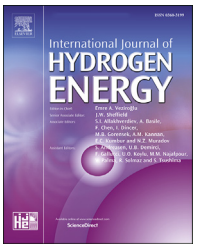
INTERNATIONAL JOURNAL OF HYDROGEN ENERGY XXX (2018) 1–7

Available online at www.sciencedirect.com

ScienceDirect

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



Nitrogen-doped carbon supported platinum catalyst via direct soft nitriding for high-performance polymer electrolyte membrane fuel cell

Dong-Jun Seo [a,b,1], *Myeong-Ri Kim* [a,b,1], *Seung Yong Yang* [a,b], *Won-Young Choi* [a,c], *Hyunguk Choi* [a,c], *Seo-Won Choi* [a,c], *Myeong-Hwa Lee* [a,c], *Young-Gi Yoon* [a], *Min-Ho Seo* [a], *Hansung Kim* [b,***], *Chi-Young Jung* [a,**], *Tae-Young Kim* [a,*]

[a] *Buan Fuel Cell Center, Korea Institute of Energy Research (KIER), Jeollabuk-do, 56332, Republic of Korea*
[b] *Department of Chemical and Biomolecular Engineering, Yonsei University, Seoul, 03772, Republic of Korea*
[c] *Department of Energy Storage and Conversion Engineering, Chonbuk National University, Jellabuk-do, 54596, Republic of Korea*

ARTICLE INFO

Article history:
Received 21 March 2018
Received in revised form
17 July 2018
Accepted 28 July 2018
Available online xxx

Keywords:
Soft nitriding
Nitrogen doping
Electrocatalyst
ORR
PEMFC

ABSTRACT

Control of doping levels of nitrogen to carbon support plays a key role to enhance the catalytic activity of the Pt/C catalyst toward oxygen reduction reaction. Mass-production of such materials is still challenging issue for the practical use. Here, we demonstrate a facile approach for fabrication of the nitrogen-doped Pt/C catalysts via direct soft nitriding of the Pt/C catalyst. The commercial 40 wt% Pt/C is first physically mixed with urea and then heat-treated at 300 °C, which allowed a massive production of the 6.6 atom% nitrogen-doped Pt/C catalysts without sacrificing the Pt catalysts. The specific activity increases by 46.9% after the thermal treatment, while the particle size and crystallinity of Pt remain similar to those before the thermal treatment. As a result, the fuel cell test showed a notable increase in the current density by 100% and 18.5% at 0.8 V and 0.5 V, respectively, for the membrane electrode assembly employing urea treated Pt/C catalyst. Hence, the soft nitriding by urea offers great promise as a simple, energy-efficient and eco-friendly way in manufacturing the nitrogen-doped Pt/C catalyst for the polymer electrolyte membrane fuel cell applications.

* *Corresponding author.*
** *Corresponding author.*
*** *Corresponding author.*
E-mail addresses: elchem@yonsei.ac.kr (H. Kim), cyjung@kier.re.kr (C.-Y. Jung), kty@kier.re.kr (T.-Y. Kim).
[1] D. Seo and M. Kim contributed equally to this work.

https://doi.org/10.1016/j.ijhydene.2018.07.173
0360-3199/

Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) are highly efficient and green energy-conversion device, regarded as one of the most promising next-generation energy technologies [1]. However, PEMFCs still face several technological challenges, despite enduring periods of research. In particular, the sluggish oxygen reduction reaction (ORR) of the carbon supported Pt (Pt/C) catalyst in the cathode plays an important role in impeding the fuel cell performance [2]. Hence, the development of electrocatalyst with high catalytic activity towards ORR has been one of the major issues that limit the commercialization.

Among many, the nitrogen-doped Pt/C catalyst has been widely accepted as one of the highly efficient electrocatalysts towards ORR [3–6]. Although the active sites of nitrogen-doped carbon materials are unclear, it is suggested that the carbon atoms adjacent to pyridinic nitrogen may play a key part in promoting ORR under acidic conditions, which may be synergistic to the Pt catalysts [7,8]. In this regard, several efforts have been made to control the doped nitrogen content and nitrogen atom configuration. Li et al. first reported that the nitrogen doping starts at 300 °C and reaches the highest doping level of 5 atom% at 500 °C when ammonia (NH_3) is used [9]. Luo et al. suggested that the surface area of the nitrogen-doped carbons increases with higher temperature and longer time while the nitrogen content decreases with increasing temperature [10]. Similarly, Zhang et al. found that the nitrogen content in the nitrogen-doped graphene varied at different temperatures, with the highest nitrogen content obtained at 500 °C and the lowest at 800 °C, and concluded that the temperatures ranging from 500 to 600 °C may be acceptable for stabilizing all the nitrogen-containing species (pyrrolic, pyridinic and graphitic nitrogen) [11]. Later, Zhao et al. reported N-doped carbon nanotubes and nanofibers interacting with various metal catalysts for ORR [12]. Furthermore, the impact of different nitrogen-containing precursors on the nitrogen contents and configurations has been studied. For instance, Lai et al. revealed that the annealing of graphene oxide with NH_3 preferentially leads to the formation of pyridinic and graphitic nitrogens [13]. Despite these efforts, the current synthetic process of the nitrogen-doped carbons, without exception, has suffered from at least partially using toxic nitrogen sources, e.g. ammonia. In addition, mass-production of such materials is still critical challenge for the practical use.

Recently, Liu et al. have synthesized the nitrogen-doped carbon supports via "soft nitriding" technique, which introduces nitrogen onto the carbon surfaces by employing NH_3 and isocyanic acid (HCNO) obtained from thermal decomposition of urea [14]. After the heat treatment, the precious metal can be loaded onto the nitrogen-doped carbon support. Their results set a useful pathway to manufacture the nitrogen-doped carbon supports for noble metal catalysts, yet have been employed in the further applications with Pt/C.

In this work, we, for the first time, fabricated the nitrogen-doped Pt/C catalyst via direct soft nitriding of the commercial Pt/C catalyst for promoting the ORR. Unlike the previous work [14], the commercial 40 wt% Pt/C is first physically mixed with urea by vigorous grinding and then mildly heat-treated up to 300 °C to facilitate the fabrication process, thus enabling efficient nitrogen doping in a large quantity. Neither high annealing temperatures above 500 °C [9,10] nor toxic gas such as ammonia [11] is required for nitrogen doping. First, the surface state of the nitrogen-doped carbon is investigated. Subsequently, the particle diameter and crystallinity of Pt catalyst are explored to examine the chemical stability during

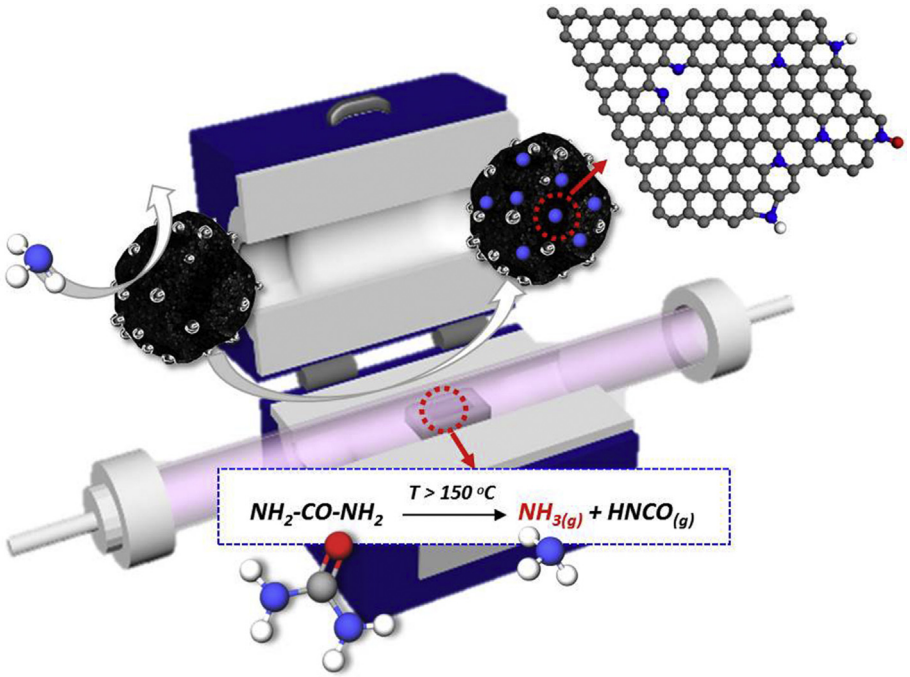


Fig. 1 – A schematic illustration for soft nitriding of the commercial Pt/C into nitrogen-doped Pt/C.

Please cite this article in press as: Seo D-J, et al., Nitrogen-doped carbon supported platinum catalyst via direct soft nitriding for high-performance polymer electrolyte membrane fuel cell, International Journal of Hydrogen Energy (2018), https://doi.org/10.1016/j.ijhydene.2018.07.173