

A General Approach to Preferential Formation of Active Fe–N_x Sites in Fe–N/C Electrocatalysts for Efficient Oxygen Reduction Reaction

Young Jin Sa,[†] Dong-Jun Seo,[§] Jinwoo Woo,[‡] Jung Tae Lim,[⊥] Jae Yeong Cheon,[†] Seung Yong Yang,[§] Jae Myeong Lee,[§] Dongwoo Kang,[†] Tae Joo Shin,^{||} Hyeon Suk Shin,[†] Hu Young Jeong,^{||} Chul Sung Kim,^{*⊥} Min Gyu Kim,^{*#} Tae-Young Kim,^{*§} and Sang Hoon Joo^{*†,‡}

[†]Department of Chemistry and [‡]School of Energy and Chemical Engineering, Ulsan National Institute of Science and Technology (UNIST), 50 UNIST-gil, Ulsan 44919, Republic of Korea

[§]Hydrogen and Fuel Cell Center, Korea Institute of Energy Research (KIER), Jellabuk-do 56332, Republic of Korea

^{||}UNIST Central Research Facility, Ulsan National Institute of Science and Technology (UNIST), 50 UNIST-gil, Ulsan 44919, Republic of Korea

[#]Beamline Division, Pohang Accelerator Laboratory, Pohang, Kyungbuk 37673, Republic of Korea

[⊥]Department of Physics, Kookmin University, Seoul 02707, Republic of Korea

Supporting Information

ABSTRACT: Iron–nitrogen on carbon (Fe–N/C) catalysts have emerged as promising nonprecious metal catalysts (NPMCs) for oxygen reduction reaction (ORR) in energy conversion and storage devices. It has been widely suggested that an active site structure for Fe–N/C catalysts contains Fe–N_x coordination. However, the preparation of high-performance Fe–N/C catalysts mostly involves a high-temperature pyrolysis step, which generates not only catalytically active Fe–N_x sites, but also less active large iron-based particles. Herein, we report a general “silica-protective-layer-assisted” approach that can preferentially generate the catalytically active Fe–N_x sites in Fe–N/C catalysts while suppressing the formation of large Fe-based particles. The catalyst preparation consisted of an adsorption of iron porphyrin precursor on carbon nanotube (CNT), silica layer overcoating, high-temperature pyrolysis, and silica layer etching which yielded CNTs coated with thin layer of porphyrinic carbon (CNT/PC) catalysts. Temperature-controlled in situ X-ray absorption spectroscopy during the preparation of CNT/PC catalyst revealed the coordination of silica layer to stabilize the Fe–N₄ sites. The CNT/PC catalyst contained higher density of active Fe–N_x sites compared to the CNT/PC prepared without silica coating. The CNT/PC showed very high ORR activity and excellent stability in alkaline media. Importantly, an alkaline anion exchange membrane fuel cell (AEMFC) with a CNT/PC-based cathode exhibited record high current and power densities among NPMC-based AEMFCs. In addition, a CNT/PC-based cathode exhibited a high volumetric current density of 320 A cm⁻³ in acidic proton exchange membrane fuel cell. We further demonstrated the generality of this synthetic strategy to other carbon supports.

