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journal homepage: www.elsevier.com/locate/apcatbDesign of active Pt on TiO₂ based nanofibrous cathode for superior PEMFC performance and durability at high temperatureYunseong Ji^{a,1}, Yong il Cho^{a,1}, Yukwon Jeon^a, Chanmin Lee^b, Dae-Hwan Park^a, Yong-Gun Shul^{a,*}^a Department of Chemical and Biomolecular Engineering, Yonsei University, Seoul 120-749, Korea^b Center of Advanced Instrumental Analysis, Kyushu University, Kasuga, Fukuoka, 816-8580, Japan

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ABSTRACT

Oxygen reduction reaction (ORR) activity and stability of the cathode catalyst are important issues for practical applications, which should be even considered for the materials in high temperature polymer electrolyte membrane fuel cells (HT-PEMFCs). To improve these properties, modification of the catalyst electronic structure and finding durable supports can be a good approach. In this study, we synthesized a noble nanofibrous composite electrode which consist of carbon nanotube (CNT)-winded Pt/TiO₂ nanofiber (CNT-Pt/TiO₂). Our approach takes advantages of the electrochemical conductivity of CNF as well as better stability from the corrosion resistivity of TiO₂ and strong metal-support interaction (SMSI) between the Pt nanoparticles and TiO₂ nanofibers for less Pt dissolution. We also found that the Pt electronic state can be changed by an interaction with neighbouring CNT and TiO₂, resulting a decrease of Pt d-band vacancy for enhanced catalytic activity. Furthermore, nanofibrous structure with a unique 3D pore structure provides higher surface area for additional improvements of the mass transfer. These results reveal that the CNT-Pt/TiO₂ nanofiber based electrode shows enhanced performance with the maximum power density of 567 mW cm⁻² compare to commercial Pt/C (461 mW cm⁻²) with a significant durability at harsh conditions of 120 °C and RH 40%.

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1. Introduction

Fuel cell is one of the most promising electrochemical energy conversion devices which withholds many advantages; high efficiency, high power density, rapid start up, any significant pollutant, etc. Especially, PEMFCs get a lot of attention because it has high power density and is relatively portable [1,2]. Primitive PEMFCs are usually operated at low temperatures (LT-PEMFC, ≤100 °C) [3]. However, these days, many researches in the field take an interest of high temperature PEMFC (HT-PEMFC, ≥100 °C) that offers several improvements such as high fuel cell efficiency, kinetics of oxygen reduction reactions, water management and tolerance to contaminants [4]. These factors can provide an efficiency and simplification of the system, and makes the system cost effective. However, still, there are many problems to commercialize the HT-PEMFC, for example catalysts with highly active and durable system.

Regardless of whether low or high temperature, platinum deposited on carbon material is a common PEMFC catalyst that has large surface area, high electrical conductivity, and appropriate pore structure [5]. However, carbon support materials usually suffer from degradation in a harsh PEMFC operation conditions [6]. Generally, carbon corrosion is occurred on the surface and it makes vacancies under the Pt nanoparticles. This mechanism gives rise to agglomeration and sinter of Pt particles via Ostwald ripening. Consequentially, carbon corrosion brings decreases of the electrochemical surface area (ECSA) and hinder long-term operations [7–9]. Thus, electrochemically stable support materials need to be developed [10].

Metal oxide supports can be an effective alternative for the electrode catalyst due to their excellent mechanical strength, corrosion resistance and inherently higher stability in various operation conditions than carbon. Through a theoretical calculation by K. Sasaki, titanium dioxide (TiO₂) can be one of the support candidates for fuel cell catalysts [11]. It has been attracted due to not only their low price for commercial availability but also their SMSI effect for better durability even under the acidic [12,13]. In addition, when the metal is loaded on TiO₂ surface, there are electron charge transfer from a TiO₂ to Pt, which provides an increase of the Pt electron

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