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Enhancing stability of octahedral PtNi nanoparticles for oxygen reduction reaction by halide treatment

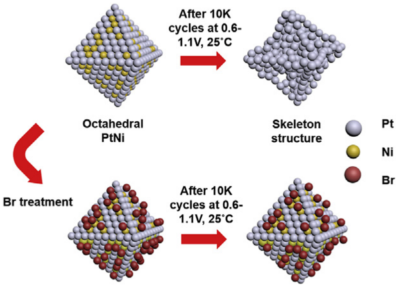
Juhyuk Choi, Youhan Lee, Jihan Kim, Hyunjoo Lee*

Department of Chemical and Biomolecular Engineering, Korea Advanced Institute of Science and Technology, Daejeon 34141, Republic of Korea

HIGHLIGHTS

- PtNi octahedral nanoparticles showed high activity for oxygen reduction reaction (ORR).
- The surface Ni is leached out in acidic solution degrading the activity for the ORR.
- Halides can be adsorbed on Ni sites more strongly than Pt sites.
- Br adsorbed on the nanoparticle surface protected Ni from being leached out.
- The Br-treated PtNi nanoparticles preserved the shape with high activity even after ADT.

GRAPHICAL ABSTRACT



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ABSTRACT

Because a reduction in the amount of Pt catalysts is essential for the commercialization of fuel cells, various approaches have been tested to maximize the mass activity of Pt-based catalysts. Among these, the most successful results so far were obtained using shaped PtNi alloy nanoparticles, preferably with PtNi(111) facets. However, these nanoparticles typically suffer from much lower activity after the durability tests due to the leaching out of the surface Ni during the oxygen reduction reaction (ORR), which leads to the disappearance of the activity-enhancing effect caused by electronic structure modification. Here, we showed that halide treatment of the octahedral PtNi nanoparticles could significantly enhance their durability. Halides are adsorbed on surface Ni more strongly than on surface Pt, and the surface halides are found to preserve the surface Ni that induces the ORR activity enhancement. Especially, Br can preserve the surface Ni effectively. Durability testing by repeating cyclic voltammetry 10,000 times in the 0.6–1.1 V range showed that the mass activity decreased by 52.6% for the as-prepared PtNi octahedral nanoparticles, whereas the mass activity decreased by only 15.0% for the Br-treated PtNi nanoparticles. The simple treatment significantly enhanced the long-term stability of the highly active PtNi alloy nano-octahedra.

1. Introduction

Fuel cells have been considered to be an environmentally friendly power source for automobiles. Although a few automobile companies have reported the production of fuel cell vehicles such as Tucson or Mirai, cost reduction is highly necessary for the

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* Corresponding author.
E-mail address: azhyun@kaist.ac.kr (H. Lee).

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realization of the commercial fuel cell market. Because current fuel cells use an excessive amount of Pt as electrode catalysts, the minimization of Pt usage has been attempted using various strategies [1,2]. Studies of the control of Pt catalyst nanostructure have been reported such as those of the formation of Pt-based alloys [3–6], Pt monolayers [7,8], and core-shell structures [9–11] to maximize the mass activity for the oxygen reduction reaction (ORR). The ORR, a cathode reaction in the fuel cell, typically exhibits a sluggish reaction rates, requiring a large amount of Pt catalyst.

The highest mass activity for the ORR was reported for the single crystalline $Pt_3Ni(111)$ surface, which was found to be a factor of 90 more active than the Pt/C catalyst [12]. Since this work was published in 2007, much effort has been devoted to the realization of the $Pt_3Ni(111)$ surface in the nanoparticles. Currently, various PtNi alloy octahedral nanoparticles with high ORR mass activity were reported [13–18]. However, these nanoparticles typically show low durability because Ni is easily leached out during the ORR under acidic conditions [19–25]. Strasser et al. clearly showed that Ni was distributed on the facets of the PtNi alloy octahedra and that these Ni atoms were selectively leached during the ORR, leaving the bare Pt skeleton [24,25]. Because the high activity of $Pt_3Ni(111)$ results from the weakening of OH adsorption on Pt surface due to the modification of electronic structure by the Ni underlying the surface Pt monolayer [12], the Ni loss and the degradation of the (111) surface would significantly reduce the high activity. Efforts to enhance the durability of PtNi alloy nanoparticles have been recently reported. The surface Ni was intentionally leached, forming a Pt shell, and the shell was annealed at a high temperature [26]. In another work, PtNi nanoparticles were treated with NH_3, forming Ni_4N in the core, surrounded by a thin Pt shell [27]. Au was used as an interlayer connecting the Ni-rich core and PtNi shell [28]. Most notably, a transition metal was doped into PtNi nanoparticles, selectively located at the surface vertex/edge sites [29]. These methods were shown to minimize Ni leaching and enhance the mass activity for the ORR even after accelerated durability tests.

Halides often play important roles in the synthesis of shaped nanoparticles [30–36]. For example, the shape of Rh nanoparticles changed significantly when $RhCl_3$ was reduced in the presence of different halides [30]. The presence of NaF induced the dendritic shape of Rh nanoparticles, whereas the presence of NaBr resulted in cubic Rh nanoparticles. It is well known that Br can be selectively adsorbed on the (100) surface, often resulting in a cubic shape [31–33]. Iodine can be selectively adsorbed on the (100) surface, inducing the deposition of metal atoms into non-(100) facets [35]. Various nanoparticles with high index facets were also synthesized using halides as auxiliary shaping agents [37–40]. Clearly, halides can be adsorbed on the metal surface, often ‘capping’ the surface. We speculated that these halides may be able to prevent the surface atoms from being dissolved. In this work, we synthesized octahedral PtNi alloy nanoparticles in dimethylformamide without organic surface capping agents to preserve clean metal surfaces as much as possible. Halides were then intentionally adsorbed on the PtNi surface. The halide-treated PtNi nanoparticles were tested as catalysts for the ORR, and their activity and stability were evaluated. The extent of the shape degradation was observed for as-prepared PtNi nanoparticles and halide-treated nanoparticles.

2. Experimental section

2.1. Chemicals

Platinum acetylacetonate ($Pt(acac)_2$, 97%, Aldrich), nickel acetylacetonate ($Ni(acac)_2$, 95%, Aldrich), anhydrous ethanol (99.9%, Samchun), N,N-dimethylformamide (DMF, 99.8%, Aldrich), NH_4F (98.0%, Aldrich), NH_4Cl (99.5%, Aldrich), NH_4Br (99.0%, Aldrich), NH_4I (99.0%, Aldrich), isopropanol (IPA, 99.7%, Junsei), 5 wt% Nafion® perfluorinated resin solution (Aldrich), $HClO_4$ (70%, Aldrich) were used as purchased.

2.2. Preparation of octahedral PtNi nanoparticles

PtNi nanoparticles were prepared using a previously reported method [14]. $Pt(acac)_2$ (0.36 mmol) and $Ni(acac)_2$ (0.12 mmol) were dissolved in 12 mL of DMF. The homogeneous solution was transferred to a Teflon-lined vessel and heated at 200 °C for 24 h. The vessel was naturally cooled down to room temperature before being opened. The black solution was sonicated for 30 min. Vulcan carbon XC-72 (281 mg) was dispersed in 50 mL of ethanol. The PtNi nanoparticle solution and carbon support solution were mixed and the mixture was sonicated for 30 min and stirred further for 8 hours. The PtNi/C were washed with ethanol and water several times and dried in a vacuum oven. The weight percentage of Pt was targeted as 20 wt%, and the actual Pt weight percentage was measured as 16.4 wt% by ICP-OES.

2.3. Halide pre-treatment

The molar ratio of halide to surface Ni was targeted as 1:1. The synthesized PtNi/C (20 mg) were dispersed in 20 mL of deionized water and sonicated for 10 min. NH_4X (X = F, Cl, Br, I; 0.17 mmol) were dissolved in 10 mL of deionized water. The halide solution (20 μL) was added to the above PtNi/C solution. The mixture was sonicated for 10 min and stirred overnight to allow the adsorption of halides on the PtNi surface. Finally, the halide-treated PtNi/C were washed by filtration to remove the remaining ions and other residues.

2.4. Characterizations

The shape of PtNi nanoparticles was observed by transmission electron microscopy (TEM, Tecnai TF30 ST, 300 kV). High angle annular dark field scanning TEM (HAADF-STEM) and line-scan images were taken by Cs-corrected TEM (Titan cubed G2 60-300, 300 kV). Powder X-ray diffraction (XRD, D/MAX-2500, RIGAKU) patterns were collected to investigate the crystalline structure. The Pt and Ni contents in the catalysts were obtained by inductively coupled plasma optical emission spectroscopy (ICP-OES, Agilent ICP-OES 720). The concentration of Pt or Ni ions leached into the electrolytes was measured by inductively coupled plasma mass spectroscopy (ICP-MS, Agilent ICP-MS 7700S). X-ray photoelectron spectroscopy (XPS, K-alpha, Thermo VG Scientific) was used to determine the surface properties of the catalysts. Electron energy loss spectroscopy (EELS, Gatan Quantum 965, resolution 0.2 eV) was used to confirm the presence of Br on the nanoparticle surface. X-ray absorption near edge structure (XANES) of the Pt L3 edge was measured using the 8C Nano XAFS beamline of the Pohang Light Source (PLS).

2.5. Electrochemical measurements

All electrochemical measurements were conducted at 25 °C. The measurements were performed using a CHI 730E potentiostat and a three-electrode cell. A platinum wire and a 3 M NaCl saturated Ag/AgCl (RE-5B, BASi) were used as the counter electrode and the reference electrode, respectively. All potentials in this paper were calibrated to a reversible hydrogen electrode (RHE) potential. The RHE potential was measured by performing hydrogen evolution and oxidation reactions in a H_2-purged electrolyte using a rotating Pt electrode prior to each measurement. The catalysts were dispersed in a mixture of deionized water (3 mL), IPA (2 mL), and