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Insight into the different ORR catalytic activity of Fe/N/C between acidic and alkaline media: Protonation of pyridinic nitrogen

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ABSTRACT

Pyrolyzed Fe/N/C catalysts have been considered as the most promising non-precious metal electrocatalysts for oxygen reduction reaction (ORR) in fuel cells. Commonly, the ORR activity of the Fe/N/C and metal-free N-doped carbon catalysts is much higher in alkaline medium than in acidic medium. The exact reason for such pH-dependent activity is not very clear yet. Herein, through the XPS test of the mixture of a Fe/N/C catalyst and a solid acid—Nafion, we found that the pyridinic N that is important for ORR, has been protonated completely. The protonation of pyridinic N in acidic medium may reduce the charge density of adjacent carbon atoms, which further influence the catalytic activity. Through comparison of ORR behaviors of three Fe/N/C catalysts prepared from different nitrogen sources, we observed that although all samples hold the same rule of ORR activity in alkaline medium higher than in acidic medium, the order the catalytic activity depends on the proportion of pyridinic N: the higher percent of pyridinic N, the higher sensitivity to the solution acidity/alkalinity. This study indicates that the pyridinic N has high ORR activity in alkaline medium, but when it is protonated in acidic medium, the catalytic activity is greatly suppressed.

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1. Introduction

The exploration of non-precious metal (NPM) electrocatalysts with high activity towards oxygen reduction reaction (ORR) is vital for large-scale applications of fuel cells. Currently, pyrolyzed Fe/N/C catalysts are considered as the most promising NMP catalysts for ORR, and proton exchange membrane fuel cells with the Fe/N/C as cathode catalysts can output a powder density as high as 0.7–1 W cm^{-2} [1–5]. The Fe/N/C can catalyze ORR in both acidic and alkaline media. However, the catalytic activity is much higher in alkaline medium than in acidic medium, and the enhancement also depends on catalyst properties. For example, Dodelet and coworkers found that the ORR activities of the Fe/N/C catalysts prepared by ball-milling and pyrolyzing are 7–10 times higher at pH 13 than at pH 1 [6]. Mukerjee and coworkers reported that pyrolyzed iron(III) meso-tetraphenylporphine chloride (FeTPPCl) exhibits an ORR activity 3–4 orders of magnitude higher in 0.1 M NaOH than in 0.1 M $HClO_4$ [7]. The reason for such big activity gap between the acidic and alkaline media is not very clear yet. Previously, Liang's group extensively investigated the pH effect on the ORR activity of the nitrogen-doped carbon catalyst [8]. They observed the ORR activity increases with increasing the solution pH values, and attributed the big gap in performance between acidic and alkaline media to the change in the active sites and their interaction with oxygen. They further speculated the protonation of doped nitrogen atoms hinders the charge delocalization, and thus decreases its catalytic activity in acidic medium [8]. However, no experimental evidences of protonation were provided.

The activity site of pyrolyzed Fe/N/C catalysts is also a long-debated issue [7,9–11]. It may consist of both Fe-N_x as macrocycle compounds (e.g., iron porphyrin), and metal-free N-doped carbon. Especially in alkaline medium, N-doped carbon materials indeed exhibit considerably high ORR activity. There are several nitrogen forms in N-doped carbon materials, such as pyridinic N, pyrrolic N, and graphitic N [12,13]. Through designing a model catalyst based on highly oriented pyrolitic graphite (HOPG), Guo et al. revealed that the ORR active site is created by pyridinic N, i.e., carbon atoms with Lewis basicity next to pyridinic N [14]. Our recent studies also indicate that the pyridinic N is important for ORR in pyrolyzed Fe/N/C catalysts.

In this study, we carried out the XPS test of the mixture of Fe/N/C catalyst and Nafion to simulate the acidic surrounding, and observed the complete protonation of pyridinic N. We further found that the proportion of pyridinic N is highly correlated with the gap in the catalytic activity between acidic and alkaline media.

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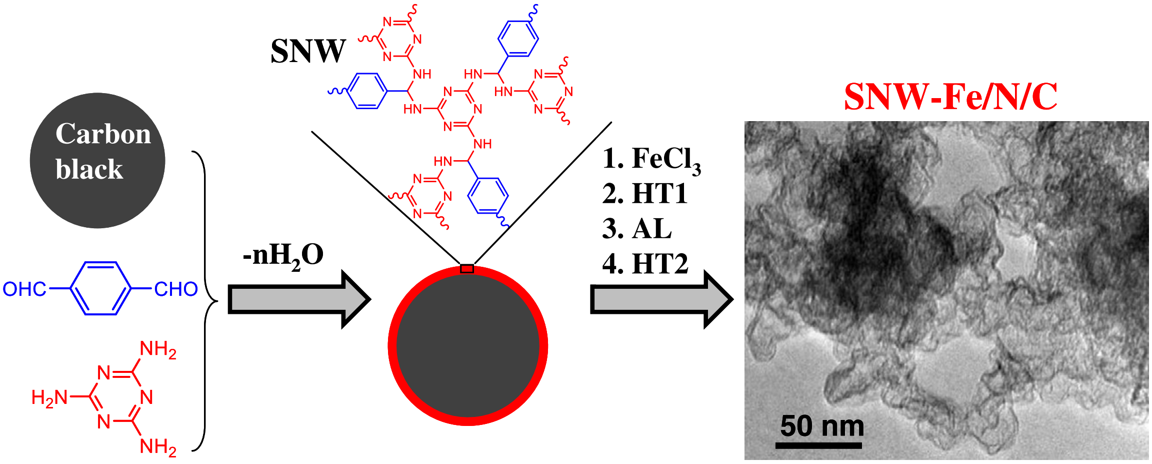

Fig. 1. Illustration of synthesizing SNW-Fe/N/C. The Schiff base networks (SNW) was prepared through the dehydration condensation between melamine and terephthalaldehyde, and coated on carbon black. The obtained sample was mixed with $FeCl_3$, and then subjected to heat treatment (HT1), acid leaching (AL) and second heat treatment again (HT2) to obtain the final SNW-Fe/N/C.

2. Experimental

To investigate the influence of nitrogen forms on the ORR activity, we synthesized three Fe/N/C catalysts from different nitrogen sources: Schiff base networks (SNW), *m*-phenylenediamine (*m*-PAD), and 2-aminothiazole (2-AT). The preparation process of SNW-Fe/N/C is illustrated in Fig. 1. The SNW was prepared through the dehydration condensation between melamine (0.626 g, 5.0 mmol), terephthalaldehyde (1 g, 7.5 mmol) with DMSO (18 mL) in 25 mL Teflon lined autoclave at 170 °C for 72 h, according to the revised literature method [15]. The formed SNW was in-situ coated on KJ600 carbon black (0.5 g). The obtained SNW/C (1.0 g) was mixed with $FeCl_3$ (3 mmol) in ethanol and the solvent was removed through rotary evaporator and further dried at 70 °C for 12 h. The resulting dried powder was subjected to the heat treatment (HT1) at 800 °C under argon atmosphere for 1 h. The pyrolyzed sample was then acid leached (AL) in 0.1 M H_2SO_4 at 80 °C for 8 h to remove unstable and inactive species, and the second heat treatment (HT2) was performed at 800 °C for another 3 h to form the final SNW-Fe/N/C catalyst. The morphology of the catalyst looks like the aggregation of porous carbon nanoparticles of ca. 30 nm in size (Fig. 1a).

The PDA-Fe/N/C and AT-Fe/N/C catalysts were synthesized as previously reported methods [16,17], and the pyrolyzed process and acid leaching were similar to those of SNW-Fe/N/C. X-ray photoelectron spectroscopy (XPS) characterization of the Fe/N/C catalysts was carried out on Omicron Sphera II hemispherical electron energy analyzer with Monochromatic Al Kα X-ray source (1486.6 eV, anode operating at 15 kV and 300 W).

The ORR activity was tested in O_2-saturated 0.1 M H_2SO_4 or 0.1 M NaOH solution on a glassy carbon (GC) rotating disk electrode (RDE, $\phi = 5.61$ mm) with a CHI-760D bipotentiostats. Rotating rate was 900 rpm. Counter electrode was a GC plate, and reference electrode was a reversible hydrogen electrode (RHE) and HgO/Hg electrode in acidic and alkaline media, respectively. All potentials in this study refer to the RHE scale. To prepare catalyst ink, the Fe/N/C catalyst (6.0 mg) was ultrasonically dispersed in a mixture of 0.45 mL water, 0.50 mL ethanol and 50 μL 5% Nafion for 1 h. The 25 μL of ink was carefully dropped onto the GC disk electrode, resulting in the catalyst loading of 0.6 mg cm^{-2}. Polarization curves were recorded by potential cycling between 0.2 and 1.2 V at 10 mV/s. Solution ohmic drop was compensated. Capacitive background current was corrected by subtracting the curve recorded in N_2-saturated solution at the same potential scan rate.

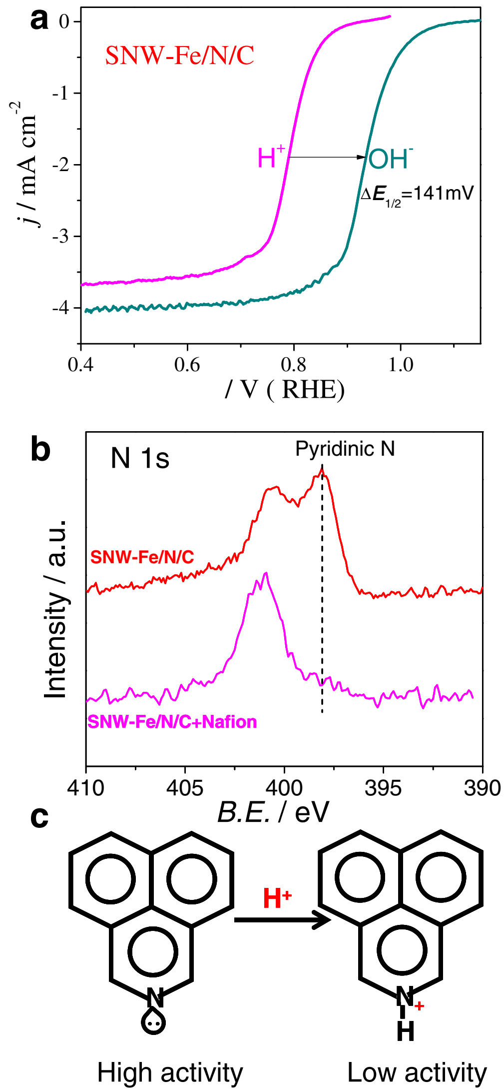

Fig. 2. (a) ORR polarization curves of SNW-Fe/N/C in 0.1 M H_2SO_4 and 0.1 M NaOH solution. Rotating speed: 900 rpm; scan rate: 10 mV/s. (b) High resolution N 1 s XPS of pristine SNW-Fe/N/C and the mixture of SNW-Fe/N/C + Nafion. The mass ratio of SNW-Fe/N/C to Nafion was 1:1. (c) Illustration of the protonation of pyridinic N in the Fe/N/C. The protonation of pyridinic N decreases the charge density (or basicity) of adjacent carbon atoms, and thus reduces the affinity to O_2 and ORR activity.

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