

Fe-N-C hollow spheres as an efficient non-precious electrocatalysts for oxygen reduction in alkaline media

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Non-precious electrocatalysts for oxygen reduction reaction (ORR) have paid lot of attention in recent times as a possible replacement of Pt and its alloy catalysts at the fuel cell cathode. Platinum nanoparticles dispersed on the carbon are the most efficient catalyst for ORR, however, the high cost, low abundance of Pt is one of the technical limitations in the commercialization of fuel cell technology. The synthesis of cost-effective and high performance electrocatalyst for the oxygen reduction reaction is one of the most critical challenges for the successful commercialization of PEMFC for portable and transportation applications. Recently, research efforts have been devoted to decrease the cost of Pt electrocatalyst by adopting innovative approaches. The development of simple and efficient method to fabricate highly active ORR catalyst is required.

We introduce a simple method to fabricate Fe-N-C hollow spheres by single step route using a single precursor. The non-precious catalyst was prepared by pyrolysis of iron organometallic complex at 700 °C under its autogenic pressure, and then the product was treated with concentrated HCl to remove oxide core, and to form Fe-N-doped carbon hollow spheres (Fe-N-C-71). The Fe-N-C hollow sphere samples were characterized by using SEM, TEM, XRD and XPS techniques. The electrochemical oxygen reduction of Fe-N-C was studied using CV, RDE, and RRDE in 0.1 M KOH. The ORR activity was almost comparable with commercial Pt/C catalyst. The details of synthesis and electrochemical oxygen reduction activities of Fe-N-C hollow nanostructures will be discussed.

The XRD pattern of Fe-N-C nanostructures showed a broad diffraction peak centered at 25.2° (2θ), which corresponds to the graphitic (002) reflection of carbon. The electron microscopic (SEM and TEM) studies reveal that the products obtained at 700 and 900 °C show the presence of core-shell sphere morphologies with uniform carbon coating and the diameter of the particles are in the range of 500-800 nm with a wall thickness of 80 nm. After acid treatment most of the particles show shell-like morphologies and all of the spheres are free from the iron oxide core. The TEM image of hollow sphere shows that the outer diameter is about 800 nm (Fig.1) To access the nature of nitrogen functional groups in Fe-N-C hollow spheres; X-ray photoelectron spectroscopy (XPS) measurements were carried out. The XPS wide spectra of spheres show the presence of only C, N, and O. The deconvoluted high resolution N 1s spectra of Fe-N-C-71 and Fe-N-C-91 showed peaks with binding energy values of 398.5 eV, 400.1 eV and 403.0 eV and they can be attributed to pyridinic-, pyrrolic-, and graphitic- type nitrogen functional groups, respectively. The amount of nitrogen in Fe-N carbon spheres prepared at 700, and 900 °C are found to be 11.4, 3.9 wt %, respectively.

The electrocatalytic ORR performance of Fe-N-Cs was carried out by rotating disc electrode (RDE) voltammetry and RDE traces were recorded in O₂ saturated 0.1 M

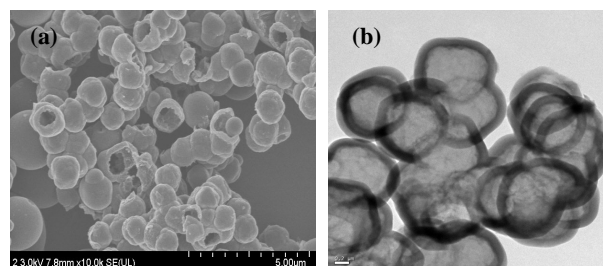


Fig.1. (a) SEM (b) TEM images of Fe-N-C-71.

KOH at a scan rate of 10 mV s⁻¹ over an electrode rotation rate of 1600 rpm, and the corresponding LSVs are shown in Fig. 2b. The LSVs show a significant oxygen reduction current on all the catalysts. For comparison, ORR activity of a commercial Pt/C was measured. Fig. 2b compares the ORR activity of Fe-N-C-71 with that of Pt/C. The onset potential of Fe-N-C-71 catalyst was approximately 0.91 V vs. RHE. The half wave potential ($E_{1/2}$) of Fe-N-C-71 catalyst calculated from Fig. 2b is negatively shifted by 50 mV compared to that of Pt/C. The rotating ring-disk electrode study reveals very high selectivity of the Fe-N-C-71 catalyst for four electron reduction to water. The H₂O₂ yield of Fe-N-C-71 remains below 5 % at all potentials. Moreover, the number of electron transfer was found to be around four with different catalyst loadings from 0.2 to 0.8 mg.

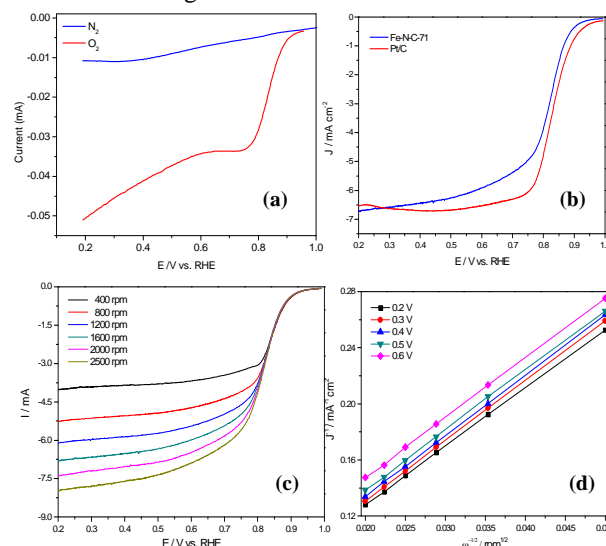


Fig.2 (a) LSVs of Fe-N-C-71 in 0.1 M KOH, (b) RDE traces of Fe-N-C-71 and Pt/C at 1600 rpm, (c) RDE traces of Fe-N-C-71 electrode in aqueous 0.1 M KOH saturated with O₂ at different rotation rates. (d) The corresponding Koutecky-Levich plots at different potentials.

The electrode stability of Fe-N-C-71 and Pt/C was evaluated by perturbing the electrodes with 0.75 V vs. RHE and the current decay for ORR current was prominent for Pt/C than that for Fe-N-C-71, which is an indication of better stability of Fe-N-C-71 catalyst for O₂ reduction. Another advantage of Fe-N-C-71 over Pt/C as an ORR electrocatalyst is that O₂ reduction on Fe-N-C-71 was not influenced by CO poisoning, on the other hand, Pt/C showed a large current decay due to CO poisoning. The high selectivity of Fe-N-C-71 hollow spheres toward ORR makes it a very promising electrocatalyst. The details of electrocatalytic oxygen reduction activities and stabilities of various Fe-N-C hollow catalysts will be discussed.

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