Nano Energy 55 (2019) 49–58

Contents lists available at ScienceDirect

Nano Energy

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

Full paper

RuO_2 nanocluster as a 4-in-1 electrocatalyst for hydrogen and oxygen electrochemistry

Han-Saem Park[a,1], Juchan Yang[a,1], Min Kyung Cho[b], Yeongdae Lee[a], Seonghun Cho[c], Sung-Dae Yim[c], Byeong-Su Kim[d], Jong Hyun Jang[b,*], Hyun-Kon Song[a,*]

[a] School of Energy and Chemical Engineering, Ulsan National Institute of Science and Technology, UNIST-gil 50, Ulsan 44919, Republic of Korea
[b] Fuel Cell Research Center, Korea Institute of Science and Technology (KIST), Hwarangno 14-gil 5, Seongbuk-gu, Seoul 02792, Republic of Korea
[c] Fuel Cell Laboratory, Korea Institute of Energy Research (KIER), 152 Gajeong-ro, Daejeon 34129, Republic of Korea
[d] Department of Chemistry, Yonsei University, 50, Yonsei-ro, Seodaemun-gu, Seoul 03721, Republic of Korea

ARTICLE INFO

Keywords:
Multi-functional electrocatalysts
Water splitting
Carbon coated metal oxides
All-pH electrolysis
Regenerative fuel cells

ABSTRACT

Partially hydrous RuO_2 nanocluster embedded in a carbon matrix (x-RuO_2@C with x = hydration degree = *0.27* or *0.27*@C) is presented as a bifunctional catalyst for hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) for water splitting. Symmetric water electrolyzers based on *0.27*-RuO_2@C for both electrodes showed smaller potential gaps between HER and OER at pH 0, pH 14 and even pH 7 than conventional asymmetric electrolyzers based on two different catalysts (Pt/C || Ir/C) that have been known as the best catalysts for HER and OER respectively. Moreover, *0.27*-RuO_2@C showed another bifunctional electroactivity for fuel cell electrochemistry involving hydrogen oxidation reaction (HOR) and oxygen reduction reaction (ORR) that are the backward reactions of HER and OER respectively. Pt-level HOR electroactivity was obtained from *0.27*-RuO_2@C, while its ORR activity was inferior to that of Pt with 200 mV higher overpotential required. The tetra-functionality of *0.27*-RuO_2@C showed the possibility of realizing single-catalyst regenerative fuel cells.

1. Introduction

Hydrogen economy is one of the possible and potential alternatives to the present hydrocarbon economy even if the concept has been criticized in terms of its low conversion efficiencies and infeasible competitive edge over other energy sources. Hydrogen production and its conversion to electricity are the starting and ending points of hydrogen economy, respectively. In the interim between them, hydrogen storage and its transportation are another important sectors in hydrogen economy [1]. Water electrolysis is one of the main production methods, which is more environmentally friendly than the steam reformation of hydrocarbons is. However, water electrolysis has the disadvantages of high cost and low efficiencies [2–5]. Electrocatalysts have been developed to improve water electrolysis efficiencies while renewable energy sources were combined with electrolyzers for cost reduction [6,7]. On the other hand, various types of fuel cells have been considered as candidates for hydrogen/electricity conversion [8]. As a more advanced hydrogen-based device, regenerative fuel cells function as water electrolyzers to produce hydrogen in its regenerative or reverse mode and as fuel cells to generate electricity in its fuel cell mode [9]. The core element of electrolyzers and fuel cells is electrocatalysts that accelerate kinetics of hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) for water electrolysis; and hydrogen oxidation reaction (HOR) and oxygen reduction reaction (ORR) for fuel cells. HER and OER are the backward reactions of HOR and ORR, respectively. In this work, we introduce a single catalyst for all the four reactions, demonstrating successful operation of symmetric water electrolyzers.

Electrochemical water splitting occurs through two reactions: HER at $E^\circ = 0\ V_{RHE}$ (E° = standard reduction potential, V_{RHE} = V versus RHE) and OER at 1.23 V_{RHE}.

	Acid	Base	
HER:	$2H^+ + 2e^- \rightarrow H_2$	$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	(1)
OER:	$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$	$2OH^- \rightarrow O_2 + 2H_2O + 4e^-$	(2)

Two issues are most challenging in the field of electrocatalysts for water electrolysis: (1) bifunctional catalysts covering both HER and OER; and (2) HER or OER catalysts working over a wide pH range [10–12].

First, high-performance monofunctional catalysts such as Pt for HER

* Corresponding authors.
E-mail addresses: jhjang@kist.re.kr (J.H. Jang), philiphobi@unist.ac.kr, philiphobi@hotmail.com (H.-K. Song).
[1] Authors contributed equally to this work.

https://doi.org/10.1016/j.nanoen.2018.10.017
Received 27 April 2018; Received in revised form 21 September 2018; Accepted 8 October 2018
Available online 23 October 2018
2211-2855/