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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 platinum-based materials.

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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 N_2 adsorption-desorption isotherms were acquired with a Micromeritics Tristar 3000 analyzer at $-196\text{ }^\circ\text{C}$. 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 $(\text{NH}_4)_2\text{S}_2\text{O}_8$ was added dropwise. The polymerization was allowed to proceed first with the container immersed in an ice bath ($0\text{ }^\circ\text{C}$) 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 $60\text{ }^\circ\text{C}$. Finally, the mixtures were ground into powder and heated under a N_2 flow at $1000\text{ }^\circ\text{C}$. 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 $25\text{ }^\circ\text{C}$. 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 cm^2 area) and dried at room temperature. The ORR was performed in O_2 -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 O_2 -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 N_2 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).

acid, thus the water solubility of the undoped PpPD was very low [24]. As a result, the PpPD sheets tended to agglomerate, thus increasing the particles size. Because the interaction between the hydrophobic surfaces of the CB and the PpPD is strong, the CB particles also aggregated on the PpPD surfaces and retarded the polymerization reaction. Thus, the PpPD particle sizes in the 0.88PpPD/CB were smaller than in the pure PpPD sample. To gain further insight into the structure of the PpPD/CB composites, N_2 adsorption-desorption measurements were carried out. Fig. 2(a) shows the adsorption-desorption isotherms, while the corresponding pore size distributions are presented in Fig. 2(b) and the results are summarized in Table 1. As expected, the Brunauer-Emmett-Teller (BET) surface area of the CB was very large, while the BET surface area of the PpPD was only 125 m^2/g , which is in good agreement with the image in Fig. 1(a). Therefore, the BET surface area of the PpPD/CB composite decreased as the amount of PpPD increased. It is interesting to observe that the micropore area of the 0.88PpPD/CB was larger than that of the 0.44PpPD/CB. This occurred because both the PpPD and the CB contributed to the micropore area, thus the 0.88PpPD/CB had a superior composite structure because it contained the optimal ratio of PpPD to CB.

3.2. Electrochemical characterization

We performed RDE measurements in KOH solution (0.1 mol/L) to evaluate the ORR activity of the prepared catalysts. As shown in Fig. 3(b), the onset potential of the PpPD was rather high, and its current density increased slowly as the potential decreased (Fig. 3(a)). This is attributed to the very low BET surface area of the PpPD (with an external surface area of only 12.7 m^2/g), because surface area is vital to mass transport in this system. Thus, the current density obtained from the PpPD was 2.2 mA/cm^2 even at -1 V, and a plateau appeared at approximately -0.5 V, suggesting the production of HO_2^- . As a result of the addition of CB, the PpPD/CB composite exhibited a substantial improvement in ORR activity and the plateau disappeared. As shown in Fig. 3(a), the ORR activity of the 0.88PpPD/CB was far superior to those of the 0.44PpPD/CB and 1.32PpPD/CB. Because these catalysts were all prepared in

Table 1

BET surface, micropore and external surface areas of the prepared catalysts.

Catalyst	BET surface area (m^2/g)	Micropore area (m^2/g)	External surface area (m^2/g)
PpPD	125	122	12.7
1.32PpPD/CB	286	127	158
0.88PpPD/CB	523	263	260
0.44PpPD/CB	590	247	342
CB	1480	618	862

the same manner, except for the amount of *p*-phenylenediamine, the differences in catalytic activity must have resulted primarily from variations in their physical properties, rather than their chemical characteristics. As noted above, the 0.88PpPD/CB had an advanced composite structure, in which the N-rich surface of the PpPD had an increased active center concentration and the high external surface area of the CB was conducive to the transport of oxygen and products. Thus the 0.88PpPD/CB outperformed the commercial Pt/C catalyst, as demonstrated by the higher current density (2.17 mA/cm^2 at -0.1 V, compared to 1.11 mA/cm^2 for the Pt/C) and the more positive half-wave potential ($E_{1/2}$).

To gain further insights into the electron transfer kinetics of the ORR over the 0.88PpPD/CB, we studied the reaction kinetics by rotating-disk voltammetry. The voltammetric profiles in O_2 -saturated KOH solution (0.1 mol/L) show that the current density was enhanced as the rotation rate increased from 400 to 2000 r/min (Fig. 3(c) inset) [25], and the corresponding Koutecky-Levich plots (J^{-1} vs. $\omega^{-1/2}$) at various potentials exhibit good linearity. In alkaline solution, the ORR generally proceeds by one of two pathways. The first is a direct 4-electron process in which O_2 is reduced to OH^- , while the other is a 2-electron reduction pathway such that the O_2 is reduced to HO_2^- , followed by further reduction of the HO_2^- [26]. We supposed that the ORR over Pt/C proceeded via the 4-electron reaction at -0.4 V, and calculated the number of electrons transferred at various electrode potentials of Pt/C and 0.88PpPD/CB. In the case of the 0.88PpPD/CB, the number of electrons transferred at various electrode potentials was constant at approximately 3.6 (Fig. 3(c)), suggesting that O_2 is

Fig. 2. N_2 adsorption-desorption isotherms (a) and the corresponding pore size distributions (b) of the prepared catalysts.

Fig. 3. RDE linear sweep voltammograms (a) of the prepared catalysts (catalyst loading: 820 $\mu\text{g}/\text{cm}^2$) and Pt/C (catalyst loading: 250 $\mu\text{g}/\text{cm}^2$); tafel plots (b) obtained from the RDE measurements; the dependence of the electron transfer number on the potential (c) for 0.88PpPD/CB and Pt/C at various potentials (Inset shows the RDE voltammograms of 0.88PpPD/CB at various rotation rates); accelerated durability test data (d) for 0.88PpPD/CB after 100 and 1000 cycles. RDE data were recorded in KOH solution (0.1 mol/L); electrode rotation speed 900 r/min; scan rate 10 mV/s.

reduced almost completely to OH^- through the 4-electron reduction process.

3.3. Durability investigations

To evaluate the electrochemical durability of the 0.88PpPD/CB, accelerated durability tests using cyclic voltammograms ranging from -0.3 to 0.2 V at 50 mV/s in O_2 -saturated KOH solution (0.1 mol/L) were carried out. It is evident from Fig. 3(d) that a slight change in the half-wave potential (~ 18 mV) is observed after 1000 cycles, indicating the good electrochemical stability of the 0.88PpPD/CB. To evaluate the durability of this material, it was exposed to air for 30 d. The results following this exposure show that the catalytic activity of the 0.88PpPD/CB decreased after air exposure; the current density at -0.1 V decreased by 1.02 mA/cm² and the diffusion-limiting current density was also reduced (Fig. 4(a)). As previously discussed, platinum-based materials tend to oxidize upon exposure to air, generating a surface oxide layer. We believe that oxidation also occurs upon exposure of the 0.88PpPD/CB to the atmosphere, decreasing the ORR activity. XPS assessments were performed to determine the chemical composition and

structure of the catalyst. As shown in Fig. 4(b), the oxygen content of the 0.88PpPD/CB increased by 1% (atomic fraction) following air exposure, while the N content decreased slightly. The increase in the oxygen content indicates the occurrence of an oxidation reaction, although this reaction cannot be directly attributed to atmospheric oxygen. Thus, in order to eliminate other factors, such as water vapor and carbon dioxide, we ran another experiment. Following heat treatment and cooling of the sample to below 100 °C, the nitrogen atmosphere was transitioned to oxygen, exposing the 0.88PpPD/CB to high purity oxygen for 1 h. XPS results reveal that the oxygen content of the 0.88PpPD/CB almost doubled after this oxygen exposure, and the $\text{O } 1\text{s}$ spectrum in Fig. 4(d) clearly shows increases in the C=O (531.2 eV) and C-O (533 eV) components [8,27]. In subsequent RDE measurements, the ORR activity of the 0.88PpPD/CB was found to have greatly decreased (Fig. 4(a)) after this oxygen exposure; the current density at -0.1 V was only 0.29 mA/cm² and the diffusion-limiting current density was less than 4 mA/cm². These data demonstrate that exposing 0.88PpPD/CB to air allows oxygen to react with the catalyst, and this oxidation decreases the ORR activity. Therefore, the 0.88PpPD/CB should be protected from oxygen exposure to

Fig. 4. RDE voltammograms (a) (KOH solution (0.1 mol/L); electrode rotation speed 900 r/min; scan rate 10 mV/s); the nitrogen and oxygen contents (b); C 1s spectra (c); O 1s spectra (d) of the 0.88PpPD/CB, following exposure to air for 30 d or to pure oxygen for 1 h after heat treatment.

preserve its catalytic ability.

4. Conclusions

In summary, nitrogen-doped carbon materials with high catalytic activity in alkaline solution were obtained via the pyrolysis of PpPD/CB composite. It was found that the exposure of this composite to the ambient atmosphere resulted in oxidation of the catalyst that in turn decreased the ORR activity. Thus stability in air must be taken into consideration when assessing the application of nitrogen-doped carbon materials as alternatives to platinum-based catalysts.

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Graphical Abstract

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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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Exposing a poly-*p*-phenylenediamine/carbon black composite to air allows oxygen to react with it, and this oxidation leads to increases in the C=O and C–O components, thus the catalytic activity decreases.

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聚对苯二胺和炭黑复合物作为高效的氧还原催化剂及其稳定性研究

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摘要: 近年来, 氮掺杂的碳材料作为碱性氧还原催化剂得到了研究者的广泛关注。掺杂的 N 原子会影响 C 原子的自旋密度和电荷分布, 导致碳材料表面产生“活性位点”, 因此掺氮碳材料具有优秀的氧还原活性, 这已经在理论计算和实验中得到了验证。我们通过调节聚对苯二胺和碳黑的比例, 之后进行热解制备了一系列掺氮碳材料。其中 0.88PpPD/CB 样品具有最好的氧还原活性, 其在 KOH 溶液 (0.1 mol/L) 中的氧还原性能超过了商业碳载铂。通过扫描电子显微镜表征, 发现碳球聚集在聚对苯二胺的表面, 这主要是因为聚对苯二胺没有进行酸掺杂, 因此其水溶性比较差。通过氮气的吸脱附表征, 发现聚对苯二胺的比表面积很小, 而碳黑样品 (BP2000) 的比表面积很大。因此, 随着聚对苯二胺量的增加, 聚对苯二胺/碳黑复合物的比表面积逐渐降低。另外, 聚对苯二胺表面几乎都是微孔, 而介孔和大孔主要来自于碳黑。研究者认为, “活性位点”主要位于微孔内 (聚对苯二胺表面), 而介孔和大孔有利于物质的传输。因此, 当聚对苯二胺和碳黑的比例合适时, 既有大量的“活性位点”暴露, 又有足够的介孔和大孔进行物质传输, 所以 0.88PpPD/CB 样品的氧还原活性最高。

但是, 对于掺氮碳材料来说, 一个主要的问题就是稳定性不足。不管是电化学稳定性, 还是放置在空气中的稳定性, 掺氮碳材料都比不上铂基催化剂, 这也阻碍了它们的大规模应用。对于电化学稳定性, 很多文章都进行了报道, 但是很少有文章报道掺氮碳材料在空气中的稳定性。我们知道, 铂基材料之所以具有优异的氧还原活性, 是因为铂和氧气的结合能比较合适, 既利于氧气吸附, 也利于之后氧气分子键的断裂。但是, 当铂基材料放置在空气中, 氧气的吸附也会发生, 而且之后会导致表面氧化层的形成。所以铂基材料需要活化才能达到最好的催化性能。对于掺氮碳材料, 放置在空气中会不会发生氧化反应? 这对氧还原活性是否有影响? 为了研究掺氮碳材料在空气中的稳定性, 我们将 0.88PpPD/CB 样品在空气中

放置了一个月,之后再进行电化学测试. 旋转圆盘电极测试表明,在空气中放置了一个月后,0.88Pd/CB 样品的氧还原活性降低了,不管是半波电位还是极限电流密度都下降了. 之后我们对其进行了 X 射线光电子能谱检测,发现在空气中放置了一个月后其氧含量提高了 1%(原子分数),而氮含量几乎没有变化. 氧含量的提高证实了氧化反应的发生,但不能直接归结于空气中的氧气. 为了排除其他因素,如水蒸气、二氧化碳等,当热处理完成,管式炉温度低于 100 °C 时,我们将高纯氮气切换为高纯氧气,一个小时后再取出样品. 电化学测试表明,在氧气中暴露了一个小时后,0.88Pd/CB 样品的氧还原活性极大地降低了,而且 X 射线光电子能谱表明其氧含量提高了一倍,接近 12%. 因此,我们证实了氧气会和 0.88Pd/CB 样品反应,导致样品的氧还原活性降低. 所以,对于未来掺氮碳材料的大规模应用,要考虑其在空气中的稳定性,以及如何避免和氧气接触.

关键词: 苯二胺; 炭黑; 复合结构; 氧气还原反应; 稳定性

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