



Contents lists available at ScienceDirect

Journal of Electroanalytical Chemistry

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

Rhodium-molybdenum oxide electrocatalyst with dual active sites for electrochemical ammonia synthesis under neutral pH condition

Sunki Chung^a, Dong Han Seo^b, Minjun Choi^a, Xin Mao^c, Aijun Du^c, Kahyun Ham^a, Sarbjit Giddey^d, Jaeyoung Lee^{a,e,*}, Hyungkuk Ju^{d,f,*}^a Electrochemical Reaction and Technology Laboratory, School of Earth Sciences and Environmental Engineering, Gwangju Institute of Science and Technology (GIST), Gwangju 61005, South Korea^b School of Civil and Environmental Engineering, University of Technology Sydney, P.O. Box 123, 15 Broadway, NSW 2007, Australia^c School of Chemistry, Physics and Mechanical Engineering, Queensland University of Technology Gardens Point Campus Brisbane, QLD 4001, Australia^d CSIRO Energy, Private Bag 10, Clayton South, Victoria 3169, Australia^e Ertl Center for Electrochemical and Catalysis, GIST, Gwangju 61005, South Korea^f Hydrogen Research Department, Korea Institute of Energy Research (KIER), 152 Gajeong-ro, Yuseong-gu, Daejeon 34129, Republic of Korea

ARTICLE INFO

Keywords:

Electrochemical ammonia synthesis

Nitrogen fixation

Green hydrogen carrier

Rhodium

Molybdenum oxide

ABSTRACT

Electrochemical nitrogen reduction reaction (NRR) process has attracted significant attention recently as an alternative route for green ammonia (NH₃) production to replace conventional, energy intensive Haber-Bosch process. However, a major challenge in NRR process is the relatively poor selectivity of NRR process over its competing hydrogen evolution reaction (HER) process. Herein, we report the synthesis of molybdenum oxide decorated on the rhodium (Rh_{MoOx}/C) catalyst for an efficient NRR with high selectivity. Rh_{MoOx}/C catalyst exhibits an outstanding NH₃ yield rate of 57.2 μg h⁻¹ mg_{cat}⁻¹ at -0.6 V vs. RHE and a high faradaic efficiency of 22% at -0.2 V vs. RHE in 0.1 M Na₂SO₄ electrolyte. This study reveals the interdependent relationship between the catalyst structure, operating conditions, and the reaction selectivity in the electrochemical NH₃ synthesis. Moreover, this study also demonstrates the effectiveness of the bimetallic materials in enhancing the NRR process which is an important finding for designing a future electrocatalyst for electrochemical NH₃ production.

1. Introduction

Ammonia (NH₃) plays an essential role in the global economy and is mostly used for the production of fertilizers, explosives, refrigerants and other chemical feedstocks [1,2]. NH₃ is also being considered as a green and effective hydrogen carrier due to its high volumetric and storage densities of hydrogen (~120 kg m⁻³ and 17.7 wt%) and being carbon-free in nature [3,4]. Haber-Bosch process which is the most widely used NH₃ production method, requires high energy consumption arising from its harsh reaction conditions (400–500 °C and ~200 bar) and high purity H₂ feedstock which is extracted from the carbon rich fossil fuels [5]. In order to overcome such limitations of conventional NH₃ production process, electrochemical synthesis route has been gaining significant attention as a promising alternative approach due to single step process, potentially low energy

consumption arising from its mild reaction condition (ambient pressure and low temperature) and the required feedstocks being water and air which are abundant in nature [6,7]. Moreover, the dropping prices of electricity from renewable sources of energy such as solar photovoltaics and wind power are making the electrochemical ammonia production process to be more viable in near future [8–15]. However, the low kinetics of the nitrogen reduction reaction (NRR) process and poor yield of ammonia arising from the low reaction selectivity over its competing hydrogen evolution reaction (HER) have been main challenges hindering its progress for adoption in industry. As a result, in the electrochemical NH₃ synthesis process, development of effective electrocatalyst materials which provide high yield and high selectivity of NRR over HER is essential.

According to the Sabatier volcano curve, amongst many NRR catalyst candidates, rhodium (Rh) is found to be a thermodynamically

* Corresponding authors at: Electrochemical Reaction and Technology Laboratory, School of Earth Sciences and Environmental Engineering, Gwangju Institute of Science and Technology (GIST), Gwangju 61005, South Korea (J. Lee), Hydrogen Research Department, Korea Institute of Energy Research (KIER), 152 Gajeong-ro, Yuseong-gu, Daejeon 34129, Republic of Korea (H. Ju).

E-mail addresses: jaeyoung@gist.ac.kr (J. Lee), Hyungkuk.ju@kier.re.kr (H. Ju).

<https://doi.org/10.1016/j.jelechem.2021.115157>

Received 27 January 2021; Received in revised form 4 March 2021; Accepted 10 March 2021

1572-6657/© 2021 Elsevier B.V. All rights reserved.