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Investigation of the durability of a poly-*p*-phenylenediamine/carbon black composite for the oxygen reduction reaction



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ABSTRACT

Nitrogen-doped carbon materials exhibiting high oxygen reduction reaction activity were prepared via the pyrolysis of a poly-*p*-phenylenediamine/carbon black composite. The as-synthesized catalyst showed excellent catalytic activity in alkaline solution, and outperformed commercial Pt/C in KOH solution (0.1 mol/L), as demonstrated by the higher current density and the more positive half-wave potential. Scanning electron microscopy and N₂ adsorption-desorption analyses indicated that a composite structure, in which the N-rich surface of the poly-*p*-phenylenediamine had an increased active center concentration and the high external surface area of the carbon black was conducive to the mass transport, is highly beneficial in terms of promoting the oxygen reduction reaction. However, the activity of this catalyst underwent an obvious decrease following exposure to air for 30 d. X-ray photoelectron spectroscopy showed that the oxygen content in the catalyst was increased by prolonged air exposure. O 1s spectrum showed increases in the C=O and C–O components, suggesting that atmospheric oxygen reacted with the catalyst. This oxidation led to the deactivation of active center, thus the catalytic activity decreased. Based on these results, the stability in air of nitrogen-doped carbon materials must be taken into consideration when assessing applications as alternatives to platinum-based materials.

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1. Introduction

The oxygen reduction reaction (ORR) is a crucial process in many energy conversion devices, such as fuel cells and metal/air batteries [1]. Although platinum-based materials have

proven to be the most efficient catalysts for the ORR, the high cost and scarcity of this metal significantly hinder the large-scale applications of these devices [2,3]. Recently, non-precious metal and metal-free ORR catalysts have attracted significant research interest as alternatives to plati-

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num-based compounds [4,5]. Nitrogen-doped carbon materials represent typical metal-free catalysts and exhibit excellent ORR activity as the result of nitrogen incorporation, as confirmed by experimental studies and quantum mechanical calculations [6–8]. Aniline derivatives have unique structures consisting of aromatic rings connected via imino groups, and so are frequently used as the nitrogen source in nitrogen-doped carbon materials [9–12]. However, a remaining challenge associated with these catalysts is their insufficient durability. The electrochemical stability and durability in air of nitrogen-doped carbon materials are substantially lower than those of platinum-based compounds, and this has hampered their applications [4,13]. Many groups have reported on the electrochemical stability of nitrogen-doped carbon materials, and great progress has been made in this respect over the past several years [4,14]. However, there have been few reports of the durability in air of nitrogen-doped carbon materials.

Platinum-based materials exhibit excellent ORR activity because of their appropriate oxygen binding and OH bonding energy values [15,16]. During the ORR, oxygen is eventually reduced to water as electrons flow through an external circuit to the anode. However, when platinum-based catalysts are exposed to air, this electrochemical reaction does not proceed [17,18]. Because the adsorption of atmospheric oxygen on the Pt surface generates an oxide coating [19], platinum-based catalysts must undergo an activation treatment to remove the surface oxidation layer before they exhibit optimal performance [20]. In the case of nitrogen-doped carbon materials, oxygen also adsorbs on the surface of the catalyst during the ORR [8,21]. This raises the question of whether or not oxygen will react with the catalyst and, if so, how this impacts the catalytic activity.

Herein, we report a poly-*p*-phenylenediamine (PpPD)/carbon black (CB) composite catalyst that shows high ORR activity, such that it outperforms a commercially available Pt/C catalyst (10% Pt, Johnson Matthey Corp) in KOH solution (0.1 mol/L). More importantly, we demonstrate that the exposure of the composite to air results in a reaction between oxygen and the catalyst, leading to a decrease in the ORR activity.

2. Experimental

2.1. Chemicals and apparatus

Both *p*-phenylenediamine (AR, 97%) and ammonium persulfate (AR, ≥98%) were purchased from the Aladdin company (Shanghai, China) and were used without further purification. All the electrochemical experiments were carried out using a Parstat 2273 electrochemical station. Scanning electron microscopy (SEM) images were obtained with a Nova NanoSEM 230 and N₂ adsorption-desorption isotherms were acquired with a Micromeritics Tristar 3000 analyzer at –196 °C. X-ray photoelectron spectroscopy (XPS, ESCALAB 250) was used to characterize the surface compositions of the samples.

2.2. Preparation of catalysts

To prepare composites consisting of PpPD and CB (Black Pearls 2000) (termed 0.44PpPD/CB, 0.88PpPD/CB and 1.32PpPD/CB), *p*-phenylenediamine (0.44, 0.88 or 1.32 g) was dissolved in 200 mL deionized water, following which 0.5 g CB was added. After stirring for 5 h, a solution of the oxidant (NH₄)₂S₂O₈ was added dropwise. The polymerization was allowed to proceed first with the container immersed in an ice bath (0 °C) for 6 h, and then at room temperature for another 18 h. The resulting products were filtered and washed with deionized water, then dried at 60 °C. Finally, the mixtures were ground into powder and heated under a N₂ flow at 1000 °C. A sample of pure PpPD was prepared in the same manner, but without adding CB.

2.3. Characterization of catalysts

The electrochemical characterization of specimens was carried out in a standard three-electrode cell using a Pt plate counter electrode and a Ag/AgCl/KCl (3 mol/L) reference electrode (0.197 V vs. NHE) at 25 °C. In brief, the catalyst was dispersed in an ethanol/Nafion (5%) mixture and ultra-sonicated for 30 min to form a uniform black ink. This well-dispersed catalyst ink was applied to a pre-polished glassy carbon disk (5 mm diameter, 0.19625 cm² area) and dried at room temperature. The ORR was performed in O₂-saturated KOH solution (0.1 mol/L) with a rotating-disk electrode (RDE) system. The accelerated durability trials were carried out by acquiring cyclic voltammograms (–0.3 V to 0.2 V) at 50 mV/s in O₂-saturated KOH solution (0.1 mol/L). All potentials were reported versus Ag/AgCl/KCl (3 mol/L).

3. Results and discussion

3.1. SEM and N₂ adsorption-desorption tests

The SEM image in Fig. 1(a) shows that the PpPD had an irregular sheet-like morphology with a smooth surface, and that the particle sizes of the PpPD were on the micrometer scale. The SEM image of the 0.88PpPD/CB (Fig. 1(b)) reveals that the CB particles aggregated on the surface of the PpPD, and that the size of the PpPD sheets was decreased [22]. The composite structure seen here is different from previously reported structures, in which the CB particles were covered with a PpPD shell [12,23]. This difference is the result of variations in the process used to polymerize the pPD. In the present work, the polymerization was conducted without adding hydrochloric

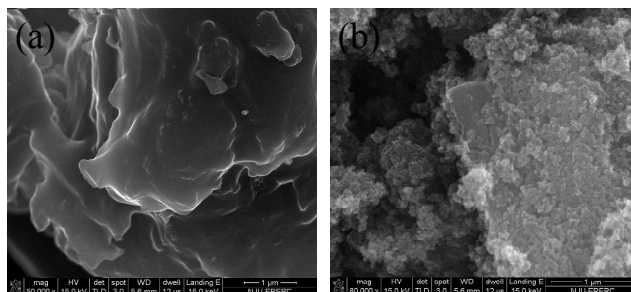


Fig. 1. SEM images of PpPD (a) and 0.88PpPD/CB (b).

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