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# The role of arginine as nitrogen doping and carbon source for enhanced oxygen reduction reaction

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## ABSTRACT

Doped carbon nanostructures as non-precious metal (NPM) catalysts for oxygen reduction reaction (ORR) in acid medium are mainly synthesized using 5, 10, 15, 20-tetrakis (4-methoxyphenyl)-porphyrin-Fe (III) chloride (Fe-TMPP) as doping and carbon sources. In this study, the doped carbon nanostructures used as cathode NPM catalysts for ORR are prepared using a mixture of iron phthalocyanine (FePc) and arginine as doping and carbon sources. The morphology and composition of the as-prepared samples are characterized using field-emission scanning electron microscopy, field-emission transmission electron microscopy, and energy dispersive X-ray (EDX) spectroscopy. The crystal and pore structures are analyzed using X-ray diffraction method, Raman spectroscopy, and nitrogen adsorption/desorption method. The sample prepared using a precursor mixture with a proper ratio of FePc and arginine exhibits significantly superior ORR performance, i.e. high specific activity, enhanced half-wave potential, and improved stability in an acid medium, as even compared to a commercial Pt/C. The improved ORR properties is mainly attributed to high portion of pyridinic N state with a relatively high specific surface area, which can result from the FePc precursor surrounded by the fused arginine.

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## Introduction

Fuel cells have been attractive as eco-friendly energy conversion devices owing to low emission of pollution and high energy efficiency [1–17]. In the fuel cells that can directly convert chemical fuels to electrical energy, hydrogen oxidation reaction (HOR) and oxygen reduction reaction (ORR) occur at an anode and a cathode, respectively. In particular, polymer electrolyte membrane fuel cells (PEMFCs) which use hydrogen as a fuel and operate at a low temperature of ~80 °C exhibit the significantly slower ORR compared to the HOR [18–27]. Thus,

since the high loading amount of Pt-based cathode catalysts for the ORR in PEMFCs is essential, non-precious metal (NPM) catalysts with low cost and electrocatalytic activity need to be intensively developed [28–32].

In recent, doped carbon nanostructures as the NPM catalysts for the ORR have been synthesized using various doping sources such as heteroatoms (N, B, P, S, Se) and non-precious transition metals (Fe, Co, Ni), representing significantly enhanced ORR performance, compared to a commercial Pt catalyst [33–43]. In particular, among the doped carbon-based NPM catalysts for the ORR, iron/nitrogen-doped structures prepared using 5,10,15,20-tetrakis (4-methoxyphenyl)-

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porphyrin-Fe(III) chloride (Fe-TMPP) as doping sources showed a superior ORR activity to the commercial Pt catalyst in acid medium [44,45]. However, since the Fe-TMPP is a still expensive compound as a doping source, the doped NPM cathode catalysts have been synthesized using various amino acids as carbon and nitrogen doping sources due to relatively inexpensive and abundant compounds. In particular, in this study, among these amino acids, arginine was chosen due to a relatively high ratio of C to N [46]. The activity of the doped carbon-based NPM catalyst for the ORR can be significantly affected by the physical structure such as porosity and surface area as well as chemical species and bonding induced by doping sources. The doped carbon-based catalysts with the increased surface area and the porous structure can maximize the catalytic reaction and facilitate the transport of oxygen and by-products, representing much improved ORR performance [47–50]. Thus, intensive studies on the synthesis of doped porous carbon nanostructures with high-surface-area and porosity using various templates need to be carried out [51–54]. In this study, a doped porous carbon nanostructure as a NPM catalyst for the ORR in acid medium was prepared using arginine as a carbon and nitrogen source with SBA-15 as a template. The electrochemical properties and catalytic activity of the catalysts in an acid media were characterized using a potentiostat in a three-electrode cell.

## Experimental

### Synthesis of doped mesoporous carbon nanostructures

The doped porous carbon nanostructures were prepared using a hard templating method with SBA-15 as a template and iron phthalocyanine (denoted as FePc) and L-arginine used as both doping and carbon sources. To prepare a silicate template (SBA-15), 4.0 g pluronic P123 (SIGMA ALDRICH) was completely dissolved in di-ionized (DI) water (30 g) and 2 M HCl (120 g, SIGMA ALDRICH). Tetraethyl orthosilicate (8.5 g, SIGMA ALDRICH) was then mixed with the solution at 35 °C with continuous stirring for 20 h and aged at 80 °C for 24 h. The precipitate was washed with DI water and ethanol several times and dried in a 50 °C oven for 12 h. The dried silicate template was calcined at 550 °C for 6 h under an air atmosphere. To obtain doped porous carbon nanostructures as cathode catalysts for ORR, FePc and arginine were utilized as nitrogen/iron doping and carbon sources with SBA-15 template. Arginine, SBA-15, and FePc, were mixed according to intentional weight ratios of 0:1:1, 1:1:1, 2:1:1, and 4:1:1 (denoted as Arg-0:1:1, Arg-1:1:1, Arg-2:1:1, and Arg-4:1:1, respectively), which the amounts of SBA-15 and FePc were fixed with increasing amount of arginine. Followed by the heating process under an N<sub>2</sub> atmosphere at 900 °C for 3 h, the samples were stirred with 10 vol% HF for 5 h to remove SBA-15 and other impurities, washed with DI water and ethanol several times, and dried in a 50 °C oven for 12 h.

### Structural analysis

The morphology of the samples was observed using field-emission scanning electron microscopy (FE-SEM, JEOL, JSM-

6700F). The structure and composition of the samples were characterized using field-emission transmission electron microscopy (FE-TEM, Philips Tecnai F20 system operating at 200 kV) and energy dispersive X-ray (EDX) spectroscopy. The specimens for FE-TEM and EDX were prepared by dropping the samples dispersed in ethanol on carbon-free Cu grids. For the structural analysis of the samples, X-ray diffraction (XRD, Burker, D2 Phase System) method was carried out with a Cu K<sub>α</sub> radiation source of  $\lambda = 0.15406$  nm and a scan rate of 0.05° min<sup>-1</sup>. The crystallinity of the doped carbon nanostructures was confirmed using a high resolution Raman spectrometer (Horiba Jobin Yvon, LabRAM HR UV/Vis/NIR photoluminescence) with a laser of  $\lambda = 532$  nm. The specific surface area and pore structure of the samples were characterized using a nitrogen adsorption/desorption method (Micromeritics ASAP 2020 adsorption analyzer). The pre-treatment of the samples was conducted at 473 K for 6 h. The starting and ending relative pressures were 0.995 and 0.01 P/P<sub>0</sub>, respectively. To analyze chemical species and composition of the doped samples, X-ray photoelectron spectroscopy (XPS, Thermo Scientific, K-Alpha) was carried out using a beam source of Al K<sub>α</sub> (1486.8 eV) and power of 200 W under a chamber pressure of  $7.8 \times 10^{-9}$  Torr. Differential scanning calorimetry (DSC, TA Instruments, TA Q600) and thermogravimetric analysis (TGA, TA Instruments, TA Q600) of the samples were performed in the temperature range of 30–700 °C under an N<sub>2</sub> atmosphere with a flow rate of 100 mL min<sup>-1</sup>.

### Electrochemical analysis

The electrochemical properties of the samples were characterized using a potentiostat (CH Instrument, CHI 700C) with a three-electrode electrochemical cell. A graphite rod and Ag/AgCl (saturated in 3 M KCl) were utilized as counter and reference electrodes, respectively. All potentials in this study were converted to reversible hydrogen electrode (RHE). The inks for electrochemical analysis were prepared by mixing the samples with isopropanol (Aldrich) and Nafion<sup>®</sup> (5 wt%, Aldrich). The ink were dropped on a glassy carbon electrode and dried in a 50 °C oven for 10 min. The total loading amounts of the NPM catalysts and Pt (20 wt%)/C were ~600 and ~200 μg cm<sup>-2</sup>, respectively. To compare the catalytic activity towards ORR, cyclic voltammograms (CVs) and linear sweep voltammograms (LSVs) of the samples were obtained in Ar or O<sub>2</sub>-saturated 0.5 M H<sub>2</sub>SO<sub>4</sub>. To identify the role of iron as a catalytic site in the doped carbon structures, the LSVs were obtained in O<sub>2</sub>-saturated 0.5 M H<sub>2</sub>SO<sub>4</sub> in the presence of 10 mM KCN. Stability test of the samples for ORR was performed in O<sub>2</sub>-saturated 0.5 M H<sub>2</sub>SO<sub>4</sub> by sweeping between 0.4 and 0.9 V vs. Ag/AgCl for 10,000 cycles. The electrode potential was converted to reversible hydrogen electrode (RHE) by the Nernst equation.

## Results and discussion

As shown in the FE-SEM images (Fig. 1), the as-prepared samples exhibited a fairly regular cylindrical shape with different particle sizes. In particular, the particle size of Arg-

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