Promotion of Oxygen Reduction to Hydrogen Peroxide by Ammonium Ions on N-doped Carbon Catalyst

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A lot of efforts have been devoted to the improvement of the catalytic activity and hydrogen peroxide (H₂O₂) selectivity of the catalysts in two-electron oxygen reduction reaction (ORR) utilized for production of H₂O₂. Little attention has been paid to the influence of the electrolyte itself. Herein, we report that the two-electron ORR catalytic performance of the catalyst strongly depends on the cations of the electrolyte. The catalytic performance of an N-doped carbon (PNC) catalyst has been evaluated in two different aqueous electrolytes: (NH₄)₂SO₄ and Na₂SO₄. The results show that the ORR catalytic activity and the H₂O₂ selectivity in (NH₄)₂SO₄ solution are much better than that in Na₂SO₄ solution, namely with H₂O₂ FE of 90.2% and current density of 13.9 mA cm⁻² in (NH₄)₂SO₄ compared to 67.8% and 2.5 mA cm⁻² in Na₂SO₄. The in-situ Fourier transform infrared (FTIR) spectroscopy shows that H₂O acts in the reaction in Na₂SO₄ solution as a proton source, but there was no evidence of the same role of H₂O in (NH₄)₂SO₄ solution. Further experimental results also show that the ORR performance of PNC is dependent on the concentration of (NH₄)₂SO₄ solution, but independent on the concentration of Na₂SO₄ solution. Thus, we reasonably infer that ammonium ions have promoted the ORR catalytic performance of PNC.

Keywords: oxygen reduction reaction, hydrogen peroxide, faradaic efficiency, electrocatalysis, ATR-FTIR

1. INTRODUCTION

H₂O₂ is widely used in various fields: as disinfectors in medicine, as green chemical oxidant and as industrial wastewater treatment agent [1-3]. Currently, H₂O₂ is mainly produced by industrial anthraquinone indirect synthesis method [4]. However, there are still serious challenges in this process such as generation of large amount of industrial waste, high storage and transportation costs [5]. An alternative approach is direct H₂O₂ synthesis from H₂ and O₂ [6-8]. However, the explosion risk in case
of mixing H$_2$ and O$_2$, as well as the necessity of noble metal catalysts usage, limiting the large-scale application of this method [9, 10]. Therefore, researchers are still searching for alternative methods for H$_2$O$_2$ production with high efficiency, low cost and high safety [11].

The two-electron electrochemical oxygen reduction reaction (ORR) is a desirable approach for H$_2$O$_2$ preparation, allowing to avoid the abovementioned disadvantages of direct and indirect synthesis methods [12,13]. The electrochemical approach can be carried out at normal temperature and pressure, which is safer and more convenient for operation, and can be powered by environment-friendly renewable energy [14]. The electrochemical ORR to H$_2$O$_2$ on non-precious carbon materials demonstrated high selectivity with a relatively low overpotential in alkaline media [11, 15]. However, H$_2$O$_2$ is extremely unstable in alkaline media [16], and the overpotential of the two-electron ORR is relative high in acidic media. Therefore, it is desired to produce H$_2$O$_2$ in a pH neutral solution [17].

Previous studies of the two-electron ORR mainly focused on the electrocatalytic materials (e.g. N-doped carbons) or active sites, whereas rare reports demonstrated the impact of the electrolytes with K$_2$SO$_4$ as the most commonly used neutral electrolyte with phosphate buffer solution [11, 18]. The reported results of high H$_2$O$_2$ Faraday efficiency (FE) are always accompanied with low current density. Therefore, it is still a challenge for non-precious catalysts in neutral electrolyte to simultaneously obtain a high H$_2$O$_2$ selectivity and high catalytic activity towards the two-electron ORR.

In this work, we explore the electrocatalytic activity and H$_2$O$_2$ selectivity of a protein derived N-doped carbon (denoted as PNC) catalyst in two different neutral electrolytes: Na$_2$SO$_4$ and (NH$_4$)$_2$SO$_4$ solution, and report a superior H$_2$O$_2$ FE of 90.2% with high current density of 13.9 mA cm$^{-2}$ in (NH$_4$)$_2$SO$_4$ solution. The in-situ FTIR spectroscopy characterization indicated that the direct proton source of ORR in Na$_2$SO$_4$ comes from H$_2$O, while the presence of ammonium ions may affect the proton transfer pathway of ORR.

2. EXPERIMENTAL SECTION

2.1 Synthesis of protein derived nitrogen-doped carbon (PNC)

Egg white (30 mL, approximately the amount from one egg) was added to ultrapure water (18.25 MΩ·cm, 10 mL), and then mixed under magnetic stirring at 40°C until a transparent solution formed. 1 g of 4MgCO$_3$·Mg(OH)$_2$·5H$_2$O was added to the protein solution, and then ultrasonically blended for 20 min after magnetic stirring for 3.5 h. A solid product was collected by centrifugation, then freeze dried under vacuum. Then the solid product was grounded to fine powders by mortar, and annealed in a tubular furnace at 600°C for 2 hours (heating rate: 5°C min$^{-1}$) under Ar atmosphere. After the pyrolysis, MgO was removed in 1.5 M HCl. The carbon material was washed 5 times with ultrapure water and freeze dried under vacuum before usage. All chemicals are analytical grade and purchased from Sinopharm Chemical Reagent Co., China.
2.2 Material characterization

Scanning electron microscope (SEM) characterization was performed by using a Zeiss Merlin Compact microscope at acceleration voltage of 5 kV. XPS studies were conducted on a Thermo Fisher EscaLab 250Xi spectrometer with Al Kα source (hν = 1486.6 eV). The N-1s spectra was analyzed and processed by XPSPEAK41 software.

2.3 Electrochemical performance measurements

5 mg of catalysts was added to 1 mL of Nafion alcohol solution (0.05 wt%), and then ultrasonically blended for 0.5 h to form uniform ink. 10 μL of the obtained ink was dropped onto a rotating ring-disk electrode (RRDE, φ = 4.57 mm, Pine Inc.) with a syringe. The coating catalyst was dried under infrared light. A rectangular carbon paper was used as the counter electrode, and an Hg/Hg2SO4 electrode was used as the reference electrode. All potentials were converted to the reversible hydrogen electrode (RHE). Electrochemical tests were performed on a CHI-700A Bi-Potentiostat. 1 M (NH4)2SO4 (pH=5.5) and 1 M Na2SO4 (pH=6) aqueous solution were separately used as electrolyte. The RRDE test was conducted in a standard 5-port electrolytic cell at 25°C. The polarization curves were recorded between 0.05 V vs. RHE and 0.85 V vs. RHE at 5 mV s⁻¹ at 1600 rpm and 1.2 V vs. RHE was applied on the Pt ring electrode in the RRDE tests. The collection efficiency of the RRDE was 0.22. The selectivity for H2O2 formation (H2O2%) and the number of transferred electrons (n) were calculated using the ring and disk currents and the collection efficiency [18].

2.4 Production of H2O2 by electrolysis

The aforementioned ink was pipetted onto both sides of a carbon paper with an area of 7×7 mm and utilized as the working electrode after drying. The bulk electrolysis was performed using H-type electrolytic cell separated by Nafion membrane (Figure S1). The three-electrode system was consisted of an Hg/Hg2SO4 electrode as a reference electrode, a Pt sheet as a counter electrode and the working electrode. 10 mL of O2-saturated (NH4)2SO4 solution or Na2SO4 solution was used as electrolyte. Bulk H2O2 production was obtained by chronoamperometry at 0.0-0.3 V vs. RHE for 10 min. The H2O2 concentration was measured using UV-vis spectroscopy calibration curve method. To obtain the calibration curve, a series of H2O2 solutions with gradient concentrations were added to 1 ml of 3 M H2SO4 and 1 ml of 0.05 M C4K2O9·2H2O solution and measured by UV-vis spectroscopy [19]. After the electrolysis, 4 mL of electrolyte was taken from the cathode compartment, and then 1 ml of 3 M H2SO4 and 1 ml of 0.05 M C4K2O9·2H2O solution were added before the UV-vis measurement. Based on the linear relationship between the UV-vis intensity and H2O2 concentration (10 ~ 40 mM), the H2O2 concentrations of the samples could be obtained (Figure S2). The H2O2 FE was calculated from the actual H2O2 product against the quantity of charge passed [20]. The current density of H2O2 (jH2O2) was calculated by the following equation:

\[
\frac{j_{H2O2}}{j_{ORR}} = \frac{H2O2 \text{ FE (\%)} \cdot j_{ORR}}{j_{ORR}}
\]

where \( j_{ORR} \) is total reaction current density (mA/cm²).
2.5 *In situ* ATR-FTIR study

To enhance the infrared signal, an Au nanofilm was deposited by a secondary chemical gilding method on a Si prism [21]. The aforementioned ink was then dropped onto the Au nanofilm and utilized as the working electrode after drying. The IR beam passed through the electrode interface by reflection (Figure S3). The *in-situ* attenuated total reflection surface-enhanced IR absorption spectroscopy (ATR-SEIRAS) study was conducted using a Thermo Fisher Nicolet 6700 spectrometer with an MCT detector with resolution of 16 cm⁻¹ and a total of 32 interferograms. All infrared spectra ordinates were expressed in absorbance (A). The infrared spectra at 0.7 V vs. RHE under Ar atmosphere were used as the background. The infrared spectra were collected while performing chronoamperometry at 0.6-0.0 V vs. RHE.

3. RESULTS AND DISCUSSION

3.1 Activity and selectivity in different electrolytes

Carbon materials are widely used in the field of electrocatalysis because of their large surface area and good conductivity, whereas nitrogen doping was reported as a feasible way for further improvement of the catalytic activity and the H₂O₂ selectivity of carbon materials [22, 23]. The PNC catalyst was synthesized by the template method and according to the SEM characterization, the PNC catalyst was obtained in the form of nanoflakes (Figure S4). XPS characterization was used to identify the various N-species in the PNC. Figure S5 displays the N-1s core level XPS spectra, which could be fitted with four distinct peaks, classified as pyridinic-N (398.4 eV), pyrrolic-N (399.9 eV), quaternary-N (400.7 eV), and graphitic-N (402.5 eV), respectively [24, 25].

The ORR catalytic performance of PNC was evaluated in Na₂SO₄ and (NH₄)₂SO₄ solutions with various concentrations. Figure 1(a, b) shows the current density of H₂O₂ production and the side reactions at different applied potentials from 0.0 to 0.3 V vs. RHE. Overall, the current density of H₂O₂ and the H₂O₂ FE in (NH₄)₂SO₄ solution (Figure 1(b)) was much higher than that in Na₂SO₄ solution (Figure 1(a)) in the investigated potential range. The current density of H₂O₂ was lower than 2 mA/cm² in all Na₂SO₄ solutions, but could reach as high as 12.5 mA/cm² in (NH₄)₂SO₄ solution. Meanwhile, the current density of H₂O₂ was independent on the Na₂SO₄ concentration (Figure 1(a)). In contrast, the current density of H₂O₂ and the H₂O₂ FE increased with the increase of (NH₄)₂SO₄ concentration at 0.0 V vs. RHE (Figure 1(b)). Solutions exhibiting best catalytic performance, namely 1 M (NH₄)₂SO₄ and 1 M Na₂SO₄, were further compared in Figure 1(c) and 1(d). 1 M (NH₄)₂SO₄ solution attributed to the highest H₂O₂ FE of 90.2% at 0.0 V vs. RHE, which was comparable to the results of the reported non-precious catalysts, while the current density of 13.9 mA/cm² is much higher than that reported in the literature (Table S1). It is worth noting that the H₂O₂ FE and the current density in 1 M (NH₄)₂SO₄ solution were 1.33 and 5.56 times higher than that in 1 M Na₂SO₄ solution respectively.

It is well known that the ORR catalytic activity and the H₂O₂ FE are sensitive to pH of the solution [17]. Therefore, in the abovementioned experiments, one might doubt that higher catalytic
performance for H$_2$O$_2$ generation resulted from lower pH of (NH$_4$)$_2$SO$_4$ solution. To eliminate this doubt, a certain amount of H$_2$SO$_4$ solution was added to 1 M Na$_2$SO$_4$ solution to adjust the pH from 6.0 to 5.5, which was the same as the pH of 1 M (NH$_4$)$_2$SO$_4$ solution.

Figure 1. Current density of H$_2$O$_2$ and side reaction and H$_2$O$_2$ Faraday efficiency (FE) in O$_2$-saturated 0.1, 0.3, 0.5, 0.7, 1 M Na$_2$SO$_4$ (a), 0.1, 0.3, 0.5, 0.7, 1 M (NH$_4$)$_2$SO$_4$ (b) solutions. Current density of H$_2$O$_2$ and side reaction in O$_2$-saturated 1 M Na$_2$SO$_4$ and H$_2$SO$_4$ (pH=5.5), 1 M Na$_2$SO$_4$ (pH=6.0) and 1 M (NH$_4$)$_2$SO$_4$ (pH=5.5) (c). The H$_2$O$_2$ FE in O$_2$-saturated 1 M Na$_2$SO$_4$ and H$_2$SO$_4$ (pH=5.5), 1 M Na$_2$SO$_4$ (pH=6.0) and 1 M (NH$_4$)$_2$SO$_4$ (pH=5.5) (d).

As shown in Figure 1(c) and 1(d), the change of pH from 6.0 to 5.5 did not strongly affect the H$_2$O$_2$ current density and the H$_2$O$_2$ FE in Na$_2$SO$_4$ solution, indicating that the reason for higher ORR catalytic performance in (NH$_4$)$_2$SO$_4$ solution was not pH.

3.2 Overall electron transfer

The electrocatalytic activity and selectivity of PNC towards ORR in 1 M Na$_2$SO$_4$ and 1 M (NH$_4$)$_2$SO$_4$ solutions were further examined by the RRDE method. Figure 2(a), 2(c) shows the experimental results in 1 M Na$_2$SO$_4$ and 1 M (NH$_4$)$_2$SO$_4$ solutions. The ORR current density was measured on the disk electrode and the H$_2$O$_2$ oxidation current was measured on the Pt ring electrode. According to the polarization curves, the ORR onset potential shifted positively from 0.52 V in 1 M Na$_2$SO$_4$ solution to 0.63 V in 1 M (NH$_4$)$_2$SO$_4$ solution, and the current was obviously higher in 1 M
(NH₄)₂SO₄. The H₂O₂% and number of transferred electrons were also derived from the RRDE polarization curves (Figure 2(b), 2(d)).

![Figure 2](image)

**Figure 2.** Linear sweep voltammetry of RRDE with the ring current (a), disk geometric current density (c), H₂O₂ selectivity (b) number of transferred electrons (n) as a function of PNC electrode potential (d). Conditions: the catalyst loading amount on the disk electrode was set to be 0.3 mg cm⁻², and measurements were performed in O₂-saturated 1 M Na₂SO₄ and 1 M (NH₄)₂SO₄ at a scan rate of 5 mV/s with 1600 rpm at 25°C.

The H₂O₂% in 1 M (NH₄)₂SO₄ solution reached ~90% at 0.4 V, in comparison to ~70% in Na₂SO₄ solution, and the electron transfer number in 1 M (NH₄)₂SO₄ solution was around ~2.2, in comparison with ~2.6 in Na₂SO₄ solution. On the basis of RRDE results, it can be concluded that the PNC performed better in 1 M (NH₄)₂SO₄ solution than in 1 M Na₂SO₄ solution, which is in consistence with the conclusion, drawn from the first discussion section.

### 3.3 In Situ FTIR observations

*In situ* ATR-SEIRAS was used to explore the ORR process in 1 M Na₂SO₄ and (NH₄)₂SO₄ solution [26]. The SEIRAS spectra on PNC surfaces were obtained in the potential range from 0.6 V to
0.0 V vs. RHE. Figure 3(a) and 3(b) are the real-time infrared spectra for ORR in 1 M Na₂SO₄ solution in Ar and O₂ atmosphere, respectively.

![Infrared Spectra](image)

**Figure 3.** SEIRAS spectra recorded in: 1 M Na₂SO₄ solution Ar-saturated (a) and O₂-saturated (b). Stark effects of the linearly adsorbed: H₂O in Ar/O₂-saturated 1 M Na₂SO₄ (c), OOH* in O₂-saturated 1 M Na₂SO₄ (d). The reference spectrum was taken at 0.7 V in Ar-saturated solution.

In the obtained SEIRAS spectra there were detected two vital bands at 3600-3000 cm⁻¹ and 1200-1000 cm⁻¹, which can be classified as the stretching of adsorbed H₂O and OOH*, respectively [27, 28]. Specifically, the H₂O stretching vibration, ν(HOH), appeared at a lower wavenumbers in O₂ than in Ar atmosphere, with Stark effects of ν(HOH) stronger in O₂ than in Ar atmosphere (Figure 3(c)), indicating a stronger PNC-H₂O interaction during ORR in 1 M Na₂SO₄ solution [26, 27]. In addition, the intensity of H₂O adsorbed at O₂ atmosphere was ~11 times higher than that in Ar atmosphere (Figure S7(a)), indicating a high coverage of H₂O on the electrode surface in 1 M Na₂SO₄ solution during ORR. These are clear evidences for H₂O participated in the ORR in 1 M Na₂SO₄ solution. Moreover, OOH* is regarded as an important intermediate for generating H₂O₂ in the ORR [17, 29]. As shown in Figure 3(b), the OOH* band turned out to be at 1100 cm⁻¹ in 1 M Na₂SO₄ solution in O₂ atmosphere. The Stark effect of ν₃(OOH*) (wavenumber shift with potential, Figure 3(d)) suggests that OOH* is an adsorbed intermediate for ORR in 1 M Na₂SO₄ solution [30].
In contrast, no H$_2$O stretching vibration bands were observed in 1 M (NH$_4$)$_2$SO$_4$ solution (Figure 4(a), 4(b)), indicating that the signal of H$_2$O$_\text{ads}$ in this condition was almost the same with the background and the reaction process related to the surface water might change in (NH$_4$)$_2$SO$_4$ solution. However, the infrared stretch vibration of surface H$_2$O is in the wave number range of 3600-3000 cm$^{-1}$ and the infrared signal of NH$_4^+$ is weak and registered at 3200-3000 cm$^{-1}$ [31]. Therefore, it is unable to obtain the infrared signal of NH$_4^+$ due to the interference with the surface H$_2$O. In addition, no OOH$^*$ band was observed in 1 M (NH$_4$)$_2$SO$_4$ solution (Figure 4(b)), indicating that protonation was too rapid in (NH$_4$)$_2$SO$_4$ solution to detect the intermediates.

Figure 4. SEIRAS spectra recorded in: 1 M (NH$_4$)$_2$SO$_4$ solution Ar-saturated (a) and O$_2$-saturated (b). The reference spectrum was taken at 0.7 V in Ar-saturated solution.

In the two-electron ORR, the adsorbed O$_2$ continuously consumes protons and electrons to generate H$_2$O$_2$ (Eq. 2, 3) [32].

\[
\begin{align*}
* + O_2 + H^+ + e^- & = OOH^* \quad (2) \\
OOH^* + H^+ + e^- & = H_2O_2 + * \quad (3)
\end{align*}
\]

Where the asterisk (*) represents the catalyst active site. Clearly, the proton transfer process is as crucial as over-potential in these reactions. Based on SEIRAS experiments, it is clear that protons were provided by H$_2$O in Na$_2$SO$_4$ solution in Eq. 2 and 3. In contrast, no surface H$_2$O-related reaction evidence was provided by SEIRAS in (NH$_4$)$_2$SO$_4$ solution. Combining with the concentration dependency relationship between the (NH$_4$)$_2$SO$_4$ solution and the H$_2$O$_2$ catalytic activity/selectivity, it can be reasonably inferred that the two-electron ORR was affected by the NH$_4^+$ concentration.

4. CONCLUSION

In this paper, we observed that the two-electron ORR catalytic activity and H$_2$O$_2$ FE of PNC were significantly improved in (NH$_4$)$_2$SO$_4$ solution, in comparison to those in Na$_2$SO$_4$ solution. The H$_2$O$_2$ FE increased from 67.8% (in 1 M Na$_2$SO$_4$ solution) to 90.2% (in 1 M (NH$_4$)$_2$SO$_4$ solution) at 0.0 V vs. RHE. Moreover, according to the in situ electrochemical SEIRAS measurement, the surface H$_2$O
directly participated in the ORR in Na$_2$SO$_4$ solution, but no surface H$_2$O-related reaction evidence was found in (NH$_4$)$_2$SO$_4$ solution. Considering the facts that the two-electron ORR catalytic activity and H$_2$O$_2$ FE of PNC were dependent on the concentration of (NH$_4$)$_2$SO$_4$ solution but independent on the concentration of Na$_2$SO$_4$ solution, we can reasonably propose that the H$_2$O$_2$ production catalytic performance of PNC was improved due to presence of NH$_4^+$ ions.

This work provides a new perspective to improve the FE and yield of H$_2$O$_2$ of the catalysts through an electrolyte point of view.

ACKNOWLEDGMENTS
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References

SUPPLEMENTARY DATA:

**Table S1.** Comparison of reaction current density and H$_2$O$_2$ Faraday efficiency in the H-type electrolytic cell in aqueous media.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Working media</th>
<th>Current density (mA cm$^{-2}$)</th>
<th>Potential (V vs. RHE)</th>
<th>H$_2$O$_2$FE (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-doped carbon</td>
<td>1 M (NH$_4$)$_2$SO$_4$</td>
<td>13.9</td>
<td>0.0</td>
<td>90.2</td>
<td>This work</td>
</tr>
<tr>
<td>N-doped carbon</td>
<td>1 M Na$_2$SO$_4$</td>
<td>2.5</td>
<td>0.0</td>
<td>67.8</td>
<td>This work</td>
</tr>
<tr>
<td>YP-80F</td>
<td>0.1M HClO$_4$</td>
<td>~3</td>
<td>~0.2</td>
<td>82</td>
<td>15</td>
</tr>
<tr>
<td>BP-2000</td>
<td>0.1M HClO$_4$</td>
<td><del>2</del></td>
<td>~0.2</td>
<td>82</td>
<td>15</td>
</tr>
<tr>
<td>N-doped carbon</td>
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<td>0.3</td>
<td>~90</td>
<td>18</td>
</tr>
<tr>
<td>N-doped carbon</td>
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<tr>
<td>N-doped carbon</td>
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<td>~0.5</td>
<td>~0.5</td>
<td>~90</td>
<td>23</td>
</tr>
</tbody>
</table>

**Figure S1.** Schematic diagram of the H-type electrolytic cell.
Figure S2. (a) Ultraviolet spectrum with a scanning range of 300-500 nm. (b) Ultraviolet standard curve.

Figure S3. Figure of electrolytic cell for ATR-SEIRAS.

Figure S4. SEM images of PNC. Scale bars = 200 nm (a); 1 μm (b, c); 2 μm (d).
**Figure S5.** XPS spectra of the N-1s core level region of N-doped carbon.

**Figure S6.** (a) Current density of H₂O₂ and side reaction in O₂-saturated 0.1, 0.5, 1, 1.5, 2 M (NH₄)₂SO₄. (b) The H₂O₂ Faraday efficiency in O₂-saturated 0.1, 0.5, 1, 1.5, 2 M (NH₄)₂SO₄.

**Figure S7.** (a) ν(H₂O) peak intensity in Ar and O₂-saturated 1 M Na₂SO₄. (b) ν₃(HOO) peak intensity in O₂-saturated 1 M (NH₄)₂SO₄.

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