

A Journal of the Gesellschaft Deutscher Chemiker A Deutscher Chemiker GDCh International Edition www.angewandte.org

Accepted Article

- Title: Overall oxygen electro catalysis on nitrogen-modified carbon catalysts: identification of active sites and in situ observation of reactive intermediates
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This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: Angew. Chem. Int. Ed. 10.1002/anie.202012615

Link to VoR: https://doi.org/10.1002/anie.202012615

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Overall oxygen electrocatalysis on nitrogen-modified carbon catalysts: Identification of active sites and in situ observation of reactive intermediates

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Abstract: The recent mechanistic understandings including active sites, adsorbed intermediate products and rate-determining steps (RDS) of nitrogen (N)-modified carbon catalysts in electrocatalytic oxygen reduction (ORR) and oxygen evolution reaction (OER), however, are still rife with controversies due to the inevitable coexistence of diverse N configurations and the technical limitation for observing formed intermediates. In this work, seven kinds of aromatic molecules with designated single N species are used as model structures to investigate the explicit role of each common N group in both ORR and OER. Specifically, dynamic evolution of active sites and key adsorbed intermediate products including O2 (ads), superoxide anion O2-* and OOH* are monitored with in situ spectroscopy. We propose that the formation of *OOH species from O_2 -* (O_2 -*+ $H_2O \rightarrow OOH$ *+OH-) is a possible RDS during the ORR process, whereas the generation of O2 from OOH* species is the most possible RDS during the OER process.

Introduction

Overall oxygen electrocatalysis, including oxygen reduction reaction (ORR) and oxygen evolution reaction (OER), represents the cornerstone for a wide range of renewable electrochemical energy conversion and energy storage technologies.^[1-3] Nitrogen (N)-modified graphitic carbon materials, as the most promising metal-free catalysts in these two reactions, have received

tremendous attention over the last decade, owing to their abundance and high sustainability compared with metal catalysts.^[4-5] Some impressive experiments and theoretical predictions regarding the possible catalytic mechanisms and active sites have been conducted through regulating the N concentration in N-modified model materials or introducing the simulation models of the active structures.[6-8] Although pyridinic N and graphitic N are recently pointed out to be the most likely species that could create active sites, the connection remains controversial due to the inevitable mixing with other N configurations (e.g. pyrrolic, amine or lactam) in doped carbon catalysts synthesized by the recently deficient doping methods. Specifically, the involved intermediate products (e.g. adsorbed O2 molecule, superoxide anion O2-*, peroxide HO2*) and ratedetermining steps (RDS) during the ORR and OER processes have been still rarely studied by experimental approaches. The precise structure-function relationship between active sites and reactivities is still unclear. The inhomogeneities of N species associated with the morphology of catalysts also hamper the exploration for active sites. Determining the genuine active sites, monitoring the important intermediate products and revealing the possible reaction pathways are therefore highly important to understand the catalytic nature and to optimize the design and development of new carbon-based catalysts.

To disclose the genuine role of each N species in oxygen electrocatalysis, preparing N-containing graphitic carbon

10.1002/anie.202012615

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In the present work, three nanocarbon supports, including onion-like carbon (OLC), high temperature-treated carbon nanofiber (HHT) and carbon nanotubes (CNTs), are chosen to support seven different model aromatic organic molecules to form model catalytic systems via a solvothermal self-assembly process (Figure 1b, here, OLC is used as an example in the preparation process). The resulting model catalytic systems not only have a high concentration of desired single N species, but also exhibit a clear structure-activity relationship. The pyridinic N species are demonstrated to be advantageous for both ORR and OER processes over a wide pH range, where it could facilitate the ORR by a four-electron-like dominated pathway associated with the local conjugated structure of N species. The activities of catalysts mainly originate from electrocatalytic reactions rather than from carbon corrosion during the OER process. The possibly adsorbed intermediate products and RDS are proposed for both ORR and OER processes.

Results and Discussion

Determination of model catalytic system with single N group

As shown in Figure 1c, the results of x-ray photoelectron spectroscopy (XPS) confirm that main four N species: pyridinic N groups (398.3 eV), lactam or amide N groups (399.2 eV) or pyrrolic N groups (400.3 eV) exist in these model catalytic systems.^[14] Due to the good symmetry and the narrow full width at half-maximum (FWHM, ~1.6 eV) of all N peaks, we can conclude that each model catalytic system contains only one type of N functional group. The content of N species on the model systems is from 1.2 to 2.3 at.%. The structural features of these model molecules on OLC support were further studied by attenuated total reflectance infrared (ATR-IR) spectroscopy (Figure S1-S5). The main characteristic peaks of CB, PTD, PTA, PAD and AD molecules can be observed clearly, meaning that the structures of various model molecules maintain the same during the preparation process. The net contents of these model molecules on OLC support are quantified to 0.72-1.31 wt % by using thermogravimetric (TG) measurements (Figure S6).



Figure 1. Structural, fabrication and elemental characterization of model catalytic systems. (a) Structures of different aromatic organic molecules with isolated N configurations (including pyrrolic, amine, lactam, and pyridinic N). (b) The preparation of aromatic molecules supported on OLC using a solvothermal method. Here, cyclohexane was used as the solvent. (c) XPS N1s spectra of OLC and model catalytic systems. The FWHM of all N peaks is approximately 1.6 eV.

Model catalysts reveal ORR active sites

The ORR activity of these model catalytic systems in alkaline is shown in Figure 2a. Only supported AD (AD+OLC) and PAD (PAD+OLC) model catalytic systems exhibit higher current densities and more positive onset potentials (Eonset) compared with pure OLC and other supported model systems with respective pyrrolic N (CB+OLC), O=C-NH (PTD+OLC) and -NH₂ (PTA+OLC) groups, while unsupported model molecules do not show the relevant activities (Figure S7), indicating pyridinic N species are the possible active species in the ORR. To further investigate the role of pyridinic N species, two other concentrations of AD molecules in AD+OLC are deliberately regulated (Figure S6f). It can be found that the current density of AD+OLC is declining with decreased concentrations of AD molecules (Figure S8a and S8c), reflecting the important role of pyridinic N species. Furthermore, the similar behavior of AD+OLC and PAD+OLC catalysts indicates that the position of the pyridinic N, noted as the edge zigzag or armchair position, negligibly affect the catalytic performance. Anthracene (AT) was additionally used to mimic the zigzag configuration of pure carbon materials (Figure S9). The lower performance of supported AT (AT+OLC) relative to AD+OLC further indicates the activity enhancement of pyridinic N species as well as non-critical role of edge configuration in the ORR process in alkaline.

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To investigate the size influence of the π -conjugated structure for the pyridinic N species on the ORR activity, two other molecules, BAD and DBAD, were chosen. The net concentrations of these two molecules are determined to be 1.18 wt% and 1.05 wt% (Figure S10). Their molecular structures exhibit good stability as confirmed by ATR-IR (Figure S11-S12). In the C K-edge X-ray absorption near-edge structure (XANES) spectra (Figure S13a), compared with pristine OLC, an additional peak of supported DBAD (DBAD+OLC), observed at 287.2 eV, can be assigned to the σ^* bond of C-N.^[15] Another weak peak appeared at about 286.6 eV for DBAD+OLC which might be attributed to π^* (ring) resonance of the DBAD molecule itself.^[16] Other carbon-nitrogen species could not be observed. In the N K-edge XANES spectra (Figure S13b), compared with pristine OLC, DBAD+OLC exhibits an obvious peak at 398.3 eV which can be assigned to a π^* feature of pyridine-like N structure,^[17] suggesting that the

dominant N species on the surface of OLC is the expected pyridinic N group. This is further supported by XPS results of DBAD+OLC (Figure S16b), which reveals that only pyridinic N species (at 398.4 eV, 1.8 at%) can be observed. The LSV results displayed in Figure 2b and Figure S14a show that the current densities are in direct proportion to the sizes of the π-conjugated structures with pyridinic N species. Further electrocatalytic results summarized in Figure 2c and Figure 2e demonstrate that the size of π-conjugated system is a critical parameter to accelerate the ORR process, showing as the gradually enhanced intrinsic current densities and the gradually positive shift in onset potential (Eonset), which might be ascribed to the enhanced electron delocalization effect from a larger π-conjugated system of model molecules. In addition, the reasonable catalytic stability of DBAD+OLC at two applied



Figure 2. Electrochemical measurements of model catalytic systems for the ORR in O2-saturated electrolytes. (a) LSV curves of model catalytic systems and pure OLC catalyst in 0.1 M KOH and (b) model catalytic systems bearing isolated pyridinic N species and extended π-conjugated structure at onset potential region. (c) The intrinsic current densities of various model catalytic systems with isolated pyridinic N species. (d) Electron transfer (ET) numbers of supported catalysts with isolated pyridinic N species and pristine OLC catalyst, respectively, based on rotating ring-disk electrode (RRDE) measurements. (e) Number of benzene units of active components with single pyridinic N species as a function of ET number. HO2- selectivity at 0.6 VRHE and onset potential (Equation of ET number. HO2- selectivity at 0.6 VRHE and onset potential (Equation of ET number. HO2- selectivity at 0.6 VRHE and onset potential (Equation of ET number. HO2- selectivity at 0.6 VRHE and onset potential (Equation of ET number. HO2- selectivity at 0.6 VRHE and onset potential (Equation of ET number. HO2- selectivity at 0.6 VRHE and onset potential (Equation of ET number. HO2- selectivity at 0.6 VRHE and onset potential (Equation of ET number. HO2- selectivity at 0.6 VRHE and onset potential (Equation of ET number. HO2- selectivity at 0.6 VRHE and onset potential (Equation of ET number. HO2- selectivity at 0.6 VRHE and onset potential (Equation of ET number. HO2- selectivity at 0.6 VRHE and onset potential (Equation of ET number. HO2- selectivity at 0.6 VRHE and onset potential (Equation of ET number. HO2- selectivity at 0.6 VRHE and onset potential (Equation of ET number. HO2- selectivity at 0.6 VRHE and onset potential (Equation of ET number. HO2- selectivity at 0.6 VRHE and onset potential (Equation of ET number. HO2- selectivity at 0.6 VRHE and onset potential (Equation of ET number. HO2- selectivity at 0.6 VRHE and onset potential (Equation of ET number. HO2- selectivity at 0.6 VRHE and onset potential (Equation of ET number. HO2- selectivity at 0.6 VRHE and onset potential (Equation of ET number. HO2- selectivity at 0.6 VRHE and onset potential (Equation of ET number. HO2- selectivity at 0.6 VRHE and onset potential (Equation of ET number. HO2- selectivity at 0.6 VRHE and onset potential (Equation of ET number. HO2- selectivity at 0.6 VRHE and onset potential (Equation of ET number. HO2- selectivity at 0.6 VRHE and onset potential (Equation of ET number. HO2- selectivity at 0.6 VRHE and onset potential (Equation of ET number. HO2- selectivity at 0.6 VRHE at 0.6 threshold current density of 1 µA/cm². (f) LSV curves measured in phosphate buffer solution (PH=7.0) and 0.1 M H₂SO₄ media, respectively.

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potentials was demonstrated by not observing significant current change for 2 h (Figure S16a). To further confirm the role of pyridinic N species, DBAD was removed from DBAD+OLC (Figure S15) by ultrasonication, the corresponding activity of the residual OLC sample returns to the level of pristine OLC, which evidences the advantageous role of pyridinic N species for the ORR activity.

The introduction of pyridinc N species significantly increases the electron transfer (ET) number from 2.4~2.7 of OLC to 2.8~3.0 for AD+OLC and can be further extended to 3.3~3.5 of DBAD+OLC at 0.2~0.7 V vs. RHE (V_{RHE}) (Figure 2d-e). The corresponding selectivity in favor of HO₂- production gradually decreases from 70~78% for OLC to 50~60% for AD+OLC, and eventually reaches 19.0~38.0% for DBAD+OLC at 0.2~0.7 VRHE (Figure S14b). Moreover, as a comparison, AT+OLC sample with single edge configuration (zigzag) and without any pyridinic N species displays higher HO₂- selectivity than that of OLC and AD+OLC (Figure S9b). All these findings indicate that (i) pyridinic N species prone to contribute the ORR in a four-electron-like manner (as clarified by increment of ET number and decrease of HO₂- production); (ii) pyridinic N species could improve the E_{onset} of ORR to more positive; (iii) the structure size of π -conjugated pyridinic N species is a critical factor to facilitate the ORR process and (iv) the edge structure in the absence of pyridinic N species (for example, only zigzag configuration) plays a negative effect in accelerating four-electron pathway of ORR. Therefore, it can be expected that carbon-based catalysts with a single pyridinic N function group in a larger π-conjugated system (e.g. nanographene) could show complete four-electron pathway.

Additionally, DBAD+OLC is selected as a representative catalyst to study the role of pyridinic N in neutral (0.1 M phosphate buffer solution, PH=7.0) and acidic (0.1 M H_2SO_4) ORR processes. Clearly, this catalyst delivered a higher current density than pristine OLC in the neutral and acidic media (Figure 2f), which suggests that the model catalyst containing pyridinic N species can exhibit an elevated catalytic performance over a broad pH range.

Model catalysts reveal OER active sites

In addition to identification of active sites for ORR, we also unveiled the catalytic function of each N species for the OER activity by evaluating the model catalytic systems in 0.1 M KOH (Figure 3 and Figure S17). In similarity to the ORR results, AD+OLC and PAD+OLC catalysts show higher current densities relative to other catalysts. This indicates that pyridinic N species are also active for OER. On the contrary, pyrrolic, amine and lactam species are inactive for OER process demonstrated by negligibly improved performance of CB+OLC, PTA+OLC and PTD+OLC relative to OLC (Figure 3a). Also, in line with the ORR results, the OER process is insensitive to the edge configurations as demonstrated by the similar current densities and Tafel slopes of AD+OLC and PAD+OLC catalyst (Figure 3a and Figure S18). By extending the π -conjugated system of the model molecules, the catalysts show an increase in the OER activity (Figure 3b). There is a direct proportional relationship between the number of benzene units and theoretical TOF values, as shown in Figure S19. Specifically, the value increases from 0.153 s⁻¹ of AD+OLC to 0.638 s⁻¹ of DBAD+OLC at 1.60 V_{RHE}. Both values are significantly higher than that of the reported highly active Ni-/Febased OER catalysts (0.028-0.075 s⁻¹ at 1.63 V_{RHE}).^[18,19] Hence, it can be concluded that the π -conjugated size of the carbon

matrix accelerates the OER process. Moreover, similar Tafel slopes (77~85 mV dec⁻¹) are obtained for AD+OLC, BAD+OLC and DBAD+OLC catalysts (Figure S20), implying the extended π -conjugation does not change the OER reaction pathway. By using the rotating ring-disk electrode (RRDE) technique (Figure S21), the OER process occurring on DBAD+OLC is dominated by a desirable four-electron pathway (99.9%) with negligible peroxide intermediate formation.



Figure 3. Electrochemical measurements of model catalytic systems for the OER in Ar-saturated 0.1 M KOH. (a) LSV curves of model catalytic systems and pristine OLC catalyst. (b) LSV curves of model catalytic systems with isolated pyridinic N species and extended π -conjugated structure catalysts. (c) Mass spectra profiles of the produced CO (m/z 28) and O₂ (m/z 32) with DBAD+OLC.

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A high Faradaic efficiency (FE(O₂)) of around 86 % at two low potentials (e.g. 1.567 and 1.60 V_{RHE}) was obtained, which are comparable to reported metal-based catalysts to some degree. $^{\left[20,21\right] }$ The loss of FE(O_2) maybe partly inflicted by the inefficient oxygen collection by the Pt ring electrode or unavoidable carbon corrosion (e.g. CO or CO2 formation) in alkaline medium. It should be emphasized that when acquiring mass spectra, a very weak CO signal and an obvious O2 signal were observed, as shown in Figure 3c, reflecting the current density originates mainly from water oxidation rather than carbon corrosion. DBAD+OLC shows a decent stability during 2 h at an applied potential (Figure S16a). All the aforementioned results suggest that pyridinic N species can efficiently accelerate both ORR and OER processes, and their catalytic performance could be regulated by the π -conjugated size of active components at molecular level. To further verify the catalytic role of pyridinic N species, two other kinds of carbon (CNT and HHT) were tested as supports for DBAD. Indeed, dramatically enhanced catalytic behavior can be observed with both DBAD+HHT and DBAD+CNT catalysts for the ORR and OER processes (Figure S22 and 23), which confirms the critical role of pyridinic N species in facilitating the catalytic processes.

Doped catalysts for OER and ORR

In general, pyridinic N and graphitic N are considered to be the most common species in oxygen electrocatalysis with Ndoped carbon as catalysts.^[8,22,23] After confirming the positive role of pyridinic N species with model molecules, four kinds of Ndoped OLC (NOLC) catalysts with enriched pyridinic N but without any graphitic N species were synthesized and tested for both ORR and OER processes (Figure S24). Among them, NOLC-4 possesses the highest N content (2.7 at%) and largest proportion (63.1%) of pyridinic N species in all the N species. As shown in Figure 4, through varying the contents of pyridinic N species in different NOLC catalysts, the current densities and onset potentials can be gradually manipulated for the ORR activity, while only the current densities are impacted for the OER activity. Some linear relationships between current densities or ET numbers and the concentrations of pyridinic N species at different applied potentials (Figure 4b, 4c and 4e) could be observed in the ORR and OER processes, reflecting that pyridinic N species are the catalytically active sites in ORR and OER processes. Moreover, the Tafel slope values (Figure 4f and Figure S25, 75~78 mV dec⁻¹) of NOLC catalysts are analogous to the model catalytic systems (77~85 mV dec⁻¹), suggesting that both model catalysts and doped catalysts have the similar kinetic reaction process.



Figure 4. Electrochemical measurements of various N-doped OLC (NOLC) catalysts with enriched pyridinic N and without any graphitic N species for ORR and OER. (a) ORR LSV curves of NOLC catalysts. (b)-(c) Dependence of current densities and ET numbers at different potentials on the concentration of pyridinic N of NOLC catalysts (based on XPS results). (d) OER LSV curves of NOLC catalysts. (e)-(f) Dependence of current densities at different potentials and Tafel slope on the concentration of pyridinic N (based on XPS results).

Mechanistic Study of ORR and OER

Density functional theory calculations predicted that the binding energy of some surface adsorbed intermediate oxygen species, such as O₂ (ads), O₂-*, OOH*, O* and OH*, governs the ORR activity,^[24-26] whereas OH*, O* and OOH* mainly dominate the OER process.^[27] It is significant to use effective experimental measurements to elucidate the evolution processes of the surface relevant species during electrochemical reactions. As shown in

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the in situ ATR-IR spectra in Figure 5a, the peak located at 1400 cm⁻¹ exhibits a quasi-reversible behavior with ORR potential change, which is attributed to the O-O vibration of adsorbed oxygen molecule O2(ads) on the catalyst.[28] Moreover, evolution processes monitored by two other peaks located at 1052 cm⁻¹ and 1019 cm⁻¹ are observed (Figure 5b). Given that the infrared vibration peaks of the O2-* and OOH* typically are located in the region 1100-980 cm^{-1,[28-33]} some control experiments were carefully introduced, to further differentiate O2-* and OOH* species. The results of Figure 5c reveal that (i) no obvious peaks at 1052 cm⁻¹ and 1019 cm⁻¹ positions can be observed in Arsaturated KOH, suggesting these two peaks corresponding to Ocontaining species and (ii) an apparent red-shift behavior ($\Delta = \sim 26$ cm⁻¹) appears at position 1019 cm⁻¹ for O₂-saturated KOD electrolyte, while the original vibration band at 1052 cm⁻¹ is unaffected (Figure 5c and Figure S26), indicating that the vibration band at 1019 cm⁻¹ is most likely to be OOH* rather than O₂-* species, thus the vibration band at 1052 cm⁻¹ is ascribed to the O₂-*. All the experiments demonstrate that O₂-* and OOH* species as the important intermediates are involved in the ORR process. Recently, the formation of O₂-* from O₂ (ads) coupled with the first electron transfer (that is $O_2+e-\rightarrow O_2-*$) or the generation of OOH* from O₂-* (O₂-*+H₂O \rightarrow OOH*+OH-) over carbon catalysts in the ORR has been considered to be the most common RDS.^[34,35] To clarify the RDS, isotopic electrochemical studies were further performed, as displayed in Figure 5e. Kinetic isotope effect (KIE) values of around 1.45-1.61 at 0.6-0.7 VRHE are obtained, suggesting that there is a potential primary isotope effect and the RDS of the ORR process involves a cleavage of the O-H bond of water molecules. Combined with the ATR-IR results, assuming the following elementary step O2-*+H₂O \rightarrow OOH*+OH- is likely to be the potential RDS in the ORR. In the case of the OER, a similar evolution behavior of OOH* species (at 1018 cm⁻¹) is observed and no distinct other oxygen species can be found in Figure 5d, implying that the RDS in the OER is mainly associated with the OOH* species. Together with the result of the primary isotope effect with the KIE values of around 1.51-1.68 at 1.567-1.6 V_{RHE} (Figure 5e), it allows us to conclude that the generation of O₂ from OOH* species is the most possible RDS in the OER.

To gain more insights into the active sites, C-N vibrational band were monitored with in situ ATR-IR spectra. The red-shift of the C-N peak at 1357 cm⁻¹ (Figure 5f and Figure S27) with potential-dependent tendency suggests that active sites should originate from pyridinic N itself or adjacent carbon atoms during the ORR and OER. To determine the real active sites, some postmortem measurements were further conducted after ORR and OER stability tests. The XPS spectrum of DBAD+OLC after ORR (Figure S16b) shows the concentration of pyridinic N is decreasing and a significant new N1s peak at 400.1 eV appears, which can be attributed to pyridonic N that transformed from pyridinic N through a reaction involving the carbon atoms next to pyridinic N and O-containing species (possibly OH or OOH).^[6] Therefore, it seems that the active sites are the adjacent carbon atoms of the pyridinic N species rather than pyridinic N itself. Similar to the case of ORR, an impressive pyridonic N peak is shown in XPS N1s peak after OER operation (Figure S16b), which also implies the active sites are likely involved with the adjacent carbon atoms of the pyridinic N species. Additionally, we do not observe any characteristics of pyridine N-oxide species at ~402 eV in N1s peak of XPS and at ~1265 cm⁻¹ in ATR-IR spectra during the ORR and OER.[36] Thus, we propose that the neighbored carbon atoms are strongly involved for accelerating both ORR and OER processes.

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Figure 5. In situ ATR-IR spectra for monitoring dynamic evolution of the involved intermediate oxygen species, determining the rate-determining steps (RDS) and identifying the active sites on DBAD. (a-c, f) ORR and (d) OER processes. The experiments including Ar-saturated KOH, O₂-saturated KOH and O₂-saturated KOD were carried out at 0.6 V_{RHE}. Here, O₂-*, OOH* and OOD* represent the adsorbed O₂-, HO₂ and DO₂ species, respectively. (e) Isotopic electrochemical studies of representative DBAD+OLC catalyst in 0.1 M KOH and 0.1 M KOD.

Conclusion

In summary, we have illustrated experimental insights into the catalytic mechanisms at a molecular level by aromatic organic molecules with designated N species as models. Pyridinic N

species play a crucial role for the electrochemical ORR over a wide pH range and alkaline OER. It can be concluded that pyridinic N species prone to facilitate the ORR process by a fourelectron-like dominated pathway, and they also improve the catalytic activity rather than carbon corrosion for the OER.

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Furthermore, the location at edge zigzag or armchair position of pyridinic N does not obviously affect the catalytic performance. The structure-function relationship of the active component can be established by delicately controlling their longitudinal extension (π -conjugated structures) and edge configurations. We believe that OOH* (that is, HO₂*) and/or O₂-* species as the key intermediates are involved in both ORR and OER processes, clarified by in situ ATR-IR spectra and isotopic labeling studies. Neighbored carbon atoms of pyridinic N species are likely the active sites clarified by the dynamic evolution in vibration peaks. To the best of our knowledge, our work provides spectral evidences for the first time to observe dynamic evolution of key intermediate products and RDS of metal-free carbon catalysts in the overall oxygen electrocatalysis at a molecular-level.

Acknowledgements

We thank Dr. Huiqing Song for his kind help in MS measurements. We also thank Prof. Robert Schlögl and Prof. Rüdiger-A. Eichel for their kind discussion about our manuscript.

Keywords: metal-free carbon • active site • nitrogen doped • in situ infrared spectroscopy • intermediate products

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RESEARCH ARTICLE

Entry for the Table of Contents



Dynamic evolution of active sites and key oxygen intermediate products during the ORR and OER on N-doped carbon catalysts are monitored experimentally with in situ ATR-IR spectra. With the assistance of isotopic labeling technical, the formation of *OOH species from O_2^{-*} ($O_2^{-*}+H_2O \rightarrow OOH^*+OH^-$) is suggested to be a possible RDS during the ORR process, whereas the generation of O_2 from OOH* species is the most possible RDS during the OER process.