Supporting Information

High-performance hydrogen fuel cell using nitrate reduction reaction on a non-precious catalyst

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Experimental Section

Synthesis of non-precious catalyst. To synthesize N-doped C cathode catalyst, a solution of 1 mM iron (III) nitrate and 3 mM melamine (C₃H₆N₆) was prepared by dissolving in a mixture solution of ethylene glycol and ethanol (50:50). The solution (3 mL) was then added to 0.2 g of carbon black (Vulcan XC-72R) at 25 °C. After the continuous stirring and sonicatesing for 1 h, the solution was completely evaporated and then the resulting powder was dried at 50 °C. The obtained powder was placed in a quartz boat and heat-treated at 700 °C for 3 h in a horizontal quartz furnace under N₂ atmosphere.

Characterizations of the catalysts. The morphology and structure of the catalysts were characterized by field-emission transmission electron microscopy (FE-TEM) using a Tecnai G2 F30 system operating at 300 kV. The TEM samples were prepared by placing a drop of catalyst suspension dispersed in an ethanol on a 3 mm carbon-coated copper grid. X-ray photoelectron spectroscopy (XPS, Thermo Scientific Co.) was carried out with the Al Kα X-ray source of 1486.6 eV at the chamber pressure below 5×10⁻⁹ Pa. The electron binding energy of N 1s was referenced at 398.4 eV and a nonlinear least-squares curve-fitting program was employed with a Gaussian-Lorentzian production function.
**Electrochemical measurements.** To characterize electrochemical properties of catalysts, electrochemical measurements were carried out in a three-electrode cell. The catalyst-coated carbon paper, a Pt wire (immersed in 1 M V$^{3+} + 5$ M HNO$_3$), and Ag/AgCl were used as working, counter, and reference electrode, respectively. In particular, the Pt counter electrode in 1 M V$^{3+} + 5$ M HNO$_3$ solution was used to reduce overpotential of the electrochemical cell. The catalyst ink was prepared by ultrasonically dispersing catalyst powders in an appropriate amount of isopropyl alcohol. The working electrode was fabricated by brushing the catalyst ink on a carbon paper. The total loading of the catalyst on the carbon paper was measured after drying at 50 °C oven. The 5 M HNO$_3$ was continuously stirred and purged with nitrogen gas. To evaluate catalytic activity of the catalyst for nitrate reduction, voltammetry was performed in N$_2$-saturated 5 M HNO$_3$ using a potentiostat (Eco Chemie, AUTOLAB) at various temperatures between 40 and 60 °C.

**Unit cell measurements.** The performance of the fabricated membrane-electrode-assembly (MEA) was evaluated using a unit cell and computer-controlled electronic load (CNLPEM005-01, CNL Energy Co.). The catalysts used at the anode and cathode were applied on PTFE-coated carbon paper (Toray) by a brushing method. The solid polymer electrolyte was a Nafion 117 (DuPont), which was pretreated with H$_2$O$_2$ and H$_2$SO$_4$ solutions. A membrane electrode assembly (MEA) was prepared by hot pressing (110 °C, 55 atm) for 3 min. The MEA with an active area of 2 cm$^2$ was placed between the graphite plates with serpentine flow-field and then the whole unit was tightened between the metal plates as a current collector with the proper pressure. The H$_2$-NO$_3^-$ cell performance was characterized at 80 °C with Pt/C (E-TEK, 0.5 mg cm$^{-2}$) at anode and N-doped C (1.0 mg cm$^{-2}$) or Pt/C (E-TEK, 1.5 mg cm$^{-2}$) at cathode. The H$_2$ gas humidified at 70 °C was supplied at anode with a flow rate of 27.8 mL min$^{-1}$. The 5 M HNO$_3$ solution was flowed at cathode with a flow rate of 2 mL min$^{-1}$. 

Supplementary Material (ESI) for Chemical Communications

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**Fig. S1** Structural analysis of N-doped C as a non-precious cathode catalyst. (a) A TEM image and (b) X-ray photoelectron spectrum of N 1s of N-doped C.

**Fig. S2** Limiting current densities of nitrate reduction reactions at various temperatures. The nitrate reduction current density of the catalysts measured at 0.9 V was expressed as a function of reciprocal absolute temperatures in 5 M nitrate solution.
**Fig. S3** TEM images of N-doped C (a,b) and Pt/C (c,d) before and after stability test, respectively. The stability tests at 0.8 V were carried out for 100 h at 80 °C with N-doped C and Pt/C as cathode catalysts.