Highly Efficient Electrochemical Synthesis of Hydrogen Peroxide (H₂O₂) Enabled by Amino Acid Glycine-Derived Metal-Free Nitrogen-Doped Ordered Mesoporous Carbon

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ABSTRACT: Electrocatalytic partial oxygen reduction has been considered a more sustainable approach to the synthesis of hydrogen peroxide (H₂O₂), as compared with current industrial anthraquinone processes. One key research need is to explore low-cost active electrocatalysts. Here, we report a facile, solvent-free method to synthesize a metal-free nitrogen-doped ordered mesoporous carbon (N-OMC) by in situ transforming of glycine (carbon and nitrogen precursors) in the mesoporous SiO₂ template (KIT-6) followed by subsequent thermal treatment at different temperatures. Among all samples, the catalyst treated at 800 °C (N-OMC-800), the nitrogen-rich carbon, exhibits outstanding structural properties and porosity, showing the dominant formation of pyrrolic-N and graphitic-N. With combined improved structural properties with the optimal ratio of N-pyrrolic/N-graphitic, P/G carbon provided an outstanding electrocatalytic activity, promoting H₂O₂ with high selectivity and production rate in alkaline mediums. The N-OMC-800 can achieve a faradaic efficiency (FE) of ∼100% to H₂O₂ at (0.6 VRHE to 0.4 VRHE) in a H-cell containing 0.1 M KOH. Furthermore, its bulk H₂O₂ electrosynthesis in our self-designed flow cell confirmed its practical capability by showing a remarkable H₂O₂ production rate of 9.43 mol gcat⁻¹ h⁻¹ at 0.35 VRHE and maintaining nearly 100% FE at the cathode potential of 0.6 VRHE for 12 h without any degradation.

KEYWORDS: hydrogen peroxide synthesis, two-electron oxygen reduction, mesoporous carbon catalyst, nitrogen-doped carbon, electrocatalysis, electrochemical flow cell

INTRODUCTION

Hydrogen peroxide (H₂O₂) is a valuable, versatile chemical, also regarded as a potential oxidant for sustainable and green chemistry. In industry, H₂O₂ is primarily produced by a multistep anthraquinone oxidation process (AO). Despite its massive and high-purity generation, the method still faces significant sustainability and safety challenges concerning energy consumption, industrial waste handling, and transportation and storage costs. Another technique that has been explored is the direct synthesis of H₂O₂ from H₂ and O₂ using noble-metal catalysts. Operating a potentially explosive H₂/O₂ mixture, however, may cause serious safety concerns. Hence, novel on-site routes to H₂O₂ production that are safe and sustainable are highly required.

The use of electrochemical technologies to on-site synthesis of H₂O₂ is efficient and sustainable since it reduces energy consumption by utilizing renewable energy sources. Electrochemically, H₂O₂ can be generated by the oxygen reduction reaction (ORR). At cathodes, electrochemical ORR can proceed through the four- (eq S1) or two- (eq S2) electron pathway. For the electrochemical H₂O₂ production through the two-electron ORR, it is critical to design low-cost, highly active, and selective electrocatalysts. Noble metals and metal-free carbon-based compounds have been found as potential 2e⁻ ORR electrocatalysts in recent years. A few noble metal alloys such as Pt–Hg, Pd–Hg, and Ag–Hg promote the two-electron pathway with low overpotential and high H₂O₂ selectivity attributed to the formation of highly active single-atomic sites. However, the need of expensive noble metal resources limits their large-scale use. Carbon materials, on the other hand, are considered feasible 2e⁻ ORR catalysts due to their abundance, good selectivity, stability, and simple preparation. More importantly, the surface and morphology of the carbon may be tuned to modify the electrochemical

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properties and thereby the ORR selectivity.\textsuperscript{9–11} Nitrogen doping is an interesting surface modification approach that provides highly efficient active sites with desirable electrochemical properties.\textsuperscript{7,12}

Nitrogen atoms are frequently found in the form of pyridinic-N, pyrrolic-N, graphitic-N, amino-N, and nitrogen oxide. Among these, pyridinic-N, pyrrolic-N, and graphitic-N have been proposed as ORR active sites.\textsuperscript{13} Studies have shown that high ORR activity in an alkaline medium can be achieved with rich graphitic-N as this specific form of N species can enhance conductivity and electron transport.\textsuperscript{14} On the other hand, pyridinic-N species have a tendency to promote the two-electron ORR process in an alkaline medium.\textsuperscript{15} It was discovered that the highly selective two-electron ORR was correlated to the pyrrolic-N content. This is because pyrrolic-N can accelerate the adsorption of the *OOH intermediate, which is later dissociated to H₂O₂.\textsuperscript{15}

Catalyst structure plays an important role in improving catalytic activity; hence, it must be considered for the development of better H₂O₂ synthesis catalysts.\textsuperscript{6} A disordered porous structure with narrow pores or micropores may cause significant mass transfer resistance.\textsuperscript{16} The ordered mesoporous carbons (OMC) have gained interest as a promising electrode material.\textsuperscript{17} Due to its high specific surface area, large pore volume, tunable pore sizes, and various pore geometries, the OMC is an attractive candidate as a 2e⁻ ORR electrocatalyst.\textsuperscript{18} The increased number of active sites and improved mass transport in OMC can greatly boost H₂O₂ production.\textsuperscript{19}

Nitrogen doped OMCs are often developed by in situ N doping, which incorporates N species into the hard template.\textsuperscript{19} Synthesizing N-OMC can be complicated and require expensive N-containing or toxic precursors.\textsuperscript{11,20} A nontoxic, low-cost, N-rich precursor is needed to create novel sustainable N-OMCs and, thus, remains an interesting area to explore. With simple synthesis using eco-friendly materials, we aim to prepare N-OMC with improved structural properties decorated with pyridinic-N and graphitic-N species to simultaneously boost 2e⁻ ORR selectivity and activity in alkaline media.

Herein, we reported a facile solvent-free method to synthesize N-rich nitrogen-doped ordered mesoporous carbon (N-OMC) with the optimal N-pyrrolic/N-graphitic ratio (P/G). The effect of annealing temperature on tuning the active N-species and catalyst morphology was investigated. The electrocatalytic activity of 2e⁻ ORR in an alkaline medium over N-OMC with different annealing temperatures was measured. Also, the N-OMC electrocatalytic performance was compared with nitrogen-free ordered mesoporous carbon (OMC) and nitrogen-doped nonmesoporous carbon (N-no/OMC) in order to individually examine the role of the mesoporous structure and N dopants on the catalytic behavior.

On-site H₂O₂ practical generation and the catalyst’s long-term stability were tested in a three-electrode flow cell over the optimal N-OMC catalyst (thermally annealed at 800 °C). The relationship between the possible N active sites and catalytic activity was examined, and the impact of morphology for further enhancement was also discussed.

### EXPERIMENTAL SECTION

**Material Preparation. Mesoporous Silica (KIT-6) Synthesis.** In a typical procedure, 0.5 g of KIT-6 was first thoroughly ground with (0.638 g) glycine (Sigma-Aldrich) in an agate mortar. The mixture was then transferred to a tube furnace. The mixed powders were first heated to 500 °C at a ramp rate of 3 °C min⁻¹ in Ar gas for 2 h. After that, the temperature was raised to 700, 800, or 900 °C at a ramp rate of 3 °C min⁻¹ for another 2 h. Next, the hard silica template, KIT-6, was removed via a two step treatment. First, 10 mL of 2 M NaOH solution was added to the product before being transferred to the oven for the heat treatment at 70 °C overnight. Next, the solution was replaced with a fresh 2 M NaOH solution and then placed in the oven at 90 °C overnight. Finally, the product was washed several times with DI water and ethanol mixture, filtered, and dried in the oven at 50 °C.

The nitrogen-doped nonmesoporous carbon (N-no/OMC-800) was synthesized using the same procedure as previously described, but without incorporating KIT-6 (hard template), and no further post-treatment was needed.

**Mesoporous Carbon (OMC) Synthesis.** Briefly, a 0.5 g of KIT-6 was added to a solution prepared by dissolving 0.625 g of sucrose (Fisher Scientific) and 0.07 g of H₂SO₄ in 2.5 g of DI water. The mixture was transferred to the oven and treated first at 100 °C for 6 h, followed by another 6 h at 160 °C. In the following step, deionized 2.5 g of water, 0.4 g of sucrose, and 0.045 g of sulfuric acid were added to the mixture, stirred, and treated under the same conditions as explained previously. After that, the mixture was transferred and thermally annealed at 800 °C in Ar gas for 2 h. Lastly, the silica was removed using the previously described method.

**Material Characterization.** Materials morphologies were determined by a FEI Quanta 250 field-emission scanning electron microscope (SEM) with resolution of 1.0 nm. Scanning transmission electron microscope (TEM) using a JEOL 2100 200 kV scanning transmission electron microscope (STEM) was added to a solution prepared by dissolving 0.625 g of sucrose (Fisher Scientific) and 0.07 g of H₂SO₄ in 2.5 g of DI water. The mixture was transferred to the oven and treated first at 100 °C for 6 h, followed by another 6 h at 160 °C. In the following step, deionized 2.5 g of water, 0.4 g of sucrose, and 0.045 g of sulfuric acid were added to the mixture, stirred, and treated under the same conditions as explained previously. After that, the mixture was transferred and thermally annealed at 800 °C in Ar gas for 2 h. Lastly, the silica was removed using the previously described method.

**Electrocatalytic Characterization.** The electrochemical measurements were carried out in a custom H-shape cell (H-cell) connected to a multichannel potentiostat (Biologic). The H-cell was composed of two compartments separated by an ion-exchange membrane (Nafion 212). One compartment had a working electrode and a silver/silver chloride (Ag/AgCl) reference electrode, while the other contained platinum foil (counter electrode). Both compartments were filled with 0.1 M KOH solutions. The membrane was sequentially pretreated with 1 M H₂O₂ and 1 M KOH at a temperature of 80 °C for 1 h. The catalyst ink used in the working electrode fabrication was a mixture of dispersed catalyst powder,
isopropanol, and a 5 wt % Nafton (Sigma-Aldrich) solution. A catalyst loading of approximately 0.05 mg cm$^{-2}$ was sprayed onto both sides of carbon paper, Toray Paper 060 (Fuel Cell Store), with an area of 1 x 1 cm$^2$. In this study, all electrode potentials were converted to RHE. Prior to the electrochemical measurements, the manual IR (MIR) compensation method was employed to correct the electrolyte resistance. Then, the ORR activity of the catalyst was examined via linear sweep voltammetry (LSV), which was performed at a 5 mV s$^{-1}$ scan rate in O$_2$ saturated electrolyte stirred at 250 rpm. To study the bulk H$_2$O$_2$ electrolysis, a chronoamperometry (CA) technique was conducted across a potential range (0.6 to 0.3 V$_{RHE}$) in an O$_2$ saturated solution stirred at 250 rpm for 1 h. The H-cell catalyst

Figure 1. (a) SEM image, (b) TEM image, (c) nitrogen adsorption–desorption isotherms, and (d) pore size distribution of N-OMC-800. (e) High-resolution N 1s XPS spectra and (f) atomic N content and N/C ratio of all N-OMCs.
durability was examined under the same conditions by running six separate 1 h tests at 0.6 V_RHE using the same catalyst. The hydrogen peroxide reduction reaction (H₂O₂RR) was examined via LSV at a scan rate of 1 mV s⁻¹ in N₂-saturated electrolyte stirred at 250 rpm before and after the addition of 30 PPM of standard H₂O₂ solution.

The practical continuous generation of H₂O₂ was examined in our self-designed three electrodes flow cell with a spacer and anode chamber, which was separated from the cathode by a Nafion 212 membrane, was pumped with 0.1 M KOH at a flow rate of 75 mL min⁻¹. Platinitized titanium fiber felt catalyst (Fuel Cell Store) of (2 × 2 cm²) was used at the anode side. For the cathode chamber, 0.1 M KOH was circulated at a flow rate of 75 mL min⁻¹ through a custom-made PTFE spacer facing the catalyst and containing an opening for the reference electrode. The oxygen gas was continuously purged at 30 mL min⁻¹ through the back of the catalyst substrate. The N-OMC-800 catalyst ink was sprayed on a carbon paper, Sigracet 22 BB (Fuel Cell Store), with an area of (2 × 2 cm²) using a spray gun, resulting in a loading mass of 0.2 mg cm⁻². The electrolysis was then carried out at various potentials to evaluate the production rate of H₂O₂ of a 3 h test. The flow cell catalyst stability was examined at 0.6 V_RHE for 12 h under the same conditions. IR compensation was used in all flow cell measurements. To quantify the generated H₂O₂ in each test, samples were first collected at specific time intervals and then analyzed by the iodide/UV–vis spectroscopy method. The iodometric spectrophotometry was described in detail elsewhere. Briefly, the collected H₂O₂ sample was added to equal parts of solutions A and B and allowed to mix for 5 min. Next, the UV–vis measurements were taken at 351 nm, and the hydrogen peroxide concentrations were estimated using a calibration curve constructed via standard H₂O₂ solution. The Faradaic efficiency of H₂O₂ was calculated using the following equation:

\[ \text{H}_2\text{O}_2 \text{ Faradaic efficiency, } \% = \frac{2VCF}{Q} \]

where \( V \) is the electrolyte volume (L), \( C \) is the H₂O₂ produced concentration (mol L⁻¹), \( F \) is the faraday constant (C mol⁻¹), and \( Q \) is the total charge passed (C).

**RESULTS AND DISCUSSION**

**Catalyst Synthesis and Characterization.** The synthesis procedure of the well-ordered mesoporous carbon, N-OMC-800 catalyst, is illustrated in Scheme 1. Briefly, the N-OMC-800 was synthesized by grinding glycine, which served as the carbon and nitrogen sources, with the mesoporous KIT-6 silica template, followed by polymerization and carbonization steps in the Ar atmosphere. The KIT-6 template was then etched away using 2 M NaOH to prepare template-free nitrogen-doped mesoporous carbon. Detailed synthesis is provided in the Experimental Section.

KIT-6 is a mesoporous silica material characterized by a three-dimensional (3D) porous network structure composed of highly interconnected bicontinuous systems. KIT-6 is an intriguing material due to its easily accessible structure and wide pore diameter (3–15 nm), which likely increase mass transfer and reactant adsorption. Glycine is an attractive precursor for upscaling mesoporous carbon synthesis due to its nontoxicity and widespread availability in large quantities at a reasonable price. Glycine was chosen for this work because it may act as a dual precursor for carbon and nitrogen with a high nitrogen/carbon ratio. Hence, it significantly increases the dopant concentration and also reduces the synthesis procedure by bypassing the need for postnitrogen doping. A further advantage of this compound is that it has a simple molecular structure with a low molecular weight which can inhibit the clogging of pores by C–N species while also assisting the formation of a stable and highly ordered mesoporous structure with a large surface area and a narrow pore size distribution.

During the initial grinding, glycine molecules fill the template’s interconnecting channels. When the carbon-template composite is heated (dehydrated), polymerization occurs. The formed carbon chains in the template structure contain a high concentration of N–H bonds, which is believed to be crucial for the formation of pyrrolic-N in the carbon framework.

In order to study the N-OMC-800 structure, scanning electron microscopy (SEM) was performed to evaluate the change in the catalyst structure created by introducing KIT-6. When glycine was heated without the KIT-6 catalyst, it tended to aggregate into glassy-like large lumps with a poor specific area, as seen in Figure S1a. On the other hand, as glycine was incorporated into the KIT-6 template, dense agglomerate with porous microstructure was obtained, demonstrating a structural similarity between N-OMC-800 (Figure 1a) and KIT-6 (Figure S1b). Furthermore, transmission electron microscopy (TEM), as illustrated in Figure 1b, was used to gain insights into the catalyst mesoporous structure. The TEM image revealed that the structure of the N-OMC-800 was an exact inverse replica of KIT-6 (shown in Figure S1c), with an ordered mesoporous arrangement being introduced into the resulting carbons, indicating successful carbonization of glycine within the silica template. To further analyze the N-OMC-800, energy-dispersive X-ray spectroscopy (EDS) was used to estimate element concentrations. The EDS spectra (in Figure S2 and inset table) revealed that the catalyst framework was mostly composed of C, N, and O atoms, with only trace amounts of Si (0.08 at%) and Na residue, suggesting that the Si template was thoroughly washed away during the washing process.

It is worth noting that varying the carbonization temperature from 700 to 900 °C affected the catalyst structure. By heating the catalyst at 700 °C, the catalyst structure appeared dense, with some of clogged mesoporous arrangements (Figure S3a). This apparent clogging could originate from the glycine-derived CN species that were not completely decomposed during the carbonization process.

On the other hand, a poor outcome was found for the 900 °C treatment (Figure S3b), in which some of the ordered mesoporous structure was deformed and resulted in random pore configuration rather than a more organized porous structure. Consequently, the randomly generated carbon layers (at 700 °C) or a deformed porous structure (at 900 °C) may reduce the surface area and pore volume of carbon catalysts, thereby reducing the 2e⁻ ORR to H₂O₂ activity.

The pyrolysis temperature, therefore, influenced tuning the catalyst morphology. The carbonization at 800 °C favored the formation of a uniform ordered mesoporous structure by diminishing the CN species clogging effect and preventing structural deformation.

To further examine the impact of temperature on the structure of the N-OMC catalysts, the BET surface areas (shown in Table S1) were determined to be 844 m² g⁻¹ (N-OMC-700), 864 m² g⁻¹ (N-OMC-800), and 850 m² g⁻¹ (N-OMC-900). Despite the fact that N-OMC-800 showed a slight increase in the surface area, varying the pyrolysis temperature did not provide a significant difference among these samples. However, the surface texture and porosity of catalysts altered as the temperature changed. Figures 1c, S4a, and S4b show N₂ adsorption–desorption isotherms of all N-OMC catalysts. 
Each of these catalysts exhibited type IV features, including a hysteresis loop, indicating the presence of mesoporous nature in the structure of the N-OMC catalysts. However, because their porous structure was subjected to varied temperatures, the size and volume of the pores changed as well. Table S1 summarizes the structural and textural properties of all samples. The pore volumes of the N-OMC-700 and N-OMC-900 were 0.88 cm$^3$/g and 0.96 cm$^3$/g, respectively, whereas the N-OMC-800 had the largest pore volume of 1.08 cm$^3$/g. Furthermore, the average pore sizes of N-OMC-700 and N-OMC-900 were 4.2 and 3.9 nm, respectively, whereas the N-OMC-800 had the largest average pore size of 5.1 nm.

Figure 2. (a) FE and H$_2$O$_2$ concentration of various carbon based catalysts at 0.6 V$_{\text{RHE}}$. (b) Linear sweep voltammetry (LSV), (c) H$_2$O$_2$ FE, and (d) H$_2$O$_2$ concentration of all N-OMCs. (e) H-cell durability test (Trail 1 vs Trail 6) of N-OMC-800 catalyst at 0.6 V$_{\text{RHE}}$. (f) H$_2$O$_2$RR performance of N-OMC-800 in N$_2$-saturated electrolyte containing 30 ppm. (g) Correlation between P/G ratio and 2e$^-$ ORR performance of all N-OMCs at 0.4 V$_{\text{RHE}}$. All the above experiments performed in 0.1 M KOH for 1 h.
and N-OMC-900, as determined by the Barrett–Joyer–Halenda (BJH) model (shown in Figure S4c,d), were 4.28 and 4.38 nm, respectively, and the difference is considerable when compared to N-OMC-800, which had a pore size of 5.12 nm. The N-OMC-800 showed the largest pore diameter and demonstrated the development of larger mesoporous pores, with sizes ranging from 9 to 14 nm, in Figure 1d.

According to the findings, the N-OMC-800 demonstrated the ideal temperature for achieving superior structural properties by maintaining a well-ordered mesoporous structure with large pores and broad size distribution, which can enhance the partial oxygen redox reaction to H₂O₂.

The surface chemical characteristics of the N-OMCs samples were then studied in detail via X-ray photoelectron spectroscopy (XPS). Figure S5 shows a wide scan XPS survey spectrum with a series of peaks corresponding to C 1s (285.5 eV), N 1s (398.5 eV), and O 1s (532.3 eV). XPS also estimated C, N, and O compositions of all samples, as shown in Table S2. As it can be seen, the element compositions varied in response to temperature changes. For instance, increasing the temperature to 900 °C resulted in a significant drop in the quantity of nitrogen in the catalyst. As a result, carbon becomes the most dominant element, with some oxygen species remaining on the structure’s frame. These observations are similar to those of some previous publications.

The narrow scan N 1s spectrum of all N-OMCs shown in Figure 1e evidenced the formation of pyrrolic-N (398.98 eV), as well graphitic-N (400.48 eV), pyridinic-N (397.42 eV), and oxidized-N (402.08 eV). The peak model used in this analysis was adapted from a prior study that explored it in detail. The atomic percentages of N species in N-OMC catalysts are shown in Figure 1f and Table S3. It is obvious that the pyrrolic-N formation favored low-temperature pyrolysis (below that contribute to the selective generation of H₂O₂ at high concentrations in an alkaline medium. Furthermore, as nitrogen was introduced to an OMC structure as for N-OMC-800, remarkably, its catalytic activity was further improved with FE of 100% and H₂O₂ production of 352 mmol g cat⁻¹. More specifically, the N-dopant species, rich pyrrolic-N, and graphitic-N contents perhaps influenced the further enhancement. It was reported that pyrrolic-N was able to improve the adsorption rate of *OOH intermediate (before being dissociated to H₂O₂) as well as inhibit the *OOH to further dissociated into *O and *OH intermediates (favoring H₂O formation). Graphitic-N, on the other hand, could improve conductivity and increase the transport of electrons, which in turn improves the overall reactivity of ORR (such as increasing the current density), resulting in a higher H₂O₂ generation rate.

The last carbon material (nitrogen-doped nonmesoporous carbon, N-no/OMC-800) was studied to evaluate the role of N-dopant alone. Despite the fact that the N configuration of N-no/OMC-800 was not optimal as more graphitic-N (the nonselective N species) formed on its structure (Table S3), it showed slightly improved efficiency over the baseline of almost 85%, indicating N-dopants (regardless of which species is most prevalent) can likely promote H₂O₂ selectivity. However, because it was synthesized in the absence of the KIT-6 template, its surface area and porosity (not shown) were significantly reduced, resulting in an H₂O₂ yield of just 35 mmol g cat⁻¹.

The results suggested that significant enhancement in H₂O₂ performance can be obtained if the catalyst morphology and N-dopant species were optimized as for N-OMC-800. Overall, the dual effect of modified morphology and N-rich dopant makes the N-OMC-800 catalyst outperform the other carbon-based catalysts in the H₂O₂ selectivity and generation rate in an alkaline medium.

Electrocatalytic Analysis. The ORR performance was studied in an H-type electrolysis cell containing an alkaline electrolyte. The N-OMC-800 catalytic activity was compared to various carbon-based catalysts, including the reference material (Ketjenblack EC-600JD), with the goal of understanding the impact of mesoporous structure and N-dopant on H₂O₂ generation performance in alkaline mediums. Figure 2a illustrates the H₂O₂ concentration and the H₂O₂ FE of several carbon-based catalysts at applied potentials of 0.6 V_RHE in O₂ saturated 0.1 M KOH for 1 h tests. The nondoped mesoporous carbon (OMC-800) was synthesized to evaluate the role of morphological modification in enhancing catalytic activity. Unlike the commercial carbon black, EC-600JD, which generated ~125 mmol g cat⁻¹ with FE of less than 82%, OMC-800 demonstrated improved performance with 258 mmol g cat⁻¹ and FE close to 92%, indicating that the ordered mesoporous structure may facilitate mass transfer and active sites accessibility, resulting in improved performance.

Furthermore, as nitrogen was introduced to an OMC structure as for N-OMC-800, remarkably, its catalytic activity was further improved with FE of 100% and H₂O₂ production of 352 mmol g cat⁻¹. More specifically, the N-dopant species, rich pyrrolic-N, and graphitic-N contents perhaps influenced the further enhancement. It was reported that pyrrolic-N was able to improve the adsorption rate of *OOH intermediate (before being dissociated to H₂O₂) as well as inhibit the *OOH to further dissociated into *O and *OH intermediates (favoring H₂O formation). Graphitic-N, on the other hand, could improve conductivity and increase the transport of electrons, which in turn improves the overall reactivity of ORR (such as increasing the current density), resulting in a higher H₂O₂ generation rate.
production of all N-OMCs were measured over various potentials, as shown in Figure 2c,d.

The N-OMC-700 showed H₂O₂ FE of above 90%, in a wide potential window. However, its production rate was the lowest, which was in line with the current density observed from LSV analysis, indicating some mass transfer issues. The observed clogging of C–N species occurred in the 700 °C doping process, which could undesirably decrease the catalyst pore volume (shown in Table S1). The reduced catalyst pore volume may hinder oxygen diffusion, thereby lowering ORR activity.

By contrast, the N-OMC-900 catalyst experienced a different activity. Despite the fact that it showed a great H₂O₂ generation over a broad potential window with a maximum H₂O₂ generation of ~1000 mmol g⁻¹ at 0.3 V_RHE, the FE was the lowest 90% at 0.6 V_RHE and it dropped dramatically to 70% as the potential was shifted negatively to 0.3 V_RHE. The loss in ORR activity was further confirmed when its partial ORR current density (J_HO2) shown in Figure S6b was estimated. The partial current density (J_HO2) of the N-OMC-900 catalyst decreased significantly as the potential increased, indicating that it became less selective and did not promote H₂O₂ generation at more negative potentials.

The significant drop in H₂O₂ selectivity or FE could be attributed to a decrease in nitrogen content (7.51 at. %), which perhaps decreased the density of the active site needed for promoting H₂O₂ generation. Nitrogen functional groups could influence the decrease in FE, as graphitic-N is the most abundant species in the N-OMC-900 sample. Although graphitic-N facilitates electrical conductivity, leading to increased catalytic activity, a graphitic-N-rich catalyst has been reported to promote 4e⁻ ORR in an alkaline medium.²⁶,²⁷ Finally, alterations in the catalyst’s texture and porosity, such as the loss of some ordered porous structures (Figure S3b), could disturb intermediates’ adsorption and desorption mechanisms. The generated H₂O₂ could not be released quickly enough and could instead be reduced further to water.

Among the three catalysts annealed at different temperatures, N-OMC-800 exhibited the best 2e⁻ ORR performance in alkaline medium, reaching 100% FE at (0.6 V_RHE) to 0.4 V_RHE and generating a maximum of 980 mmol g⁻¹ at 0.3 V_RHE. This outstanding selectivity and activity toward electrochemical H₂O₂ production are superior to most previously reported results (Table S4). This remarkable performance likely can be attributed to the development of catalytically active N-species (pyrrolic-N and graphitic-N) and the formation of an ordered mesoporous structure, both of which can only be achieved at 800 °C. While the N-species could tune the catalyst’s electronic structure, creating more active sites to promote H₂O₂ generation and improve its conductivity and electron transfer, ordered mesoporous structure with extra-large pores sizes could provide a large surface area and accessible active sites. These improved structural properties may facilitate the mass transfer, allowing the rapid release of H₂O₂, therefore, H₂O₂ can be produced with extremely high selectivity, outperforming the other N-OMC catalysts.

**Catalyst Durability and Hydrogen Peroxide Reduction Reaction H₂O₂RR.** The catalyst durability was examined in the H-cell in an alkaline environment by running six separate 1 h tests at 0.6 V_RHE using the same catalyst. As shown in Figure 2c, the H₂O₂ FE could be maintained as high as 99.8% after the sixth trial with only a 0.2% drop from the first test (100%). The accumulated H₂O₂ was close to 325 mmol g⁻¹ cat, which is approximately 42 mmol g⁻¹ cat less than the amount collected in the first trial. Moreover, N-OMC-800 catalytic activity toward the electrochemical H₂O₂ reduction reaction (H₂O₂RR) was investigated to examine whether the catalyst would react with the generated H₂O₂, which is an undesired reaction for practical operations. A control experiment in a H-cell with N-saturated 0.1 M KOH electrolyte containing 30 ppm of H₂O₂ (equivalent to the actual generated amount per hour) was conducted, and LSVs were obtained pre- and postaddition of H₂O₂ content (Figure 2f). The LSV curves collected before and after the control experiment were nearly identical, suggesting that N-OMC-800 does not promote H₂O₂RR. The findings imply that N-OMC-800 is a suitable candidate for H₂O₂ generation in practical continuous operations like a flow cell configuration since it can maintain superior 2e⁻ ORR performance with high selectivity and yield for an extended period.

**Insights into the Role of N Species and the Morphological Structure on 2e⁻ ORR Performance.** The synthesized N-OMC-800 exhibited the optimal performance that could be ascribed to the dual effect of the tuned nitrogen concentrations and the catalyst morphology. Despite the fact that oxygen dopants have also been claimed to promote the 2e⁻ ORR process,²⁸ our results show that nitrogen doping, not oxygen doping, is more crucial in the 2e⁻ ORR process as there was no correlation between oxygen concentration and 2e⁻ ORR activity. For instance, the N-OMC-800 catalyst with the highest oxygen content showed the lowest H₂O₂ selectivity among the other tested N-OMCs. In order to gain deeper insights into the role of N species in ORR activity, XPS was used to characterize all N-OMCs. The narrow scan N 1s peak was then deconvoluted into four peaks, assigned to pyridinic-N, pyrrolic-N, graphitic-N, and oxidized-N structures (Figure 1e). Interestingly, a correlation can be observed between the ORR activity and these active N species when they are linked with the 2e⁻ ORR performance of N-OMC catalysts. Figure 2g shows the correlation between the P/G ratio and the 2e⁻ ORR performance of all N-OMC catalysts treated at temperature range from 600 to 1000 °C. It can be observed that the P/G ratio increased as the annealing temperature deceased. The samples with the high P/G ratio (with dominant pyrrolic-N content) exhibited H₂O₂ selectivity over 95%, suggesting that pyrrolic-N can promote 2e⁻ ORR activity, which is in line with prior findings.¹³,¹⁵,²⁹ On the other hand, H₂O₂ generation was significantly increased for samples with a low P/G ratio, which could be attributed to a higher graphitic-N concentration. It has been reported that graphitic-N can enhance the electrical conductivity and thus raise the current density, leading to higher H₂O₂ generation.¹³ What makes N-OMC-800 outperform the other N-OMCs is that it has the optimal P/G ratio of about 1.14, which can simultaneously boost both H₂O₂ selectivity and generation. The N-OMC-800 was the only catalyst capable of maintaining a high FE and producing a significant amount of H₂O₂ over a broad potential range. Additionally, to better understand the association between the P/G ratio and the 2e⁻ ORR performance, the N-OMC-800 was compared to a range of previously reported nitrogen-doped carbons, as illustrated in Figure S7. Several nitrogen-doped carbons were explored to determine their P/G ratios, and the overall trend revealed that
when the P/G ratio decreased (to less than 0.8), the H$_2$O$_2$ FE (%) proportionally decreased as well. This correlation supports the findings of this study. A high P/G ratio (close to 1) is desirable for high selectivity, as is the case with the N-OMC-800. Furthermore, N-OMC-800 was able to reach 100% FE and can be maintained in a wide potential range, which could be attributed to its enhanced morphology. The high degree of ordered mesoporous structure can be found only in N-OMC-800 with high pore volume and large pore diameters. These enhanced structural properties are proposed to provide a large surface area and accessible active sites, allowing very short contact time due to its facile mass transport. Hence, H$_2$O$_2$ can be generated with extremely high selectivity, making N-OMC-800 outperform the other N-OMC catalysts.

**Flow Cell Performance and Long-Term Catalyst Stability.**

The flow cell is ideal for upscale synthesis since it can enhance oxygen gas diffusion to achieve higher ORR current densities while providing more uniform and better mass transport than the H-type cell. Figure 3a shows our custom-designed three-electrode flow cell used to examine the 2e$^-$ ORR performance of the N-OMC-800 catalyst in 0.1 M KOH alkaline electrolyte. The oxygen gas was purged to the back of the catalyst substrate, while the KOH electrolyte was circulated in a spacer on the other side facing the catalyst. The N-OMC-800 performance in a flow cell was tested at various potential windows; the current density and corresponding average FE of 3 h tests are shown in Figure 3b. Remarkably, the catalyst was able to maintain 100% FE in a broad potential range even at a high current density of 149 mA/cm$^2$, implying that it exclusively promotes H$_2$O$_2$ formation in an alkaline media. Furthermore, the H$_2$O$_2$ production rate (shown in Figure 3c) started at 0.35 mol g$_{cat}^{-1}$ h$^{-1}$ at 0.6 V$_{RHE}$ and almost doubled as the overpotential increased to a maximum of 9.43 mol g$_{cat}^{-1}$ h$^{-1}$ at 0.35 V$_{RHE}$. The N-OMC-800 catalyst outperformed or was comparable to a number of other ORR carbon-based catalysts modified with heteroatom dopants or transition metals, indicating that it would be a great candidate for generating H$_2$O$_2$ in practical uses (Table S5). In addition to its considerably increased H$_2$O$_2$ activities in a flow cell, the stability of the N-OMC-800 catalyst is an essential factor and should be considered for its potential industrial uses. A stability test of the N-OMC-800 was conducted under the same conditions at 0.6 V$_{RHE}$ for 12 h. The results (shown in Figure 3d) show that the N-OMC-800 exhibited FE of above 99% for 12 h without experiencing any degeneration, indicating its excellent catalytic stability for long-term H$_2$O$_2$ production. In comparison to recently published state-of-the-art 2e$^-$ ORR catalysts in alkaline, our N-OMC-800 catalyst demonstrated substantial improvements, most notably in maintaining FE over 99% (Table S6).

**CONCLUSIONS**

We successfully synthesized the N-OMC-800 catalyst, with high nitrogen content and ordered mesoporous architecture, for highly selective and stable electrochemical generation of H$_2$O$_2$ in an alkaline medium. The N-OMC-800 catalyst has demonstrated outstanding electrocatalytic activity and dominant generation of H$_2$O$_2$ (with FE of 100%). The ordered mesoporous structure further boosted both electron transport...
rates and oxygen diffusion, resulting in significantly improving the 2e− ORR current density. We also demonstrated the onsite H2O2 generation in a flow cell, which showed a high H2O2 production rate and long-term stability. Accordingly, our catalyst should be applicable for the electrochemical reduction of O2 to H2O2 in alkaline, and it will likely be incorporated into the cathode of more practical applications like paired electrolysers to produce two valuable products simultaneously or other environmental applications using H2O2 for mineralizing or removing organic pollutants electrochemically.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acssuschemeng.1c08285.

Equations, additional structural characterization, and supporting electrochemical characterization (PDF)

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Notes

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