

Supporting Information

Reduction of NO with Fe(II) and subsequent regeneration of Fe(II) in fuel cell

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Experimental Section

Synthesis of non-precious catalyst. To synthesize N-doped carbon, a solution of 1 mM iron (III) nitrate and 3 mM melamine ($C_3H_6N_6$) was prepared by dissolving in a mixture solution of ethylene glycol and ethanol (50:50) as described in the previous study.⁸ 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 sonicating 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 N_2 atmosphere.

NO reduction measurements. A solution of 1 M $FeSO_4$ and 2 M H_2SO_4 was prepared in 1000 mL of deionized water. The solution was continuously stirred and purged with NO (5% NO in a balance N_2) until completely saturated. The change of color in the saturated solutions was observed at 50 and 80 °C.

The NO reduction rates of the solutions were studied by UV-Vis absorbance spectroscopy ($\lambda=454$ nm). The selectivity of NO reduction reaction was measured by calibrating UV-Vis absorbance at $\lambda=190$ nm. The spectra were recorded at 25 °C using a Jasco V-650 spectrophotometer.⁷

Electrochemical measurements. To characterize electrochemical properties of Fe²⁺/Fe³⁺ redox couples, electrochemical measurements were carried out in a three-electrode cell using a potentiostat (Eco Chemie, AUTOLAB) at 25 °C. The N-doped carbon catalyst-coated rotating disc electrode, a Pt wire, and Ag/AgCl were used as working, counter, and reference electrode, respectively. All potentials are reported with respect to Ag/AgCl.

Electrochemical cell measurements. The performance of electrochemical cell was evaluated using membrane-electrode-assembly (MEA) and computer-controlled electronic load (CNLP005-01, CNL Energy Co.). The catalysts used at the anode and cathode were applied on carbon papers (Toray Co.) by brushing method. The solid polymer electrolyte was a Nafion 117 (DuPont Co.), which was pretreated with H₂O₂ and H₂SO₄ solutions. The MEA was prepared by hot pressing (110 °C, 55 atm) for 2 min. The MEA with an active area of 2 cm² was placed between the graphite plates with serpentine flow-field and then the whole unit was tightened between the metal plates with the proper pressure. The electrochemical cell performance was characterized at 70 °C with Pt/C (E-TEK, 0.5 mg cm⁻²) at anode and N-doped carbon (1.0 mg cm⁻²) at cathode. The H₂ gas humidified at 70 °C was supplied at anode with a flow rate of 27.8 mL min⁻¹. The Fe-NO solution kept at 80 °C for 4 h was flowed at cathode with a flow rate of 2 mL min⁻¹.

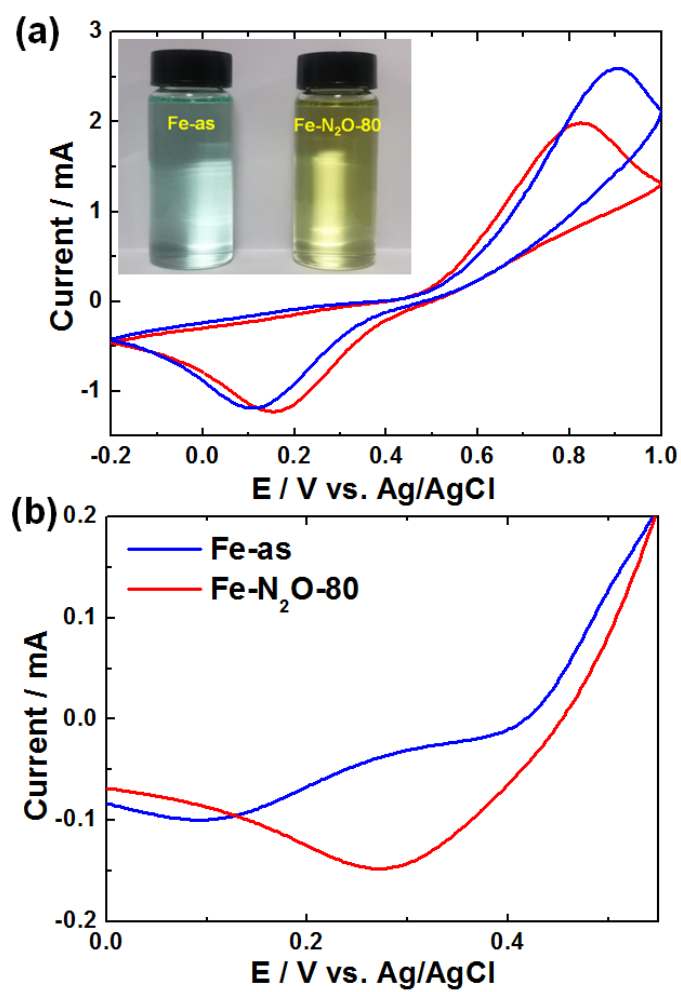


Figure S1. Electrochemical reduction reactions on N-doped carbon in N₂O(100%)-absorbed solution for 4h at 80 °C (referred to as Fe-N₂O-80). (a) Cyclic and (b) linear sweep voltammograms for iron reduction reactions in Fe-as and Fe-N₂O-80.

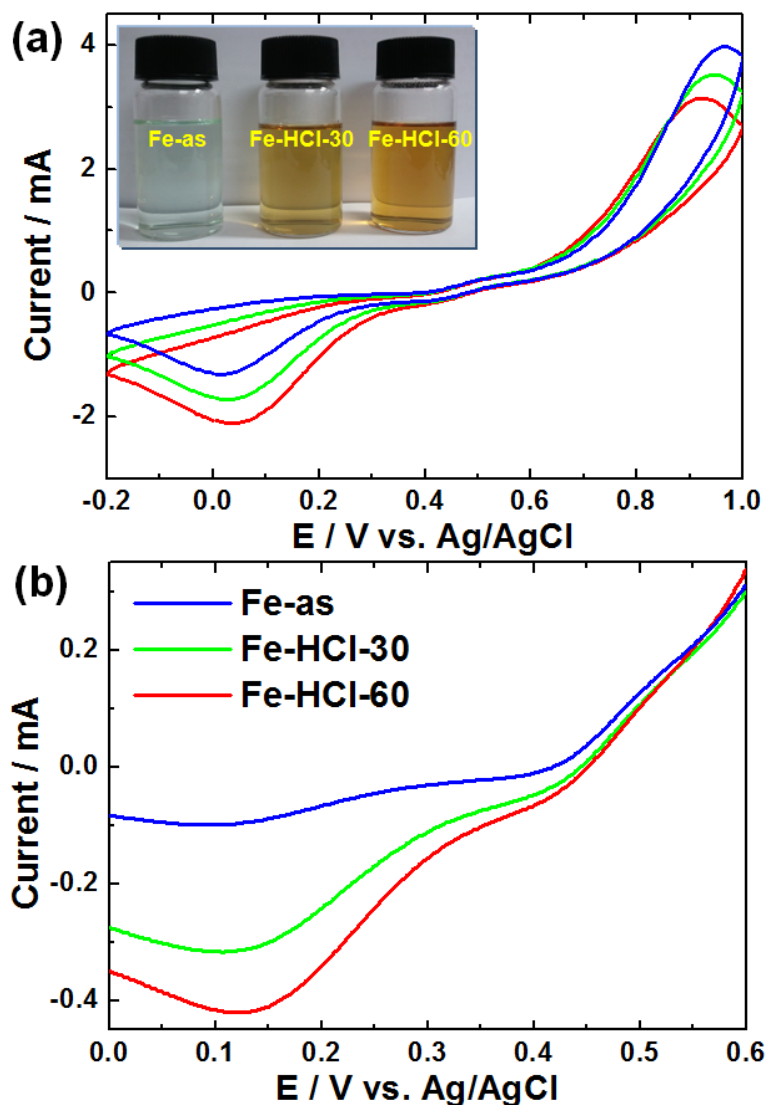


Figure S2. Electrochemical reduction reactions on N-doped carbon in Cl_2 -absorbed solutions for 30 and 60 min (referred to as Fe-HCl-30 and Fe-HCl-60, respectively). (a) CVs and (b) linear sweep voltammograms for iron reduction reactions in Fe-HCl-30 and Fe-HCl-60.