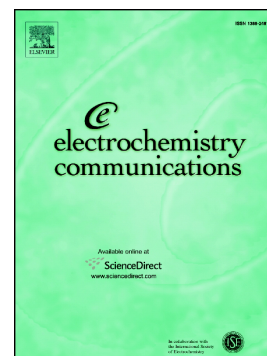


Accepted Manuscript

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PII: S1388-2481(18)30267-4
DOI: doi:[10.1016/j.elecom.2018.10.014](https://doi.org/10.1016/j.elecom.2018.10.014)
Reference: ELECOM 6318
To appear in: *Electrochemistry Communications*
Received date: 25 August 2018
Revised date: 14 October 2018
Accepted date: 15 October 2018

Please cite this article as: Hui-Juan Yang, Jiao Dong, Yu-Hao Hong, Wen-Feng Lin, Zhi-You Zhou, Shi-Gang Sun, Comparative investigation of CO₂ and oxygen reduction on Fe/N/C catalysts. *Elecom* (2018), doi:[10.1016/j.elecom.2018.10.014](https://doi.org/10.1016/j.elecom.2018.10.014)

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**Comparative investigation of CO₂ and oxygen reduction on Fe/N/C
catalysts**

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Abstract

Fe/N/C catalysts have been investigated as promising non-noble metal catalysts for both CO₂ reduction reaction (CO₂RR) and oxygen reduction reaction (ORR). However, it is unclear whether both reactions hold the same active sites. In this study, the Fe/N/C catalysts were subjected to oxidation treatment in O₂ at different temperatures to tune the reactivity. It was found that the oxidation treatment exhibits inverse effects on the CO₂RR and ORR. The CO₂RR activity was enhanced while ORR activity was suppressed after the oxidation treatment at temperatures from 80 to 240 °C. This result indicates that CO₂RR and ORR occur at different active sites. Furthermore, it was evidenced that pyrrolic N increases significantly upon the oxidation treatment, similar to the variation tendency of the CO₂RR activity, which suggests that pyrrolic N is highly relevant to the CO₂RR on Fe/N/C catalysts.

Keywords: CO₂ reduction; O₂ reduction reaction; Fe/N/C catalysts; N species; electrocatalysis

1. Introduction

Recently, carbon materials have attracted substantial attention as promising catalysts for electrochemical CO₂ reduction reaction (CO₂RR) due to low activity for side reaction of H₂ evolution as compared with metal catalysts [1-3]. For instance, it has been reported that N-doped carbon nanotubes could convert CO₂ to CO at low overpotential with a high faradaic selectivity of 80%, and the high catalytic activity was linked to graphitic and pyridinic N defects [4]. On the other hand, metal centers are also attributed to the active sites for the CO₂RR to CO [5-7]. For example, Yan et al reported that coordinatively unsaturated Ni-N sites exhibit high activity for CO₂ reduction to CO, and Ju et al. have demonstrated that M-N_x (M = Mn, Fe, Co, Ni, Cu) sites are crucial to CO₂RR [8]. Fe-N_x and Ni-N_x sites in carbon materials present a unique reactivity and faradaic efficiency for reducing CO₂ into CO, however, Co-N_x sites enhance the H₂ evolution. However, molecular catalysts with Co-N_x sites, such as cobalt meso-tetraphenylporphyrin and cobalt phthalocyanine, were anchored on carbon nanotubes to improve the selectivity for CO [9, 10]. The latter was contrary to Ju's report [11]. Obviously, there are contestations about the active sites in M/N/C catalyst materials. Apart from these, Xu et al. suggest that the intrinsic activity seems to correlate best with the quaternary N species [12]. Furthermore, Cui et al. used hot water steam to etch pyridinic and graphitic N species [10], and they found that pyrrolic N was retained to improve the performance of CO₂ reduction. All in all, the active sites of CO₂RR are still under debate.

It remains similar controversy about active sites of heteroatom-doped carbon materials for oxygen reduction reaction (ORR). Metal and nitrogen-doped carbon materials have been extensively studied for ORR. M-N_x sites are usually considered to be active sites [13-15]. The other viewpoint is that electron-rich N can introduce *sp*² carbon materials with abundant free-flowing π electrons to activate carbon materials [16, 17]. At present, the pyridinic N has been regarded as an important site associated with ORR activity for metal-free N-doped carbon materials. Guo et al. designed highly oriented pyrolytic graphite (HOPG) model catalysts and demonstrated that ORR active site was created by pyridinic N [18]. Obviously, heteroatom-doped carbon materials can catalyze both CO₂RR and ORR [9, 19-21]. A question arises naturally: Do both reactions hold the same active sites? We found there are yet no such comparative investigations between CO₂RR and ORR on heteroatom-doped carbon materials, which may provide useful insight for the mechanism of these two important reactions.

In this study, we studied the relevance of ORR and CO₂RR on pyrolyzed Fe/N/C catalysts. The catalytic activity of the Fe/N/C catalysts was tuned by post-oxidation-treatment from 80 to 240°C in O₂ atmosphere. Interestingly, we found that ORR activity decreases gradually with the increase of oxidation temperature, while the activity of CO₂RR to CO exhibits the opposite tendency, indicating different active sites for both reactions. We further analyze the changes in the N contents of various N bonding types by X-ray photoelectron spectroscopy (XPS) and found that pyrrolic N is highly relevant to the CO₂RR to CO.

2. Experimental

The Fe/N/C catalyst was prepared according to the established approach we reported previously [22]. In brief, phenylenediamine (PAD) monomer was oxidized and polymerized by $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and coated onto KJ600 carbon black. The precursor was mixed with FeCl_3 solution, dried at 80°C then subjected to pyrolysis at 950°C for 1 hours under Ar atmosphere. The obtained powder was subjected to acid leaching and then secondary pyrolysis at 950°C for 3 hours. The as-prepared Fe/N/C catalyst was labeled as Origin. The Origin sample was further oxidation treated by in O_2 for 2 h at 80, 160, and 240°C , and the obtained samples were labeled as 80°C-O_2 , 160°C-O_2 and 240°C-O_2 , respectively. The near-surface composition and chemical state were analyzed by XPS on an Omicron Sphera II hemispherical electron energy analyzer with Monochromatic Al $\text{K}\alpha$ X-ray source (1486.6 eV, anode operating at 15 kV and 300 W), and peak deconvolution was carried out by XPSPEAK software.

The CO_2RR activity test was performed in a standard three-electrode glass cell, by bubbling CO_2 in 0.1 M NaHCO_3 solution ($\text{pH} = 6.8$) at room temperature, using the CHI 760E potentiostat. The ORR activity test was performed using a rotating ring-disk electrode (RRDE) system, by bubbling O_2 in 0.1 M H_2SO_4 solution at 30°C . The catalyst ink was prepared as follows: 6 mg catalyst was ultrasonically dispersed in a mixture of 500 μL ethanol, 500 μL ultrapure water and 50 μL 5 wt% Nafion solution. The catalyst ink was dropped onto a glassy carbon working electrode with a loading of 0.6 mg cm^{-2} . A graphite sheet was used as the counter electrode for both

CO₂RR and ORR. Saturated calomel electrode (SCE) was used as the reference electrode in CO₂RR and reversible hydrogen electrode (RHE) in ORR. All the potentials were reported versus the RHE scale. Nafion-117 proton-exchange membrane was used to separate H-type cell for CO₂RR. Gaseous products were analyzed by on-line gas chromatography (GC9790II, Fuli).

3. Results and discussion

Fig. 1A shows the Raman spectra of the above four Fe/N/C catalysts, clearly indicating the local distortion (D-band at around 1350 cm⁻¹) and the extent of graphitization of the carbon materials (G-band at around 1580 cm⁻¹) [23, 24]. The intensity ratio of the D to G bands (I_D/I_G) is relevant to defects [25]. The I_D/I_G (1.04-1.10) of the oxidation-treatment samples is considerably higher than that of the Origin sample ($I_D/I_G=1.02$), indicating that the oxidation treatment can induce carbon defects on the surface.

To further verify the influence of oxidation treatment, the chemical states and element composition of the four samples were analyzed by XPS. All samples contained C, O, N, and tiny Fe elements (as seen in Fig. 1B). The emphasis is put on to the N species, because it is the key factor determining the catalytic activity for both CO₂RR and ORR. Weight contents of N changed from 5.6% for the untreated one, to 8.28%, 7.6%, and 7% for the oxidation-treated samples at 80, 160, and 240°C, respectively. Fitting high-resolution N 1s XPS of Origin and 240°C-O₂ samples (as shown in Fig. 1C and 1D) exhibits the pyridinic N (398.6 eV), Fe-N_x (399.7 eV),

pyrrolic N (400.8 eV), graphitic N (401.6 eV), and pyridinic-like oxide N (402.5 eV) [4, 15, 26]. The pyrrolic N is the most obvious N species changed after oxidation treatment. It increases from 1.23% in the Origin sample to 2.47% in 240°C-O₂.

Linear sweep voltammetry (LSV) was used to evaluate the CO₂RR performance of these catalysts in a CO₂-saturated 0.1 M NaHCO₃ solution (Fig. 2A). Compared with N₂-saturated solution, the reduction current increases significantly in CO₂-saturated solution, which demonstrates that CO₂RR took place in addition to H₂ evolution. The higher the oxidation treatment temperature of the catalyst sample, the larger the reduction current was observed at high overpotentials. It is worth mentioning that this reduction current includes both CO₂RR and HER. In N₂-saturated 0.1 M NaHCO₃ solution, 160°C-O₂ and 240°C-O₂ samples show larger reduction current than the untreated Origin and 80°C-O₂ samples. This indicates that 160°C-O₂ and 240°C-O₂ have better performance for HER. Therefore, the reaction products should be analyzed by gas chromatography (GC) and ¹H nuclear magnetic resonance (NMR) to evaluate the CO₂RR activities. It was found that no considerable liquid-phase products could be detected by NMR. As for gas-phase products, only CO and H₂ were observed through GC quantitatively and qualitatively analysis. The CO₂RR to CO partial current density (j_{CO}) was calculated using equation (1):

$$j_{CO} = \frac{C_{CO} \times F_{CO_2} \times 10^{-3} \times 96485 \times 2}{22.4 \times 60 \times A} \quad (1)$$

where C_{CO} is the volume fraction of the gas-phase product CO, F_{CO_2} is the flow rate of CO₂ (24 mL min⁻¹), and A is the geometric area of the working electrode [17]. The influence of oxidation temperature on the j_{CO} was shown in Fig. 2B, especially at high

overpotentials. The j_{CO} increases from 0.88 to 0.97, 1.95, and 3.2 mA cm⁻², corresponding to the untreated catalyst, oxidation treated ones at 80, 160, and 240 °C, respectively. That is, CO₂RR catalytic activity increases with increasing oxidation treatment temperature. At the oxidation temperature beyond 240 °C, the CO₂RR activity decreased due to the decomposition of active sites by the over-oxidation. As for Faradaic efficiency of CO, it was slightly improved from 77.9% @ -0.646 V on the untreated catalyst to 86.7 % on the 160°C-O₂ sample, but decreased to 83.2% on the 240°C-O₂ sample. However, the 240°C-O₂ sample showed the maximum CO partial current density.

In contrast to the enhancing effect of the oxidation treatment on the Fe/N/C catalyst for the CO₂RR, the ORR activity decreased. Fig. 2C shows ORR polarization curves of the four catalysts in O₂-saturated 0.1M H₂SO₄ solution. The ORR half-wave potential ($E_{1/2}$) was 0.813 V (vs. RHE) for the Origin sample. The ORR activity decreases after the oxidation treatment, yielding $E_{1/2}$ of 0.785, 0.762, and 0.732 V for 80°C-O₂, 160°C-O₂, and 240°C-O₂, respectively. The kinetic current was calculated by Koutecky–Levich equation [27], and then normalized with catalyst loading to obtain mass activity (j_m), which represents the intrinsic activity of catalyst samples. The j_m of the Origin catalyst is 11.5 A g⁻¹ at 0.80 V vs. RHE, that of the oxidation-treated ones are 2.5, 1.4 and 0.45 A g⁻¹ for 80°C-O₂, 160°C-O₂, and 240°C-O₂, respectively. Clearly, the ORR activity of the Fe/N/C catalyst decreased significantly after the oxidation treatment. To get insight into the impact on ORR mechanism, Tafel plots were obtained and shown in Fig. 2D for the untreated and oxidation-treated catalysts.

Tafel slopes are very similar, being 76, 73, and 72 mV dec⁻¹ for Origin, 80°C-O₂ and 160°C-O₂, respectively. Clearly, there is no significant change in the reaction mechanism of the ORR on the oxidation-treated catalysts.

To compare more clearly the effects of the oxidation treatments upon the activity of the Fe/N/C catalyst towards CO₂RR and ORR, the partial current density of CO₂RR to CO (at -0.646 V) and the kinetic current density of ORR (at 0.8 V) of the four catalysts are compared in Fig. 3A. The inverse effects of the oxidation treatment upon the activity for two reactions are distinctly observed. The j_{CO} of the 240°C-O₂ was 3.2 mA cm⁻², which was nearly 4 times higher than that of the untreated catalyst (0.88 mA cm⁻²). However, the untreated catalyst exhibited the highest ORR kinetic current density, and the $E_{1/2}$ decreases for all the treated catalysts and along the rise of oxidation treatment temperature. It is clear that the oxidation treatment of Fe/N/C catalyst can promote its CO₂RR activity but suppress ORR activity. This result indicates that the active sites of the Fe/N/C catalyst for CO₂RR and ORR are different. For the CO₂RR, Zheng et al. reported the active sites are possibly related to pyrrolic N [28]. To get an insight into this, Fig. 3B shows the relationship between CO₂RR activity and N content of different N-bonding type in the Fe/N/C. Only pyrrolic N has the similar variation tendency to the CO₂RR activity. Our experimental data also support that the active sites are related to pyrrolic N for CO₂RR in Fe/N/C catalysts. Previously, we prepared a Fe-free N-doped carbon material (N_xC) from ZIF-8 and tested its CO₂RR activity [29]. As shown in Fig. 3C, the content of pyrrolic N shows a good correlation with CO₂RR activity for both Fe/N/C and the N_xC

catalysts. As for ORR, it was observed that the content of graphitic N decreases with increasing the oxidation treatment temperature from 80 to 240 °C (Fig. 3B). This trend is consistent with that of ORR activity shown in Fig. 3A. Previously, Chen's group reported that graphitic N serves as the active sites for ORR on N-doped carbons [30]. Therefore, the graphitic N may also be responsible for the ORR in our study. Furthermore, the roles of Fe played in CO₂RR and ORR are still needed further studies.

Conclusion

In summary, the Fe/N/C catalyst was prepared and subjected to oxidation treatment in oxygen at three different temperatures, and the untreated and treated catalysts were tested for CO₂RR and ORR. It was found that the CO₂RR activity was enhanced, while ORR activity was suppressed after the oxidation treatments at temperatures from 80 to 240°C. This observation suggests that the active sites of the Fe/N/C catalyst for CO₂RR and ORR are different. Furthermore, it was also found that the amount of pyrrolic N increases significantly upon the oxidation treatment, and only pyrrolic N has the similar variation tendency to the CO₂RR activity, indicating that the active sites are related to pyrrolic N for CO₂RR in Fe/N/C catalysts. This work not only provides evidence for understanding different active sites exist in the Fe/N/C catalysts for the two important reactions but also suggests a new approach for increasing the CO₂RR activity through engineering pyrrolic N content.

Acknowledgements. This study was supported by grants from National Key Research and Development Program of China (2016YFB0101202), National Natural Science Foundation of China (91645121 and 21621091), Fundamental Research Funds for the Central Universities (20720150109) and Loughborough University (H10841).

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Figure captions

Fig. 1. Raman spectra (A) and XPS (B) of the four Fe/N/C catalysts: Origin, 80°C -O₂, 160°C -O₂ and 240°C -O₂; also shown are the high-resolution XPS for the region of N 1s for the Origin (C) and 240°C -O₂ (D) samples.

Fig. 2. (A) linear scanning voltammograms for the four Fe/N/C catalysts of Origin, 80°C -O₂, 160°C -O₂ and 240°C -O₂ in CO₂-saturated 0.1 M NaHCO₃ at 50 mV s⁻¹. The dash lines are the corresponding data in N₂-saturated electrolyte as for references; (B) Partial current density of CO₂ reduction to CO at different electrode potential; (C) ORR polarization curves in O₂-saturated 0.1 M H₂SO₄ at 10 mV s⁻¹ with a rotating speed of 900 rpm; (D) Tafel plots of the four Fe/N/C catalysts for ORR.

Fig. 3. (A) Comparison of catalytic activity between CO₂RR and ORR on the four Fe/N/C catalysts. Partial current density of CO₂ reduction to CO at -0.646 V (Right axis) and ORR kinetic current density at 0.80 V (Left axis). (B) N species content and partial current density of CO₂ reduction to CO at -0.646 V (Right axis) obtained on the four Fe/N/C catalysts of Origin, 80°C -O₂, 160°C -O₂, and 240°C -O₂. (C) The relationship between CO₂RR activity and pyrrolic N content. The data of Fe-free N-doped carbon (N_xC) was derived from Ref 29 (Sample number was ZIF-CNT-FA-p).

Figures

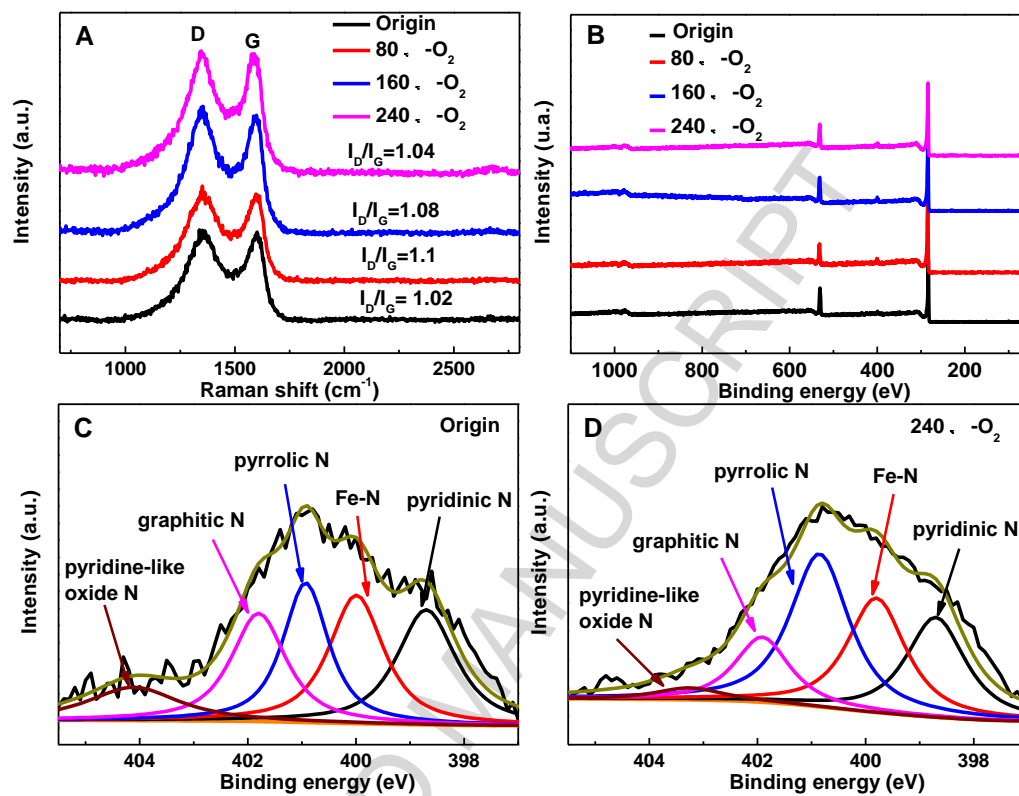


Fig. 1

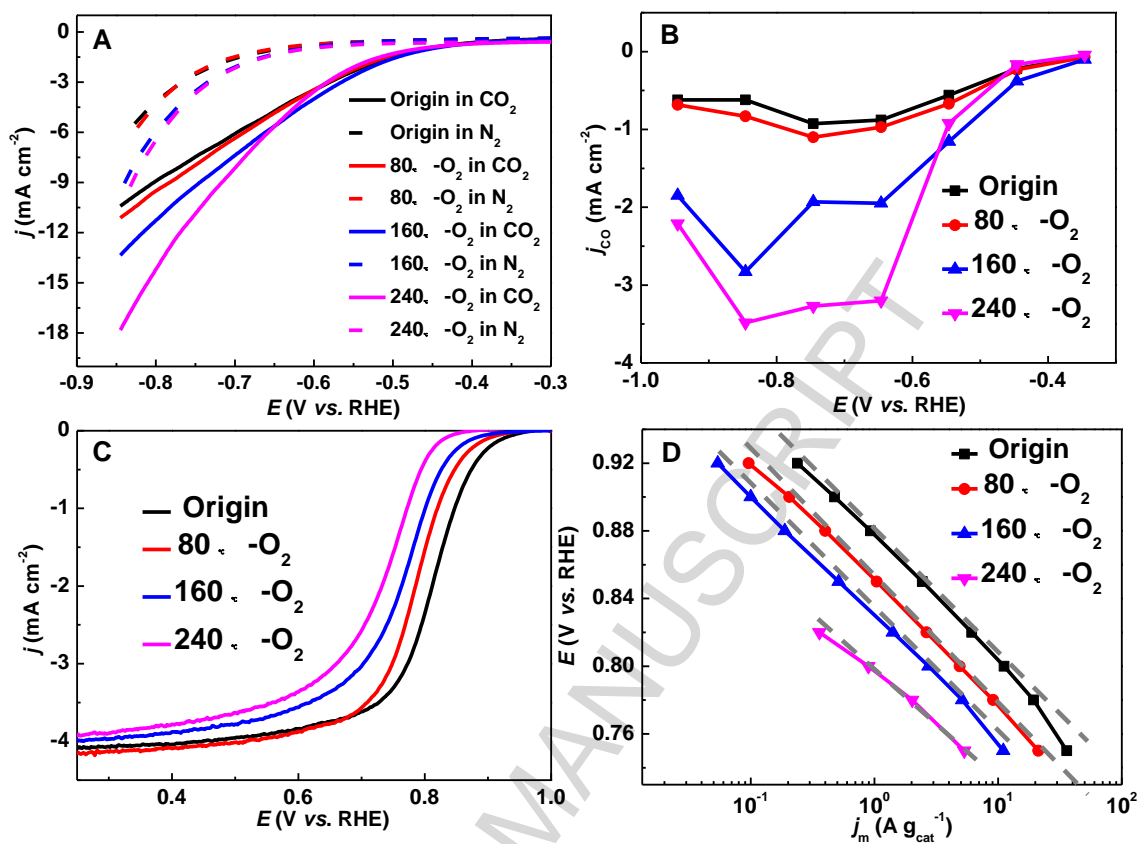


Fig. 2

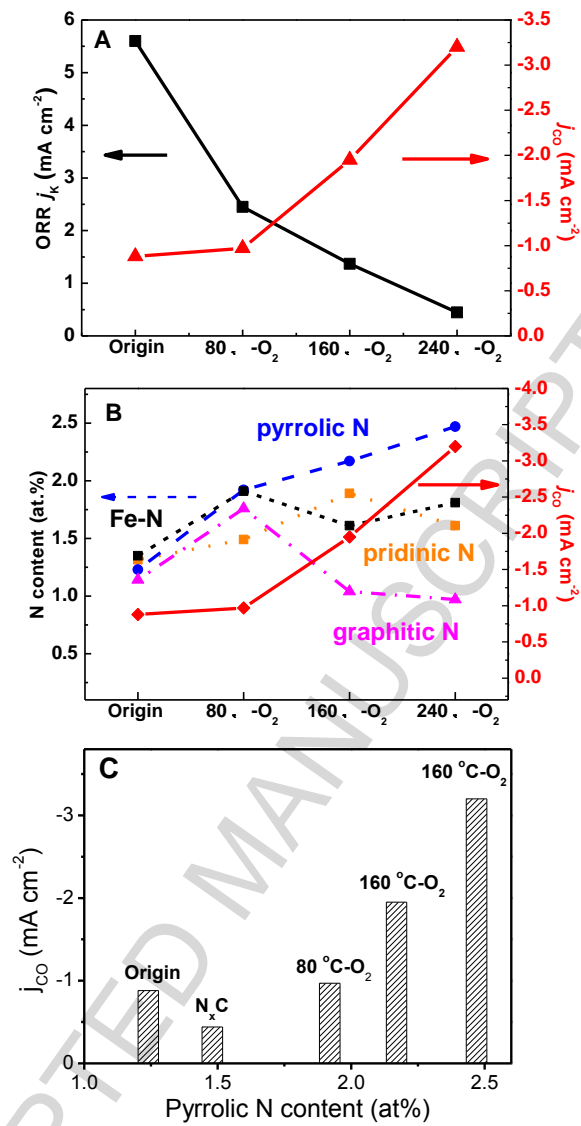


Fig. 3

Highlights

- ◆ Comparative investigation of CO₂ and O₂ reduction on Fe/N/C catalysts was carried out.
- ◆ CO₂ and O₂ reduction occur at different active sites.
- ◆ Thermal oxidation treatment of Fe/N/C catalysts can promote the activity for CO₂ reduction.

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