



Electronic structure modification of platinum on titanium nitride resulting in enhanced catalytic activity and durability for oxygen reduction and formic acid oxidation

Sungeun Yang^a, Dong Young Chung^{b,c}, Young-Joo Tak^d, Jiwhan Kim^e, Haksu Han^a, Jong-Sung Yu^f, Aloysius Soon^d, Yung-Eun Sung^{b,c}, Hyunjoon Lee^{e,*}

^a Department of Chemical and Biomolecular Engineering, Yonsei University, Seoul 120-749, Republic of Korea

^b Center for Nanoparticle Research, Institute for Basic Science, Seoul 151-742, Republic of Korea

^c School of Chemical and Biological Engineering, Seoul National University, Seoul 151-742, Republic of Korea

^d Department of Materials Science and Engineering, Yonsei University, Seoul 120-749, Republic of Korea

^e Department of Chemical and Biomolecular Engineering, Korea Advanced Institute of Science and Technology, Daejeon 305-701, Republic of Korea

^f Department of Energy Systems Engineering, Daegu Gyeongbuk Institute of Science & Technology, Daegu 711-873, Republic of Korea

ARTICLE INFO

Article history:

Received 17 October 2014

Received in revised form 25 February 2015

Accepted 25 February 2015

Available online 26 February 2015

Keywords:

Titanium nitride

Platinum

Metal-support interaction

Oxygen reduction reaction

Formic acid oxidation

ABSTRACT

It is very important to improve the mass activity and durability of platinum (Pt) catalysts for oxygen reduction and the oxidation of small organic molecules for fuel cell applications. A strong interaction between Pt and the support materials can change the electronic structures of platinum, enhancing catalytic activity and durability. Here, we deposited various amounts of Pt on TiN supports and characterized these catalysts using electron microscopy, H₂ uptake, XANES, XPS, and valence-band XPS. The Pt nanoparticles had very small sizes (<2 nm) with a narrow size distribution. Compared to a commercial Pt/C catalyst, the Pt surface in Pt/TiN catalysts was in a higher reduction state, and the Pt d-band center was downshifted. The results of DFT calculations confirmed that Pt could be stabilized on the TiN surface and that the Pt d-band center is downshifted relative to bulk Pt. The activity and durability of the Pt/TiN catalysts was enhanced for the oxygen reduction reaction and formic acid oxidation over that of the Pt/C catalyst. For the oxygen reduction reaction at 0.9 V (vs. RHE), the mass activity was 0.29 A/mg_{Pt} for the 10 wt% Pt/TiN catalyst and 0.17 A/mg_{Pt} for the Pt/C catalyst. After 5000 cycles of an accelerated durability test, the Pt/TiN exhibited a mass activity of 0.24 A/mg_{Pt}, whereas the Pt/C catalyst exhibited a mass activity of 0.12 A/mg_{Pt}. The Pt/TiN catalyst followed a direct pathway with fewer surface-poisoning intermediates for formic acid oxidation, which enhanced the activity of the Pt/TiN catalyst over that of the Pt/C catalyst. The modification of the electronic structure of Pt catalysts by interaction with TiN supports can significantly enhance the activity and durability of the catalyst.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Pt minimization has been a key issue in the commercialization of polymer electrolyte membrane fuel cells (PEMFCs) and will become increasingly important as the market grows in size [1,2]. It is important to utilize Pt effectively without affecting either its activity or durability. Many strategies have been applied to maximize the catalytic activity of Pt catalysts, such as alloying, inducing a surface strain, using a core-shell structure, shape-control, and surface modification by organic molecules [3–12]. These appar-

ently disparate strategies are all based on modifying the electronic structure of the Pt surface. Alloying Pt with Ni, Co or Y is known to produce high catalytic activity for the oxygen reduction reaction (ORR) by downshifting the d-band center of Pt and weakening oxygen adsorption [9–11]. The Pt₃Ni(1 1 1) surface has a downshifted d-band center and it exhibits ORR activity that is 10-fold higher than the Pt(1 1 1) structure [13]. Research on the Pt₃Ni(1 1 1) surface led to the development of Pt₃Ni nano-octahedra with high ORR activity [5,14,15]. The annealed alloy often has a core-shell structure, for which a Pt skin forms at the shell from surface segregation. The dissolution of Co in the alloy results in the formation of a Pt skeleton containing only Pt atoms with a modified electronic structure at the alloy surface [3]. Attaching different amounts of oleylamine to

* Corresponding author. Tel.: +82 42 350 3922; fax: +82 42 350 3910.
E-mail address: azhyun@kaist.ac.kr (H. Lee).

a commercial Pt/C catalyst was found to increase the mass activity of the catalyst for the ORR by downshifting the Pt d-band center [7].

A strong metal-support interaction (SMSI) between Pt and ceramic supports has been used to simultaneously improve the activity and durability of Pt catalysts [16,17]. A strong interaction usually increases the Pt dispersion and causes the lower particle aggregation, because small Pt nanoparticles are more strongly anchored to the support. Most importantly, SMSI changes the electronic structure of the metal catalyst. SMSI can be used to suitably modifying the electronic structure of Pt to enhance ORR activity. TiO₂-based materials have been widely used as supports with SMSI [18–25]. Oxygen vacancies have been intentionally created with a chemical composition of TiO_x, where x was less than 2, or by doping with F or Cr [19,22]. Treating a TiO₂ support with HF was found to reduce the electronic state of TiO₂ [20]. Pt/Ti_{0.7}Mo_{0.3}O₂ or Pt/Nb–TiO₂ have also exhibited enhanced activities for electrochemical reactions [21,23]. This enhanced activity was attributed to the electron transfer between the support and the Pt catalyst [22,23], a compressive strain that modified the Pt electronic structure [19], or a bifunctional effect whereby the support alleviated surface poisoning [24]. Other unconventional supports have also been used, such as In-doped SnO₂ [26], TiC [27], Ti₃C₂X₂ (X = OH and F) [28], or TaB₂ [29]. Notably, the use of SMSI has improved the durability of Pt catalysts over other strategies used for Pt minimization.

TiN can be an effective support material for electro-catalysis because of its high electrical conductivity and resistance to oxidation and acid corrosion [30–33]. Although enhanced activity has been reported using TiN as a support for ORR and methanol oxidation [30–34], the origin of this enhancement has not yet been thoroughly studied. In this study, various amounts of Pt were deposited on TiN, and the effect of Pt content was evaluated. The change in the Pt electronic structure was investigated using density functional theory (DFT) calculations, X-ray absorption near edge structure (XANES) measurements, X-ray photoelectron spectroscopy (XPS), and valence-band XPS. Interestingly, post-treatment significantly changed the electronic structure of Pt. The activity and durability of the Pt/TiN catalysts were tested for ORR and formic acid oxidation.

2. Experimental

2.1. Preparation of Pt/TiN catalysts

Pt/TiN catalysts were prepared using a previously reported method [31]. One hundred and fifty milligrams of TiN nanoparticles (NanoAmor) were added to 65 ml of ethylene glycol (Sigma–Aldrich, 99.8%) and dispersed by ultra-sonication (Sonics, Vibra-cell) for 20 min. Appropriate amounts of H₂PtCl₆·6H₂O (Sigma–Aldrich, ≥37.50% Pt basis) were dissolved in 5 ml of ethylene glycol and added dropwise to the TiN-dispersed ethylene glycol. The solution pH was controlled at 11.5 by adding 1 M NaOH (Sigma–Aldrich, ≥97.0%) to the ethylene glycol. The mixture was heated to 160 °C and maintained at the same temperature for 3 h under a nitrogen atmosphere. After the mixture had cooled down to room temperature, a 10 wt% aqueous HCl solution was added to control the pH at 0.5. The mixture was then stirred overnight. The resulting Pt/TiN was thoroughly washed with deionized water and dried at 80 °C. The Pt/TiN catalyst was reduced in a 10 vol% H₂ flow (the balance was N₂) at a flow rate of 200 sccm for 1 h at 200 °C.

2.2. Electrochemical measurements

A conventional three-electrode electrochemical cell was used to perform electrochemical measurements along with a potentiostat

(CHI 760E), a platinum wire that served as a counter electrode, and a 3 M NaCl Ag/AgCl (RE-5B, BASi) electrode that served as a reference electrode. The temperature of the cell was controlled at 25 °C using a water bath. All of the potentials were reported vs. reversible hydrogen electrode (RHE) measured for hydrogen evolution and hydrogen oxidation reactions at a rotating platinum electrode in a H₂-purged electrolyte. Equal masses of the Pt/TiN catalyst and carbon black (Vulcan, XC72R) were dispersed in ethanol (Samchun, 99.9% anhydrous) by ultra-sonication for 20 min. Carbon black was added to ensure that the catalyst was sufficiently conductive. The exact amount of Pt was measured using inductively coupled plasma (ICP) elemental analysis for each sample, and 3 μg of platinum were cast onto a glassy carbon electrode. Then, 10 μl of a 0.05% Nafion solution were cast onto the electrode to adhere the catalyst firmly to the electrode surface. The catalyst-coated glassy carbon electrode was used as a working electrode. Before testing the electrocatalytic activity, 50 cycles of cyclic voltammetry were performed from 0.05 V to 1.1 V in an Ar-saturated 0.1 M HClO₄ (Sigma–Aldrich, 70%) solution to obtain stable signals. Then, either the oxygen reduction reaction (ORR) or the formic acid oxidation (FAO) reaction was performed. The ORR measurements were conducted in an O₂-saturated 0.1 M HClO₄ solution at a rotation rate of 1600 rpm and a sweep rate of 10 mV/s in the positive direction. Accelerated durability tests were performed in an O₂-saturated 0.1 M HClO₄ solution by cycling the voltage from 0.6 V to 1.0 V at a scan rate of 100 mV/s for 5000 cycles. The FAO was conducted independently from the ORR. After activating the catalysts in a 0.1 M HClO₄ solution, formic acid (Sigma–Aldrich, ≥95%) was added to the 0.1 M HClO₄ solution to form a 0.5 M HCOOH + 0.1 M HClO₄ solution. Argon was purged for 30 min, and cyclic voltammetry was conducted between 0.05 V and 1.1 V at a scan rate of 50 mV/s. A long-term stability test was conducted by maintaining the potential at 0.7 V at an electrode rotation rate of 1600 rpm. A 20 wt% Pt/C catalyst that was purchased from Johnson–Matthey was used as a comparison.

2.3. Characterizations

The morphologies and particle sizes of the Pt nanoparticles on TiN supports were characterized using various electron microscope techniques. Transmission electron microscopy (TEM) images were taken using a JEM-2100 (JEOL). High resolution (HR) TEM and scanning-TEM (STEM) images were taken using a TF30 ST (Tencai) and a JEM-ARM 200F (JEOL). The crystalline structures of TiN and TiO₂ were studied using X-ray diffraction (XRD) with a D/MAX-2500 (Rigaku). X-ray photoelectron spectroscopy (XPS) was used to measure the binding energy of the Pt 4f electrons and the Ti 2p electrons using a Sigma Probe (Thermo VG Scientific). The binding energy was corrected using the C 1s peak of the advantageous carbon at 284.8 eV as a reference. Valence-band XPS was measured to estimate a Pt d-band center (Thermo VG Scientific). The data from bare TiN served as backgrounds for the Pt/TiN catalysts. The d-band center was calculated by $\int N(E)E dE / \int N(E) dE$ [7,34]. X-ray absorption near-edge structure (XANES) experiments were conducted using the 8C Nano XAFS beamline of the Pohang Light Source (PLS). Inductively coupled plasma atomic emission spectrometry (ICP-AES) was used to measure the actual weight percentages of Pt on TiN using an OPTIMA 7300 DV (PerkinElmer). The H₂ uptake was determined from pulsed chemisorption measurements using a BELCAT-M (BEL JAPAN, Inc.). The electrical conductivity of TiN, Vulcan carbon, and a mixture of TiN and Vulcan carbon was measured using a homemade four-point probe apparatus by varying the applied pressure as reported previously [35,36]. Keithley model 6220 and model 2182A were used as the DC current source and voltmeter, respectively. The current was varied from 0 to 10 mA, and the corresponding voltages were measured.

Download English Version:

<https://daneshyari.com/en/article/6500047>

Download Persian Version:

<https://daneshyari.com/article/6500047>

[Daneshyari.com](https://daneshyari.com)