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journal homepage: www.elsevier.com/locate/apcatbSelf-healing Pd₃Au@Pt/C core-shell electrocatalysts with substantially enhanced activity and durability towards oxygen reductionSang-Young Lee^{a,b}, Namgee Jung^c, Dong Yun Shin^d, Hee-Young Park^a, Docheon Ahn^e,
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ABSTRACT

Pt shells were synthesized on Pd-based alloy-cores via the chemical reduction method. Pt shells containing 1, 2, or 3 layers were prepared by controlling the amounts of Pt precursor used during synthesis. The thicknesses of Pt shell layers were calculated using the difference in the particle size between core and core-shell nanocatalysts, as determined from Cs-corrected scanning transmission electron microscopy (Cs-STEM) data. The shape and elemental distribution in the core-shell structured nanoparticles were analyzed using line profiles and elemental mapping from Cs-STEM. High-resolution X-ray diffraction and X-ray photoelectron spectroscopy analyses suggested that the structural and electronic properties of core-shell nanocatalysts were dependent on the number of shell layers. The activity and durability of the core-shell nanocatalysts were analyzed by the electrochemical method. Accelerated durability tests (ADT) were conducted in the potential range of 0.6–1 V for 10000 cycles, and the mass and specific activities of ADT were shown to be stable for the carbon-supported core-shell nanocatalyst with two Pt shell layers (core@Pt[2](*)/C). In addition, excellent electrochemical performance was observed for the core@Pt[2]/C sample before and after the ADT compared to the commercial samples as well as other samples prepared in this study. Importantly, the optimized Pt usage demonstrated in this study would significantly contribute to the commercialization of proton exchange membrane fuel cells.

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1. Introduction

Proton exchange membrane fuel cells (PEMFCs) are one of the important type of fuel cells that allows the direct conversion of chemical energy into electricity at high efficiencies PEMFCs utilize hydrogen and oxygen as reactants for producing electricity [1]. Over the last several years, significant attention has been paid towards developing high-efficiency nanocatalysts that enhance the oxygen reduction reaction (ORR) in PEMFCs. Among the various nanocatalysts for the ORR at the cathode of the PEMFCs, Pt has been widely used. However, Pt dissolves during the operation of PEMFCs and therefore, exhibits low mass activity compared to high ORR performance [2–5]. Furthermore, in view of the limited Pt resources on

Earth, many researchers have investigated methods for reducing the amount of Pt used in the catalyst by alloying with other transition metals [1,6–13] or by designing catalysts that have a Pt shell on a pure metal or alloy-core composed of other elements [14–16].

Studies have been conducted on alloy-core catalysts involving metals other than Pt because of the high costs of Pt. In particular, PdM (M=Fe, Co, Ni, Cu, Y, W, Sc, Au, etc.) alloy nanocatalysts have been investigated for achieving enhanced ORR activities [17–23]. In addition to reducing Pt utilization, the synthesis of nanocatalysts with core-shell structures has led to improved ORR activities. When Pt is deposited on different metal, compressive or tensile stresses can occur, owing to lattice mismatch [2,24]. The structural changes caused by Pt deposition would affect the electronic structure of the core-shell alloy, owing to d-band shifts [25–28]. Among the various types of alloys, the effect of Au on the stability and durability of the nanocatalysts has been investigated at various composition ratios between the core and surface materials using density functional

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