Efficient Electrochemical Hydrogen Peroxide Production from Molecular Oxygen on Nitrogen-Doped Mesoporous Carbon Catalysts

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Supporting Information

ABSTRACT: Electrochemical hydrogen peroxide (H₂O₂) production by two-electron oxygen reduction is a promising alternative process to the established industrial anthraquinone process. Current challenges relate to finding cost-effective electrocatalysts with high electrocatalytic activity, stability, and product selectivity. Here, we explore the electrocatalytic activity and selectivity toward H₂O₂ production of a number of distinct nitrogen-doped mesoporous carbon catalysts and report a previously unachieved H₂O₂ selectivity of ∼95−98% in acidic solution. To explain our observations, we correlate their structural, compositional, and other physicochemical properties with their electrocatalytic performance and uncover a close correlation between the H₂O₂ product yield and the surface area and interfacial zeta potential. Nitrogen doping was found to sharply boost H₂O₂ activity and selectivity. Chronoamperometric H₂O₂ electrolysis confirms the exceptionally high H₂O₂ production rate and large H₂O₂ faradaic selectivity for the optimal nitrogen-doped CMK-3 sample in acidic, neutral, and alkaline solutions. In alkaline solution, the catalytic H₂O₂ yield increases further, where the production rate of the HO₂⁻ anion reaches a value as high as 561.7 mmol g⁻¹h⁻¹ with H₂O₂ faradaic selectivity above 70%. Our work provides a guide for the design, synthesis, and mechanistic investigation of advanced carbon-based electrocatalysts for H₂O₂ production.

KEYWORDS: nitrogen-doped carbon, two-electron oxygen reduction, hydrogen peroxide production, selectivity, electrocatalysis

1. INTRODUCTION

Hydrogen peroxide (H₂O₂) is highly sought worldwide as an important chemical feedstock for industries and environmental treatments, as well as a possible promising energy carrier and oxidant in renewable energy conversion technologies. Currently, the industrial synthesis route to H₂O₂ is based on the anthraquinone process involving the sequential hydrogenation/oxidation of anthraquinone molecules. Despite its state-of-the-art large-scale production, there still exist serious practical sustainability challenges such as industrial waste handling and a lack of energy efficiency as well as the high cost associated with storage and transportation. The other alternative method is the direct catalytic H₂O₂ production from molecular oxygen and hydrogen. However, during this process, the potential explosion hazard from the mixtures of oxygen and hydrogen and the use of platinum-group noble-metal catalysts make the success of this method doubtful. This is why new, facile, efficient, and ecofriendly routes to H₂O₂ production are needed.

The four-electron electrochemical reduction of molecular oxygen (oxygen reduction reaction, ORR), proceeding in acidic environments according to eq 1

$$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O} \quad E^0 = +1.229 \text{ V vs SHE}$$

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has gained tremendous attention due to its key role in various energy conversion/storage systems such as fuel cells and metal–air batteries.10–12 Currently, most research is focused on the development of improved catalysts for the four-electron pathway from oxygen to water in order to maximize the energy conversion efficiency of the devices. However, the energetically undesirable two-electron oxygen reduction pathway (eq 2)

\[
\text{O}_2 + 2\text{H}^+ + 2e^- \rightarrow \text{H}_2\text{O}_2 \quad E^0 = +0.695 \text{ V vs SHE}
\] 

(2)
generates hydrogen peroxide and is an interesting pathway for chemical synthesis purposes. In an aqueous electrolytic device, by combining the anodic half-cell reaction (eq 3)

\[
2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4e^- \quad E^0 = +1.229 \text{ V vs SHE}
\] 

(3)
the overall \( \text{H}_2\text{O}_2 \) electrolysis cell reaction proceeds according to eq 4

\[
\text{O}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{H}_2\text{O}_2 \quad E^0_{\text{cell}} = 0.534 \text{ V}
\] 

(4)
This reaction makes the in situ \( \text{H}_2\text{O}_2 \) production from renewable power sources possible, and the scalability of electrochemical devices enables local, on-demand \( \text{H}_2\text{O}_2 \) production, reducing costs associated with storage and transportation. Besides, if the reaction (eq 2) is performed in a fuel cell, it is possible to recover the energy released accompanied by the production of \( \text{H}_2\text{O}_2 \). Based on the discussions above, electrochemical two-electron oxygen reduction provides a promising method for \( \text{H}_2\text{O}_2 \) production, with its key challenge being the design and synthesis of oxygen electrocatalysts displaying high activity and selectivity.

Recently, oxygen reduction electrocatalysts based on noble metals (e.g., Pt, Pd, and Au) have been explored for \( \text{H}_2\text{O}_2 \) production, with its key challenge being the design and synthesis of oxygen electrocatalysts displaying high activity and selectivity.

Compared to the noble-metal materials reported above, carbon-based materials are more promising alternative electrocatalysts for \( \text{H}_2\text{O}_2 \) production due to their high abundance, low cost, and acceptable stability under mass transport limited operating conditions.13–16 Indeed, Berl et al. first proposed \( \text{H}_2\text{O}_2 \) production from oxygen reduction on a carbon electrode in 1939.22 Since then, various carbon materials such as carbon fibers and graphite have been reported to be active for \( \text{H}_2\text{O}_2 \) production.23,24 In particular, mesoporous carbon offers advantages over other carbon materials thanks to high surface area and favorable mass transport.25 The catalytic activity and selectivity of mesoporous carbon with respect to the oxygen reduction were reported to be further improved upon heteroatom doping.25,26 In particular, nitrogen doping was reported as an effective method for improving the electrochemical performance of carbon materials.27–29 However, prior works of ORR on N-doped carbons focused largely on optimizing the catalyst synthesis, whereas reports dedicated to the systematic exploration of the correlations between \( \text{H}_2\text{O}_2 \) reactivity, selectivity, and surface physicochemical properties have been missing. This report attempts to change that.

Here, we explore the electrocatalytic activity and selectivity toward \( \text{H}_2\text{O}_2 \) production of a number of distinct nitrogen-free and nitrogen-doped mesoporous carbon catalysts and report a previously unachieved \( \text{H}_2\text{O}_2 \) selectivity of \(-95−98\%\) in acidic solution. To explain our observations, we correlate their structural, compositional, and other physicochemical properties with their electrocatalytic performance and uncover a close correlation between the \( \text{H}_2\text{O}_2 \) product yield and the surface area and interfacial zeta potential. Balanced amount of nitrogen doping was found to sharply boost \( \text{H}_2\text{O}_2 \) activity and selectivity. Chronoamperometric \( \text{H}_2\text{O}_2 \) electrolysis confirms the exceptionally high \( \text{H}_2\text{O}_2 \) production rate and large \( \text{H}_2\text{O}_2 \) faradaic selectivity for the optimal nitrogen-doped CMK-3 sample in acidic, neutral, and alkaline solutions. In alkaline solution, the catalytic \( \text{H}_2\text{O}_2 \) yield increases further, where the production rate of the \( \text{HO}_2^- \) anion reaches a value as high as \( \text{561.7 mmol g}_{\text{catalyst}}^{-1} \text{ h}^{-1} \) with \( \text{H}_2\text{O}_2 \) faradaic selectivity above 70%. Our work provides a guide for the design, synthesis, and mechanistic investigation of advanced carbon-based electrocatalysts for \( \text{H}_2\text{O}_2 \) production.

2. EXPERIMENTAL SECTION

2.1. Chemicals. Ketjen black EC 300J and Ketjen black EC 600JD were supplied by AkzoNobel polymer chemistry. Black pearls 2000 and Vulcan XC 72R were obtained from Cabot. Graphene nanoplates (2–10 nm) were purchased from ACS Material. CMK-3 was obtained from East High Tech Limited. 1-Ethyl-3-methylimidazolium dicyanamide (EMIM-dca, a kind of ionic liquid) was purchased from Sigma-Aldrich. Hydrogen peroxide test kits were acquired from Merck. All chemicals were used without further treatment.

2.2. Synthesis of Nitrogen-Doped Mesoporous Carbon. Prior to nitrogen doping, CMK-3 was first pretreated in 2.4 M \( \text{HNO}_3 \) overnight to modify its surface area and the porosity,30 and then dried at 100 °C. In a typical procedure for nitrogen doping, 30 mg acid-treated CMK-3 were dispersed in 5 mL of deionized water by ultrasound for about 15 min, and then mixed with different amount of ionic liquid (IL) (EMIM-dca, 25, 50, 100 µL) overnight under magnetic stirring for homogenization. Subsequently, the resulting mixture was first heated at 180 °C for 2 h and then heated to different annealing temperature (600, 700, 800, and 900 °C) for 4 h at the rate of 5 °C/min in a porcelain boat under a continuous flow of nitrogen gas. To clarify, the resultant N-doped CMK-3 samples were labeled as CMK3IL-X_Y (with X the IL in microliters and Y is annealing temperature in degrees Celsius).

2.3. Characterization. Powder X-ray diffraction (PXRD) patterns were recorded on a Bruker D8 Advance device with Cu Kα radiation (\( \lambda = 1.54056 \text{ Å} \)) in the range of 10–90°. The surface area was determined by nitrogen adsorption measurements (Quantachrome Autosorb-1-C). The morphologies of the catalysts were investigated with a scanning electron microscope (SEM, JEOL 7401F) at an acceleration voltage of 10 kV and a transmission electron microscope (TEM, FEI Tecnai G2 20 S-TWIN) at an accelerating voltage of 200 kV. Cu grids with 300 mesh and a lacey carbon layer were used for preparation. X-ray photoelectron spectroscopy (XPS) measurements were conducted on an ultrahigh vacuum (UHV) system, equipped with a monochromatic Al Kα source (\( h\nu = 1486.5 \text{ eV} \)) operated at 14.5
kV and 300 W, and Phoibos 150 (SPECS GmbH) analyzer. For each sample a survey and high-resolution C 1s, O 1s, and N 1s regions were measured. The C 1s signal of graphitic-like carbon was used for binding energy calibration and assigned to 284.5 eV. The CASA XPS software with pseudo-Voight Gaussian–Lorentzian product functions and Shirley background was used for peak deconvolution. Atomic ratios were calculated from XPS intensities corrected by the corresponding sensitivity factors provided by the manufacturing company (SPECS). Raman spectra were recorded on a Bruker SENTERRA Raman system. Zeta potential was determined by Zetasizer Nano instrument (Malvern, Z). The solutions for zeta potential measurement were prepared by dissolving catalysts into Milli-Q water. Thermo Gravimetric Analysis (TGA) was used to investigate the thermal behavior of CMK3, IL, and NCMK3IL50_800T using a thermal analyzer (PerkinElmer STA 8000). All the samples as well as the empty crucible were measured following the subsequent procedure: with the nitrogen gas flow at 100 mL/min, first hold for 60 min at 30 °C and then heat from 30 to 900 °C at 5 °C/min, and at 900 °C hold for 240 min. Finally, let the sample cool down naturally and then record weight loss.

2.4. Electrochemical Measurement. All electrochemical measurements were conducted in a home-made three-compartment electrochemical glass cell with a Biologic bipotentiostat and a rotator (PINE Instruments model: AFMRSCE, USA). The three electrodes arrangement consisted of a Pt mesh as counter electrode, mercury/mercurous sulfate (AMETEK USA) as reference electrode, and a glassy carbon electrode including rotating disk electrode (RDE, 0.19653 cm²) and rotating ring-disk electrode (RRDE, 0.2475 cm²) measurement with a Pt ring as the working electrode. All potentials are referred to the reversible hydrogen electrode (RHE).

The oxygen reduction activity was investigated by cyclic voltammetry (CV) in O₂-saturated electrolyte at a scan rate of 5 mV s⁻¹. Prior to the measurement, the Pt ring of the RRDE electrode was first electrochemically cleaned using cyclic voltammetry by sweeping the potential between 0.05 and 1.2 V at a scan rate of 20 mV/s in N₂-saturated electrolytes until steady CVs were obtained. Then, the nonfaradic current as the capacitive current could be determined by collecting CV sweeping the potential between 0.05 and 1.1 V at a scan rate of 5 mV/s in N₂-saturated 0.5 M H₂SO₄. After purging with O₂ at least 30 min, the linear sweep voltammetry (LSV) of ORR was collected in O₂-saturated 0.5 M H₂SO₄ at the rotation speed of 1600 rpm. Finally, the faradaic currents were corrected by subtracting the corresponding capacitive current. The ring currents were recorded by fixing the ring potential at 1.2 V in order to detect the H₂O₂ produced on disk electrode. The catalyst ink was prepared through suspending the catalyst in a mixture containing Milli-Q water, isopropanol, and Nafion solution (5 wt %, Sigma-Aldrich). After sonication, the catalyst ink was dropped onto the freshly polished glassy carbon electrode and dried in the oven at 60 °C for 10 min. The collection efficiency (N, 37%) of the RRDE electrode used (Pine AFE6R2GCPT) was determined by using the reversible [Fe(CN)₆]₄⁻/[Fe(CN)₆]₃⁻ system. Selectivity of the catalysts toward H₂O₂ formation was calculated according to the well-known relation (eq 5):

\[ \text{H}_2\text{O}_2 \text{selectivity} (\%) = \frac{200 I_{\text{ring}}}{N I_{\text{disk}} + I_{\text{ring}}} \]  

where \( I_{\text{ring}} \) is the ring current and \( I_{\text{disk}} \) is the disk current. The number of transferred electrons (n) at the disk electrode during oxygen reduction process was calculated as follows (eq 6):

\[ n = \frac{4 I_{\text{disk}}}{I_{\text{disk}} + I_{\text{ring}}} \]  

Bulk H₂O₂ production was carried out in a custom-made two-compartment cell with Nafion 212 membrane as separator. The Nafion membrane was pretreated with 5% (v/v) H₂O₂ for 1 h at 80 °C and 10% (v/v) H₂SO₄ for 1 h at 80 °C. Both the cathode compartment and anode compartment were filled with 145 mL of the same electrolyte including 0.5 M H₂SO₄ (pH = 0.3), 0.1 M K₂SO₄ (pH = 7), and 0.1 M KOH (pH = 13), respectively. The loading amount of catalyst on the working electrode was fixed at 0.05 mg/cm². H₂O₂ production was conducted by chronoamperometry at 0.1, 0.2, and 0.3 V with 85% manual r compensation. To quantify the amount of H₂O₂ produced (yield), samples collected at certain time intervals were analyzed using a commercial hydrogen peroxide test (Merck KGaA, Germany). In detail, 2 mL aliquot of the electrolyte was taken from the cathode compartment of the electrochemical cell. Then commercial peroxide test solutions were added rapidly to the solution above according to the instruction. It should be here noted that, since the pH of the measurement solution for the commercial peroxide test kit must be within the range of 6.6–7.7, the electrolytes from the electrochemical cell need to first be neutralized using 0.1 M Na₃PO₄ for 0.5 M H₂SO₄ or 0.1 M KH₂PO₄ for 0.1 M KOH. After 10 min (reaction time) at room temperature, the resultant mixture solution was filled into a standard 70 μL cuvette for UV–vis absorption spectra measurements. The UV–vis spectra were recorded on an AvaSpec-2048TEC-2 equipped with a deuterium halogen light source (Avantes, Broomfield, USA). During the process, the color of the resultant mixture solution changed from colorless to orange since hydrogen peroxide reduces copper(II) ions to copper(I) ions in the presence of a phenanthroline derivative, which exists in the commercial peroxide test solution. The UV–vis measurements were then performed at 433 nm. The concentration–absorbance curves were calibrated using standard hydrogen peroxide solutions including 0.05, 0.1, 0.3, 0.5, 1, 2, and 2.5 mg/L of hydrogen peroxide. The hydrogen peroxide concentrations were subsequently determined based on the calibration curve. In order to ensure a precise result, the absorbance value should be under 1. If the absorbance value exceeds 1, the solution after neutralization should be further diluted before adding the test kits. The H₂O₂ faradic selectivity was calculated from the H₂O₂ yield against the quantity of charge passed:

\[ \text{H}_2\text{O}_2 \text{ faradic selectivity} (\%) = \frac{2CVF}{Q} \]

where C is the H₂O₂ concentration (mol/L), V is the volume of electrolyte (L), F is the Faraday constant (C/mol), and Q is the amount of charge passed (C).

3. RESULTS AND DISCUSSION

3.1. Structure–Activity Relationship Screening of Suitable Carbon Catalysts. Our study sets out with a broad exploration of a variety of suitable carbon materials for H₂O₂ production, followed by a down selection and a more detailed investigation of structure–composition–activity relationships of the selected materials after heteroatom doping and under varying preparation conditions. The initial set of suitable carbons was
selected as to span a diverse range of crystallinities, surface areas, and structural morphologies.

Our broader screening of six potentially suitable carbon materials involved the correlation of their physicochemical properties and O₂-to-H₂O₂ activity. Properties considered include crystal structure (PXRD), BET surface area, and zeta potential. Figure 1a reports the diffraction patterns (top to bottom) of CMK-3, Black pearls 2000, Vulcan XC 72R, Ketjen black EC 300J, Ketjen black EC 600JD, and graphene nanoplates. As shown, all carbon materials display characteristic peaks of amorphous carbon at 25° and 44°. Raman spectra were also acquired to judge the degree of graphitization, the defect content and disordered structures. As shown in Figure S1a, the Raman data demonstrated that all carbon materials exhibit typical D band (1328 cm⁻¹) and G band (1582 cm⁻¹), where the D band is related to disordered graphitic structures and edge defects, the G band reflects the degree of graphitization. It can be also observed that CMK-3 possesses characteristic features of amorphous carbon with moderate intensity ratio of the D to G band (I_D/I_G). In addition, given that the apparent electrocatalytic performances may sensitively depend on their true surface areas, nitrogen adsorption isotherms were taken to determine BET surface areas (Figure 1b), which varied from 1314.7 m²/g for Black pearls 2000 to 16 m²/g for the graphene nanoplates. Besides, the surface charge of carbon-based catalysts were reported to control their dispersion behavior and stability and therefore play an essential role in the electrocatalytic performance, which is why the zeta potential was considered as a second screening parameter. Generally, large absolute values of the experimental zeta potential suggest that there are large amounts of surface charges, which prevent the aggregation of particles, improving the dispersion stability due to the strong repulsive force. Of particular importance in the present case is the fact that large surface charge may aid in the catalytic oxidation and reduction process of reactant present in the system. As shown in Figure 1c, three carbon materials showed negative zeta potentials from −0.036 to −31.1 mV, whereas the other three exhibited positive zeta potentials from 6.85 to 16.9 mV, indicating different surface charges for different carbon materials.

Finally, we conducted rotating ring disk electrode (RRDE) measurements to examine the electrocatalytic activity of all carbon materials toward oxygen reduction to H₂O₂. Figure 2b represents the linear sweep voltammetry curves during the H₂O₂ generation process. It can be clearly observed that none of the carbon materials reaches a diffusion-limited current plateau highlighting the kinetic hindrance of this surface electrochemical process. Among them, CMK-3 exhibited the highest overall catalytic reactivity for oxygen reduction (disk current density, j_disk up to −1.06 mA/cm²), and the largest HO₂⁻ specific productivity (ring current, j_ring up to 0.07 mA) at 0.1 V (Figure 2a and b). Moreover, CMK-3 displayed the most positive onset potential around 0.44 V. The H₂O₂ selectivity trends and the number of transferred electrons derived from the RRDE voltammograms are displayed in Figure 2c and d. For all carbon materials investigated, both H₂O₂ selectivity trend and the number of transferred electrons depend on the applied potential. Nevertheless, the number of transferred electrons for CMK-3 at 0.1 V is most close to 2, thus indicating that it mainly follows two-electron oxygen reduction pathway.

To get a deeper understanding of the physicochemical properties controlling the catalytic H₂O₂ selectivity, we analyzed the relationship between BET surface area, zeta potential, and H₂O₂ selectivity at 0.1 V in 0.5 M H₂SO₄ (Figure 3). We can clearly observe that relative large BET surface area and the positive zeta potential value are beneficial for H₂O₂ production, like CMK-3, Black pearls 2000, and Ketjen black EC 600JD. These results indicate that BET surface area and zeta potential are important descriptors for determining electrocatalytic selectivity of the catalysts. On one hand, high surface areas reflect a large number of active sites and are thus beneficial for the overall catalytic performances. On the other hand, Terakura’s group reported recently the reaction mechanism for H₂O₂ production on carbon material catalysts (CMCs), where the special hydroxide site is first formed by the hydrogenation of the catalytic site on CMCs, then is abstracted by the approached O₂ molecules to form an OOH⁻ ion, and finally reacts with H⁺ to form a H₂O₂. This mechanism proposed is mainly based on the barriers for the O₂ molecule abstracting H on CMCs being lower than that for O₂ adsorption. Meanwhile, the catalysts with high H₂O₂ selectivity reported in the present work were found to generally possess a positive zeta potential, implying that the
surface of these catalysts is easily protonated and thus may be beneficial for the formation of the special hydrogen site. From this viewpoint, the H$_2$O$_2$ production process over these reported carbon catalysts follows this mechanism, which also explains why the positive value of zeta potential is beneficial for H$_2$O$_2$ production. Based on the above considerations, the reaction step scheme of H$_2$O$_2$ production is displayed in Figure S2. Besides, we also draw the relationship between the $I_D/I_G$ ratio and H$_2$O$_2$ selectivity to uncover the effect of the degree of graphitization and defect sites on H$_2$O$_2$ selectivity (Figure S1b). It can be found that H$_2$O$_2$ selectivity gradually increases as $I_D/I_G$ ratio increases from 0.02 to 1.13, whereas H$_2$O$_2$ selectivity declines slightly by further increasing $I_D/I_G$ to 1.29, indicating that the defect sites are favorable for H$_2$O$_2$ production.

### 3.2. Preparation and Characterization of Nitrogen-Doped Mesoporous Carbons

Based on its excellent faradaic H$_2$O$_2$ selectivity and its balanced BET surface area, CMK-3 was selected as the carbon scaffold to be functionalized with nitrogen atoms using a combination of an acid wash and thermal treatment in the presence of a N-rich ionic liquid (IL) (Figure 4a). In our work, CMK-3 here not only serves as carbon source but also it is used as a template for nitrogen-doped carbon. The PXRD results in Figure S9 shows that the (002) graphite reflections of pristine CMK-3 are downshifted by 4°−6°, evidencing that the interlayer distance of graphite (002) is expanded. Furthermore, SEM and TEM measurements were conducted to investigate the morphological changes upon N-doping. SEM results (Figure 4b, c, e, and f) showed no obvious change in carbon morphology. TEM results (Figure 4d and g) also indicate that ordered structures were maintained after functionalization.

Elemental analysis (Table S1) confirmed that the N-content of the catalyst samples could be tuned by simply changing the mixing ratio of the IL and CMK-3, and annealing temperature. The resulting N-content followed the initial IL amount, whereas the N-content declined with higher annealing temperature. The TGA curves of CMK-3, IL, and NCMK3IL$_{50_800T}$ (Figure S10) suggested the onset of IL decomposition at around 300 °C under a N$_2$ atmosphere with weight losses increasing with temperature, which is consistent with the element analysis.

We hypothesize that the decomposition of the IL at high temperature actually promotes the formation of micro- and mesopores. Our hypothesis is supported by the trends in BET surface areas with IL doping and temperature in Figure 5. There

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**Figure 2.** Linear sweep voltammetry of rotating ring disk electrode (RRDE) with (a) the ring current collected on the Pt ring at a constant potential of 1.2 V$_{RHE}$, (b) the disk geometric current density, (c) H$_2$O$_2$ selectivity, and (d) the number of transferred electrons ($n$) as a function of electrode potential of various carbon materials including CMK-3, Black pearls 2000, Vulcan XC 72R, Ketjen black EC 300J, Ketjen black EC 600JD, and graphene nanoplates. In all cases, measurements were performed in O$_2$-saturated 0.5 M H$_2$SO$_4$ at a scan rate of 5 mV/s with 1600 rpm at room temperature and the catalyst loading amount on the disk electrode was set to 0.05 mg/cm$^2$. The result of three measurements H$_2$O$_2$ % selectivity and the mean number of transferred electrons with error bars for CMK-3 were also shown in Figure 2c and d.

**Figure 3.** Relationship between zeta potential and BET surface area of the structurally different carbon materials: graphene nanoplates, Vulcan XC 72R, Ketjen black EC300J, CMK-3, Black pearls 2000, and Ketjen black EC 600JD. Note: The radii of the circles scale, and the numbers in circles denote the H$_2$O$_2$ selectivity at 0.1 V in 0.5 M H$_2$SO$_4$. 

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exists an optimal level of N doping (Figure 5a and c) and the BET values actually increase with annealing temperature due to formation of micropores (Figure 5b and d). The effect of N doping amount and annealing temperature on the zeta potential is reported in Figure 5e and f. Consistent with our discussion above, acid treatment introduces negative oxygen-containing functional groups,43 which are then offset by increasing amounts of N-doping seen by the zeta potential variation from $-24.4$ to $11.3$ mV. Similarly, heat treatment is detrimental to the negatively charged surface groups,28 which is why the zeta potential essentially increases from $-27$ to $+24.6$ mV with annealing temperature.

To gain qualitative and quantitative information on the chemical nature of the N-functionalities embedded into the CMK-3 carbon matrix, high resolution X-ray photoelectron spectroscopy (XPS) spectra were used to identify and distinguish various N-species by means of their core level energies. Figure 6a displays high-resolution XPS spectra of the N 1s core level region for all N-doped carbon materials. It can be observed from Figure 6b and Figure S11 that the N 1s spectra of all N-doped carbon materials except NCMK3IL50_900T can be fit with four distinct peaks, which are assigned to pyridinic-N (398.8 eV), pyrrolic-N (400.4 eV), quaternary-N (401.2 eV), and graphitic-N (402.5 eV), in increasing binding energy order, respectively.44 The total content of nitrogen doping and the relative amount of different types of N-species are summarized in Table 1. According to Table 1, several features can be observed: (1) the total content of nitrogen increases with increasing IL concentration but decreases with increasing annealing temperature; (2) as the annealing temperature increases, the relative amount of quaternary-N and graphitic-N increases whereas the relative amount of pyridinic-N and pyrrolic-N decreases since the stability of quaternary-N and graphitic-N is superior to that of pyridinic-N and pyrrolic-N at higher annealing temperature.34

3.3. Nonstationary Faradaic H$_2$O$_2$ Selectivity and the Number of Transferred Electrons. The electrocatalytic activities and selectivity of the obtained samples toward ORR were further examined through the RRDE method. We first investigated the effect of different loading amount of catalysts on their electrocatalytic activities and selectivity, and the results are...
shown in Figure S12. It can be seen that as the loading amount decreases, the selectivity of H\textsubscript{2}O\textsubscript{2} production increases, which is accordance with the previously reported literature.\textsuperscript{45} It is demonstrated that a lower catalysts loading results in the sparse distribution of active sites and the smaller probability that H\textsubscript{2}O\textsubscript{2} molecules are further reduced to H\textsubscript{2}O. Thus, the optimal loading amount is fixed as 0.05 mg/cm\textsuperscript{2} thereafter. After the introduction of nitrogen (Figure S13), an increased oxygen reduction current is observed, and the onset potential of oxygen reduction shifts positively from 0.44 to 0.55 V with increasing nitrogen doping. Nevertheless, there is no obvious effect of annealing temperature on the electrocatalytic activity except at 900 °C (Figure 7). The H\textsubscript{2}O\textsubscript{2} selectivity and the number of transferred electrons of the oxygen reduction during electrochemical reaction were also determined from RRDE experiment. As shown in Figure S13, nitrogen doping boosted the selectivity of H\textsubscript{2}O\textsubscript{2} and the number of transferred electrons dropped from 2.5 to 2.1 (Figure S13c, d). Also, the annealing temperature had a strong effect on catalyst selectivity with an optimum at 800 °C (Figure 7c, d). Finally, the effect of different pH environments on the electrocatalytic activity of the most promising NCM3IL50_800T catalyst was also addressed (Figure S14). In alkaline environment, the resultant NCM3IL50_800T exhibited the highest catalytic activity, whereas the highest selectivity can be obtained in acid solution. We ascribe this difference to the reactivity of hydroxyl species which were reported to promote an outer-sphere electron transfer process during ORR in alkaline solution, which predominantly leads only to two-electron peroxide intermediate as the final product.\textsuperscript{46} Meanwhile, peroxide reduction is also reported to be more kinetically favorable in alkaline solution than in acidic solution.\textsuperscript{46} It should be highlighted that the H\textsubscript{2}O\textsubscript{2} selectivity of NCM3IL50_800T prepared at 800 °C reached 95−98% in the potential range from 0.1 to 0.3 V, which exceeds those reported previously under similar conditions including noble-metal alloys,\textsuperscript{1,17} transition-metal-based,\textsuperscript{47} and metal-free catalysts\textsuperscript{21,28,48} (Figure S15 and Table S3).

In order to identify factors controlling the H\textsubscript{2}O\textsubscript{2} selectivity, the relationships of the BET surface area and zeta potential with H\textsubscript{2}O\textsubscript{2} selectivity at 0.1 V in 0.5 M H\textsubscript{2}SO\textsubscript{4} were investigated as a function of the level of N doping and annealing temperature (Figure 8). It can be seen that, after nitrogen doping, the H\textsubscript{2}O\textsubscript{2} selectivity increased with BET surface area increasing up to a value of 1541 m\textsuperscript{2}/g (see catalyst annealed at 800 °C, after which a sharp decline was observed (see catalyst annealed at 900 °C). This may be due to the fact that when the annealing temperature was further increased to 900 °C, the ratio of micropores increased, which is detrimental for H\textsubscript{2}O\textsubscript{2} production.\textsuperscript{28} Interestingly, we also observed that the resultant nitrogen-
doped CMK-3 catalysts such as NCMK3IL50_600T, NCMK3IL50_700T, and NCMK3IL50_800T have very negative zeta potential values; however, they performed much better in terms of selectivity than pristine carbon materials like graphene nanoplates and Vulcan XC 72R. Further, the relationship between the $I_D/I_G$ ratio and $H_2O_2$ selectivity was also investigated to uncover the effect of the degree of graphitization and defect sites on $H_2O_2$ selectivity of the nitrogen-doped CMK-3 catalysts (Figure S16−S17). The analysis revealed that for the nitrogen-doped catalysts, the $H_2O_2$ selectivity generally increased with decreasing ratio of $I_D/I_G$ (see Figure S16 at constant annealing temperature and S17 at constant N-precursor amount) whereas the two samples annealed at 700 and 800 °C are considered virtually identical. These results illustrated that compared to zeta potential and defect effects, the nitrogen doping effect may play a more dominant role for the $H_2O_2$ selectivity of the nitrogen-doped CMK-3 catalysts (Figure S16−S17). The analysis revealed that for the nitrogen-doped catalysts, the $H_2O_2$ selectivity generally increased with decreasing ratio of $I_D/I_G$ (see Figure S16 at constant annealing temperature and S17 at constant N-precursor amount) whereas the two samples annealed at 700 and 800 °C are considered virtually identical. These results illustrated that compared to zeta potential and defect effects, the nitrogen doping effect may play a more dominant role for the $H_2O_2$ selectivity of the nitrogen-doped CMK-3 catalysts during ORR. This is why we went a step further and analyzed the correlation between the total amount of nitrogen and the amount of different types of N-species and $H_2O_2$ selectivity (Figure 9). This analysis revealed that $H_2O_2$ selectivity represents a volcano trend as a function of nitrogen content. The N functionalities do play a beneficial role at low nitrogen content; however, they appear to be detrimental for the $H_2O_2$ selectivity at high nitrogen content. Further, the relationship between $H_2O_2$ selectivity and active surface site density (ASSD) was also plotted (Figure S18). It can be observed that the N-functionalities also play a beneficial role at low active surface site density; however, they appear to be detrimental for the $H_2O_2$ selectivity at high active surface site density. These relations make us believe that the “nitrogen doping” outweighs the other parameters investigated and that a balanced ASSD of about 0.004 mg/m² is optimal for the $H_2O_2$ yield in the present system. As mentioned by Stephens’s group,1 $H_2O_2$ can be electrochemically further reduced into $H_2O$ at those close N functionality. It is thus reasonable that an excess surface density of N-functional sites would facilitate the decomposition of $H_2O_2$, which is detrimental for the free $H_2O_2$ yield. Thus, we propose that in order to maximize $H_2O_2$ producing on nitrogen-doped carbon catalyst, a balanced active surface site density is required. The notion of a balanced active surface site density can be reformulated that the individual N sites should maintain an optimal distance from each other in order to keep the undesired 4-electron pathway to water to a minimum; this reaction/catalyst couple thus exhibits what is known as “site isolation effect”.59−51 From this viewpoint, the low $H_2O_2$ selectivity for NCMK3IL50_700T and NCMK3IL50_600T arises from an insufficient site isolation of neighboring N-sites at high nitrogen doping amounts.

### 3.4. $H_2O_2$ Productivities during Bulk Electrolysis over Extended Test Time.

$H_2O_2$ faradaic selectivity is one of the important parameters for evaluating the performance of catalyst, which requires the real $H_2O_2$ production during the ORR process. The amount of $H_2O_2$ produced in the bulk electrolyte...
can be detected through a photometric method reported in our previous work.\textsuperscript{25,48} Figure 10a shows the accumulated amount of H$_2$O$_2$ normalized by catalyst loading amount over the reaction time for NCMK3IL50\_800T at the different applied potentials from 0.3 to 0.1 V in O$_2$-saturated 0.5 M H$_2$SO$_4$. It can be observed that the H$_2$O$_2$ production rate increases as the potential is shifted negatively in the investigated potential range. Remarkably, the H$_2$O$_2$ production rate of 159.9 mmol g$^{-1}$h$^{-1}$ at 0.1 V (Figure 10a) and H$_2$O$_2$ faradaic selectivity of more than 70% (Figure 10b) can be achieved in the investigated applied potential, which was comparable or even better than that of the reported catalysts such as nitrogen-doped carbon\textsuperscript{25,48} and transition-metal-based catalysts\textsuperscript{47,52} (Figure S19a and Table S4). Besides, the as-prepared NCMK3IL50\_800T also exhibits excellent stability during the successive electrochemical H$_2$O$_2$ production within 6 h in acid solution (Figure S20a). We also measure the corresponding H$_2$O$_2$ faradaic selectivity in neutral (0.1 M K$_2$SO$_4$) and alkaline (0.1 M KOH) solutions. Obviously, the pH has a pronounced influence on the H$_2$O$_2$ production rate (Figure 10a, c, e). It can be seen that H$_2$O$_2$ production rate of 547.07 mmol g$^{-1}$h$^{-1}$ can be achieved in neutral solution, which is obviously higher than that reported in the literature (Figure S19b and Table S5). In alkaline solution, the resultant NCMK3IL50\_800T exhibits the highest H$_2$O$_2$ production rate at 0.1 V and can achieve the H$_2$O$_2$ production rate of 561.7 mmol g$^{-1}$h$^{-1}$ (Figure 10e), which is 1.17 and 3.51 times higher than that in 0.1 M K$_2$SO$_4$ and 0.5 M H$_2$SO$_4$, respectively. Generally, concentrated basic solution containing H$_2$O$_2$ are widely used in the pulp and paper industry.\textsuperscript{47} Thus, an on-site high H$_2$O$_2$ production rate in alkaline solution is very attractive.

Figure 7. Linear sweep voltammetry of RRDE with (a) the ring current, (b) the disk geometric current density, (c) H$_2$O$_2$ selectivity, and (d) the number of transferred electrons ($n$) as a function of electrode potential of NCMK3IL50\_YT (Y = 600, 700, 800, 900 °C). Conditions: the catalyst loading amount on the disk electrode was set to 0.05 mg/cm$^2$, and measurements were performed in O$_2$-saturated 0.5 M H$_2$SO$_4$ and a scan rate of 5 mV/s with 1600 rpm at room temperature. H$_2$O$_2$ % selectivity and number of electrons were based on three independent repeated measurements.

Figure 8. Relationship between zeta potential and BET surface area of (a) the resultant CMK-3, CMK-3 after acid treatment, and different IL doping amounts (NCMK3IL25\_800T, NCMK3IL50\_800T, and NCMK3IL100\_800T) and (b) different annealing temperatures (NCMK3IL50\_600T, NCMK3IL50\_700T, NCMK3IL50\_800T, and NCMK3IL50\_900T). Note: The radii of the circles scale, and the numbers in circles denote the H$_2$O$_2$ selectivity at 0.1 V in 0.5 M H$_2$SO$_4$.\textsuperscript{48}
for this application. However, the H$_2$O$_2$ faradaic selectivity of the resultant NCMK3IL50_800T in neutral and alkaline solutions are both lower than that in acid solution (Figure 10b, d, f), which may be attributed to the different production/decomposition mechanism of peroxide over the catalysts in different electrolytes with different pH value. Despite this, the resultant NCMK3IL50_800T also exhibits good stability in both neutral and alkaline solutions (Figure S20b, c). These results indicate that the as-prepared NCMK3IL50_800T is a promising electrocatalyst for H$_2$O$_2$ production.

4. CONCLUSION

We have screened different chemically distinct carbon and N-doped carbon catalyst materials for electrochemical H$_2$O$_2$ production by means of measuring their BET surface areas, zeta potentials, Raman, and XPS spectra. For pristine carbon materials, BET surface areas, zeta potentials, and defect sites were found to play a key role in determining the catalytic activity and selectivity. In fact, large BET surface area and positive zeta potential, and high defect sites were beneficial for H$_2$O$_2$ production. Moreover, nitrogen doping further improved the H$_2$O$_2$ selectivity. Different from pristine carbon materials, the H$_2$O$_2$ selectivity of N-doped carbon catalyst materials is more dominated by nitrogen doping effect, not zeta potentials and defect sites. Besides, the effect of electrolyte’s pH on the selectivity toward H$_2$O$_2$ and H$_2$O$_2$ production rates was also observed. It should be noted that for CMK-3 with the optimal nitrogen-doping, high selectivity, H$_2$O$_2$ production rate, and large H$_2$O$_2$ faradaic selectivity in acidic, neutral, and alkaline solution can be achieved. Our work not only describes a facile and low-cost synthetic method for H$_2$O$_2$ production, but also provides new insights for the design and mechanistic investigation of metal-free heteroatom-doped carbon materials.
Figure 10. (a, c, e) $\text{H}_2\text{O}_2$ production amount normalized by catalyst loading amount over the reaction time and (b, d, f) $\text{H}_2\text{O}_2$ faradaic selectivity of NCMK3IL50_800T catalysts in O2-saturated 0.5 M $\text{H}_2\text{SO}_4$ (a, b), 0.1 M $\text{K}_2\text{SO}_4$ (c, d), and 0.1 M KOH (e, f).

■ ASSOCIATED CONTENT

Supporting Information
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Additional structural characterization and supporting electrochemical characterization (PDF)

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Notes
The authors declare no competing financial interest.

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■ REFERENCES


