

Fluorescence detection of hydroxyl radical generated from oxygen reduction on Fe/N/C catalyst

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Pyrolyzed Fe/N/C catalyst has been considered as the most promising candidate to replace Pt for oxygen reduction reaction (ORR) in fuel cells. However, poor stability of Fe/N/C catalyst, mainly attributed to the oxidation corrosion by aggressive •OH radical, severely hampers its applications. However, the exact mechanism for generation of •OH is unclear yet. Herein, we developed a fluorescent method to effectively detect •OH generated from ORR on Fe/N/C catalyst by using coumarin as a fluorescent probe. A great difference in potential dependence between •OH and H₂O₂ generated from the ORR was observed, which suggests that •OH is not generated from the decomposition of H₂O₂ as traditional viewpoint.

oxygen reduction reaction, Fe/N/C catalysts, radical, coumarin, fluorescent probe

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Ternary Fe/N/C catalysts are promising non-precious metal electrocatalysts for oxygen reduction reaction (ORR) in electrochemical energy devices [1–4]. However, poor stability in acid media severely hampers their applications [5]. The speculated instability reasons include demetallation, protonation of N-groups, and oxidative attack by active oxygen species (e.g., •OH and H₂O₂) [6–9]. The oxidative attack by H₂O₂ is material-intrinsic and a widely accepted mechanism for the performance decay of Fe/N/C catalysts [10–12]. There are two main pathways for oxidative corrosion by H₂O₂. One is the direct attack by H₂O₂, and the other one is H₂O₂ decomposition into aggressive •OH, and the latter attacks Fe/N/C catalysts [13–18]. As early as 2003, Dodelet's group [15,19] suggested that •OH is the main

cause of H₂O₂ degradation, and latter •OH attacks the active site of the catalyst into degradation products. This mode of catalyst degradation is still considered as a strong possibility. Therefore, many studies have focused on the detection of the yield of H₂O₂, but little work reveals the exact mechanism for generating •OH, which makes it still unclearly [12,20].

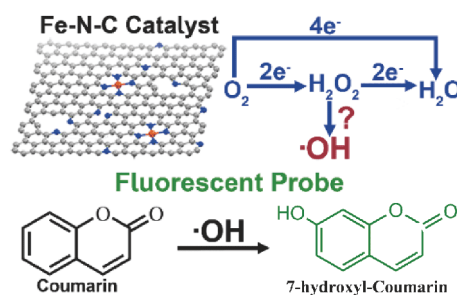
Oxygen reduction kinetics and H₂O₂ yield can be readily evaluated by rotating ring disk electrode (RRDE), but this technique cannot detect •OH radical. The life time of •OH radical is very short (about 10⁻⁹ s), and there are few reports involved in the detection of •OH during ORR on the Fe/N/C catalysts yet. Several techniques were developed to detect •OH in the ORR process, such as the combining radical footprinting with scanning electrochemical microscope (SECM) to reveal the production of •OH in ORR on Pt surface and coupling surface enhanced resonance Raman

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spectroscopy with rotating disk electrochemistry to investigate the oxygen species intermediates in ORR process of iron porphyrin compounds [21,22]. However, these techniques focused on the extended metal surface or the well-defined compounds, and were not suitable for the complex ternary Fe/N/C catalysts. Inspired by the extensive studies of active oxygen species in biological system, the methods of the electron spin resonance (ESR) spectroscopy and fluorescent probes are mainly employed to the detection of the active oxygen species [23–25]. For the ESR spectroscopy, several groups have applied it into the detection of $\bullet\text{OH}$ in ORR, but this method can only provide the qualitative conclusions, and is difficult to apply to quantitatively analyse $\bullet\text{OH}$ production due to low sensitivity [12]. Fluorescent probe method is hydroxyl radical-sensitive and a powerful tool to estimate the amount of $\bullet\text{OH}$ through the fluorescence intensity. Therefore, to pick up a suitable fluorescent probe for the detection of $\bullet\text{OH}$ in Fe/N/C ORR is prerequisite. Previous work proposed that $\bullet\text{OH}$ is common intermediate for ORR and OER in the bio-inspired copper catalyst by using the coumarin as a fluorescent probe in ethanol-diluted alkaline solution [26]. Note that coumarin would decompose in alkaline solution, and the existence of $\bullet\text{OH}$ is qualitatively conclusive. Therefore, more detailed experimental evidence is required to further understand the nature of $\bullet\text{OH}$ generated from ORR on the Fe/N/C catalysts.

Among the M/N/C catalysts, rare fluorescent probes have been employed into the detection of the $\bullet\text{OH}$, and the relationship between the $\bullet\text{OH}$ and H_2O_2 remains unclear. As coumarin is effective in acid solution and its detection limit for $\bullet\text{OH}$ is 5 nM [25,27,28], in this study, we use coumarin as the fluorescent probe to distinguish the role of $\bullet\text{OH}$ in the Fe/N/C ORR. As depicted in Scheme 1, during the Fe/N/C ORR, non-fluorescent coumarin will react with the $\bullet\text{OH}$ to generate the intense fluorescent 7-hydroxyl coumarin. According to the fluorescent intensity of 7-hydroxyl coumarin, the $\bullet\text{OH}$ can be quantitatively analysed. We found that as potential decreased from 0.70 to 0.60 V, the amount of $\bullet\text{OH}$ generated from the ORR process on Fe/N/C catalyst increased, reached a maximum at 0.65 V, and then declined. This variation of $\bullet\text{OH}$ amount is greatly different from that of H_2O_2 , and the latter increased monotonically with decreasing potentials. Our result indicates that $\bullet\text{OH}$ is not mainly generated by the H_2O_2 decomposition as traditional viewpoint.

The synthesis of Fe/N/C catalyst was similar to that reported in our previous work [29]. To avoid the micropore adsorption of coumarin which can block the mass transfer channels for ORR, we used the external-surface graphene oxide as the carbon source. The Fe/N/C catalyst was prepared by heat treatment of the graphene oxide at 950 °C in an NH_3 (10%)+Ar (90%) atmosphere for 1 h with the heat treatment of FeCl_3 in next zone at 310 °C as the Fe source. The transmission electron microscopy (TEM) showed that



Scheme 1 Schematic illustration of the conversion from non-fluorescent coumarin to fluorescent 7-hydroxyl-coumarin by $\bullet\text{OH}$ generated in ORR on Fe/N/C catalyst (color online).

the as-prepared Fe/N/C catalyst remained the layered structure as shown in Figure S1 (Supporting Information online).

The ORR test was carried out in O_2 -saturated 0.1 M H_2SO_4 solution with a glassy carbon RRDE at 900 r/min. Figure 1 (a) shows the stability test of the Fe/N/C catalyst at 0.65 V with and without 0.5 mM coumarin. With the addition of the coumarin, cathodic current decreased more quickly than that in the blank solution. Meanwhile, the electrolyte with 0.5 mM coumarin showed a fluorescence emission at 472 nm and the fluorescence signal grew continuously with the electrolyzing time varying from 0 to 6 h as shown in Figure 1 (b). The appearance of the fluorescence emission at 472 nm was due to the formation of the 7-hydroxyl coumarin [26,30]. This result indicates that $\bullet\text{OH}$ was involved in the Fe/N/C ORR process.

In order to confirm that the fluorescence was generated from $\bullet\text{OH}$ via the ORR on the Fe/N/C catalyst, we carried out a series of control experiments as shown in Figure 2. Firstly, to exclude the influence of electrooxidation, the potential was cycled between 0.2 to 1.0 V for 6 h in Ar-saturated 0.1 M H_2SO_4 solution with 0.5 mM coumarin. The fluorescence intensity at 472 nm was extremely low (66 vs. 1,083). This result is consistent with the previous reports because the oxidation potential of coumarin is above 2.1 V (vs. NHE) [28,31]. Secondly, during the Fe/N/C ORR process, the counter electrode occurs oxidation reaction. We performed the stability at 0.65 V for 6 h in 0.1 M H_2SO_4 containing 0.5 mM coumarin with a Nafion 211 proton exchange membrane to separate the work electrode and counter electrode. There was no significant fluorescence emission that was observed in the solution in counter electrode compartment. Thirdly, the O_2 oxidation effect was also ruled out by treating the Fe/N/C catalyst solely with the O_2 -saturated 0.1 M H_2SO_4 containing 0.5 mM coumarin without applying potential, and the fluorescent intensity was also very low (79 vs. 1,083). Lastly, we checked the influence of H_2O_2 . 35 μM H_2O_2 was mixed with 0.5 mM coumarin and Fe/N/C catalyst in 0.1 M H_2SO_4 , and the fluorescence intensity was also quite low (88 vs. 1,083). So, the chemical oxidation of coumarin by H_2O_2 in Fe/N/C ORR process can be excluded

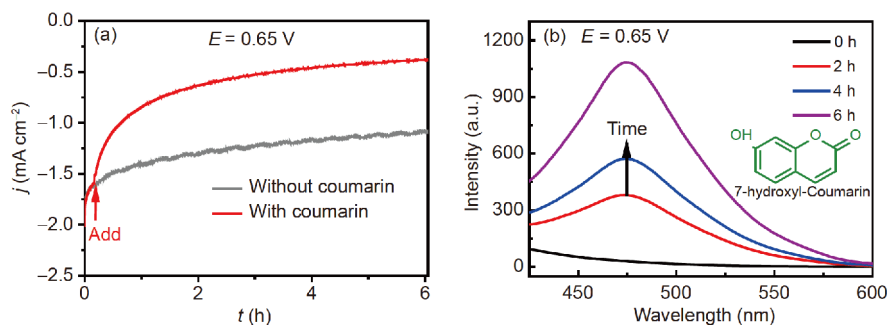


Figure 1 (a) I - t curve of ORR on Fe/N/C at 0.65 V in O₂-saturated 0.1 M H₂SO₄ solution with and without addition of 0.5 mM coumarin. The red arrow denotes the addition of coumarin into the solution. (b) Fluorescence emission spectra of the solution with coumarin collected at different ORR times (0–6 h). The emission at 472 nm indicates the presence of •OH (color online).

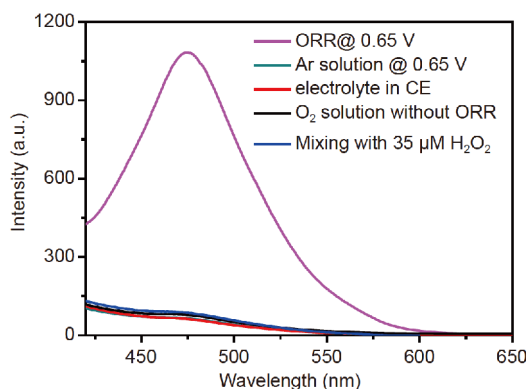


Figure 2 Control experiments for the detection of •OH generated from ORR on the Fe/N/C catalyst. The fluorescence emission spectra of five samples were tested: normal ORR at 0.65 V; Ar-saturated solution at 0.65 V; electrolyte in counter electrode compartment; O₂-saturated solution without applying potential (i.e., without ORR), and mixing with 35 μM H₂O₂ (color online).

as well. All these control experiment results further confirm that the •OH comes from the ORR process on the Fe/N/C catalyst.

We further tested the •OH produced from ORR at potentials varying from 0.60 to 0.70 V (Figure S2), and the obtained fluorescent spectra are shown in Figure 3(a). The electrolysis time was fixed at 6 h. Clearly, the fluorescence

emission increased with increasing potential, and reached a maximum at 0.650 V, and then decreased. This results demonstrates that the ORR at 0.65 V produces the maximal •OH, whose amount is about one order of magnitude than that at 0.60 or 0.70 V. To confirm the electrochemical stability of 7-hydroxyl coumarin under the Fe/N/C ORR, three potentials, 0.50, 0.60, and 0.70 V, were performed with the 3 μM 7-hydroxyl coumarin in 0.1 M H₂SO₄ solution for 2 h. As shown in the Figure 3(b), the fluorescent intensity of 7-hydroxyl coumarin changed little under the three potentials by comparing with the same concentration of 7-hydroxyl coumarin without applying potential. This result indicates that 7-hydroxyl coumarin is stable under the ORR conditions. Therefore, the generation of 7-hydroxyl coumarin through the •OH capture by coumarin fully represents the amount of •OH produced during the Fe/N/C ORR.

The generation of •OH from ORR on the Fe/N/C catalysts was mainly attributed to the catalytic decomposition of H₂O₂ by Fe^{3+/2+} through Fenton's reaction previously [6,13–15], and the detection of H₂O₂ was used to evaluate the stability of ORR catalysts. We then investigated the correlation between •OH and H₂O₂ intermediate. Figure 4(a) shows the ORR polarization curve and ring current of the Fe/N/C catalyst in O₂-saturated 0.1 M H₂SO₄ solution. The onset potential of ORR was about 0.80 V. As the potential decreased,

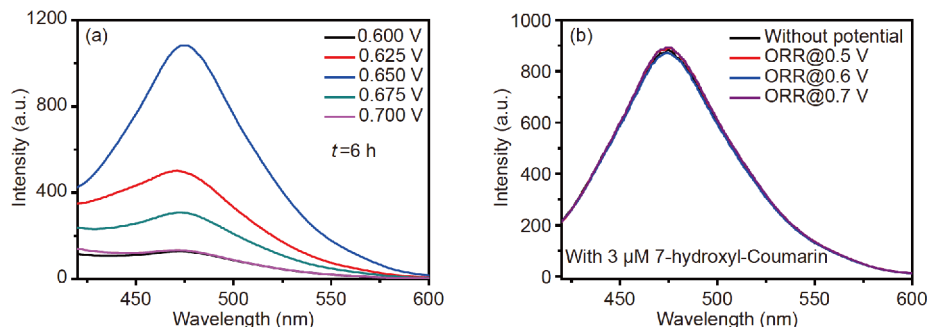


Figure 3 (a) Fluorescence emission spectra of the solution with coumarin collected from ORR at different potentials. The time for ORR was 6 h. (b) Fluorescence emission spectra of the solution with 3 μM 7-hydroxyl coumarin collected from ORR at different potentials for 2 h (color online).

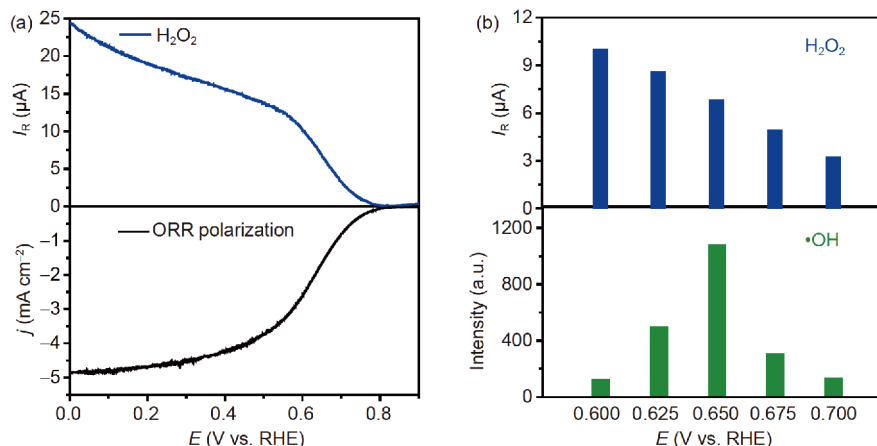


Figure 4 (a) ORR polarization curves and ring current of Fe/N/C catalyst in O_2 -saturated 0.1 M H_2SO_4 solution. The ring current comes from H_2O_2 oxidation. (b) Comparison of the ring currents from H_2O_2 oxidation with the fluorescence intensity induced by $\bullet\text{OH}$ (color online).

both disk current from ORR and ring current from H_2O_2 oxidation increased. Figure 4(b) shows the comparison of the amount between $\bullet\text{OH}$ and H_2O_2 generated from ORR on the Fe/N/C catalyst at 0.60–0.70 V. The $\bullet\text{OH}$ data were extracted from Figure 3(a). Clearly, the variation of $\bullet\text{OH}$ is quite different from that of H_2O_2 as the potential decreases from 0.70 to 0.60 V. The former increases with decreasing potential, and reaches a maximum at 0.65 V, and then decreases. By contrast, the amount of H_2O_2 monotonously increases with decreasing potential. Such great difference in potential dependence between $\bullet\text{OH}$ and H_2O_2 suggests that $\bullet\text{OH}$ is not likely to be produced from the decomposition of H_2O_2 , but may be directly derived from other ORR intermediates (e.g., $\ast\text{OOH}$).

Traditionally, $\bullet\text{OH}$ radical is considered to be generated from the decomposition of H_2O_2 through Fenton's reaction during ORR on the Fe/N/C catalysts. The intermediate of H_2O_2 can be further reduced to H_2O by 2-electron reduction and this reaction occurs faster at a lower potential [32]. To further investigate the influence of H_2O_2 on the production of $\bullet\text{OH}$ radical, we tested the fluorescence spectroscopy by adding 0.5 mM H_2O_2 into the electrolyte with 0.5 mM coumarin during ORR at 0.625 V. As shown in Figure S3, there is essentially no change in fluorescence spectra with and without the addition of 0.5 mM H_2O_2 . The saturated solubility of O_2 is 1.2 mM, and H_2O_2 yield is about 9% in this study, so that the addition of 0.5 mM H_2O_2 is enough high to evaluate the influence of H_2O_2 generated from ORR on the $\bullet\text{OH}$ radical. This control experiment supports that $\bullet\text{OH}$ radical is not generated from the decomposition of H_2O_2 .

In summary, we developed a fluorescent method with coumarin as a probe, which can effectively detect $\bullet\text{OH}$ generated from ORR on Fe/N/C catalysts. The $\bullet\text{OH}$ and H_2O_2 show great difference in potential dependence, indicating that $\bullet\text{OH}$ is not mainly produced by the decom-

position of H_2O_2 . This study provides new insight to the ORR process on the Fe/N/C catalysts.

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Conflict of interest The authors declare that they have no conflict of interest.

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