transformation of nickel sulfide to nickel hydroxide in an oxygen evolution reaction

Minoh Lee^a, Hyung-Suk Oh^a, Min Kyung Cho^b, Jae-Pyoung Ahn^b, Yun Jeong Hwang^{a,c,*},
Byoung Koun Min^{a,d,*}^a Clean Energy Research Center, Korea Institute of Science and Technology, Seoul 02792, Republic of Korea^b Advanced Analysis Center, Korea Institute of Science and Technology, Seoul 02792, Republic of Korea^c Division of Energy and Environmental Technology, KIST School, Korea University of Science and Technology (UST), Seoul 02792, Republic of Korea^d Green School, Korea University, Seoul 02841, Republic of Korea

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ABSTRACT

Ni-sulfide compounds synthesized on Ni foam by simple thermal sulfurization are employed as electrocatalysts for water oxidation, resulting in superior activity in alkaline electrolyte media. The role of sulfur in Ni-sulfide was found to be an activator that transformed sulfide into hydroxide, which was eventually transformed into (oxy)hydroxide. The Ni-(oxy)hydroxide phase was also found to be layered and/or amorphous. This activated catalyst showed significant enhancement in water oxidation performance with a low overpotential value of 256 mV at current density of 10 mA cm⁻². Our observation could offer important insight into metal-chalcogenide electrocatalyst for water oxidation.

1. Introduction

Electrochemical water splitting is considered to be an attractive and efficient method to produce pure hydrogen in connection with renewable energy [1]. In general, the overall water splitting process can be divided into two half-cell redox reactions: a hydrogen evolution reaction (HER) and an oxygen evolution reaction (OER) [2]. In particular, a high overpotential is required for OER due to the sluggish kinetics associated with O–H bond breaking and attendant O–O bond formation. Therefore, the OER has been regarded as a bottle-neck in commercializing a water splitting system [3,4]. Hence, an efficient OER electrocatalyst is highly desired to address this challenge by efficiently coupling multiple protons and electron transfers for O₂ evolution at low overpotential [5]. Currently, RuO₂, IrO₂, and their mixed oxide (e.g., Ru_{1-x}Ir_xO₂) are regarded as the most efficient OER electrocatalysts [6–8]. However, these noble metal-based catalysts have obvious disadvantages for practical applications due to their low earth abundance and high cost.

To overcome this issue, several studies have developed non-noble metal based OER electrocatalysts, including low-cost transition metal oxide/hydroxides [9–13], perovskite, [14–16] chalcogenides, [17–19] phosphates [20], and molecular electrocatalysts [21–23]. Among these metal-chalcogenide OER electrocatalysts such as MX, MX₂, M₉X₈, M₃X₄, and M₃X₂ (M = Co and Ni, X = S, Se, and Te) have recently received

attention as strong alternatives due to their prominent electronic structure and low cost [24–27].

Ni-sulfides compounds (Ni₃S₂, NiS, NiS₂ etc) have recently shown huge potential as efficient OER electrocatalysts [27–32]. In the case of Ni₃S₂ metal-chalcogenide, Ni₃S₂ nanorods/Ni foam composite electrode has been demonstrated as an excellent OER catalyst with a low overpotential of 157 mV [17]. The high activity of this catalyst was explained in terms of unusual Ni mixed valence states (Ni⁰, Ni⁺, and Ni²⁺) due to synergetic chemical coupling effects among hydrated Ni₃S₂ nanorods, the nickel oxide layer, and the Ni foam support. On the other hand, the role of sulfur in the high activity has also been studied in Ni-sulfide. For example, when Ni_xS_y film is synthesized by pulse-electrodeposition, it has been proposed that sulfur anion is depleted in the electrocatalyst surface layer while Ni_xS_y is converted into an amorphous Ni oxide [29]. This implies that metal sulfide can act as a precursor to a highly active Ni oxide electrocatalyst for oxygen evolution. Despite several important insights from previous studies, the origin of the enhanced performance of Ni₃S₂/Ni electrocatalyst has not been clearly understood yet. The physical origin of the experimentally-observed enhanced performance of activated Ni_xS_y OER electrocatalyst in alkaline condition has not been elucidated either. Therefore, a more detailed study is needed to advance metal-chalcogenide electrocatalysts for OER.

The objective of this report was to address these issues mentioned

* Corresponding authors at: Clean Energy Research Center, Korea Institute of Science and Technology, Seoul 02792, Republic of Korea.

E-mail addresses: yjhwang@kist.re.kr (Y.J. Hwang), bkmin@kist.re.kr (B.K. Min).