Iron and nitrogen-doped double gyroid mesoporous carbons for oxygen reduction in acidic environments

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Abstract
Iron- and nitrogen-doped carbon (Fe-N-C) represents a promising class of alternative electrocatalysts to noble metals for the oxygen reduction reaction (ORR) in acidic environments. To make Fe-N-C active, one of the most critical parameters is microporosity, which must be controlled to maximize the active site density. However, the use of microporosity must be optimized for the requirement of high-flux mass transport. Here, we synthesized and demonstrated gyroidal mesoporous Fe-N-C with microporous pore walls as an avenue to combine a high active-site density with favorable mass transport at high flux. The gyroidal mesoporous Fe-N-C catalysts have competitive gravimetric and volumetric ORR activities, comparable to the ORR activity obtained in purely microporous configurations despite having mesoporous features. Our result suggests that the ORR activity of microporous Fe-N-C electrocatalysts can be combined with mesoporosity through the use of mesoporous Fe-N-C with microporous pore walls. We further investigate effects of the nitrogen incorporation method on mesoporous N-doped carbon electrocatalysts. We find that despite having \( \sim 2 \times \) higher N concentration, nitrogen incorporation via \( \text{NH}_3 \) yields similar ORR activity to incorporation via a chemical additive, a finding we attribute to the role of pyridinic and quaternary N in the ORR.

1. Introduction

Electroactive materials containing carbon, nitrogen, and transition metals such as iron and cobalt are one of the few highly active platinum-group-metal-free (PGM-free) electrocatalysts for the ORR in acidic environments [1–4]. Unfortunately, a number of issues have hindered their adoption in proton-exchange membrane fuel cells (PEMFCs). These issues include a limited incorporation of the transition-metal and nitrogen species that make up the active sites [5, 6]. As a result, it has been challenging to realize a high active site density necessary to attain high volume-normalized (‘volumetric’) ORR activity [7]. In response to this issue, many groups have examined the use of high surface area microporous carbons to increase the internal surface area. The benefit is two-fold: to increase the active site density and create a microstructure that favors the formation of sites that are shared between two carbon grains, which have been proposed to be ORR-active. However, these microporous channels (< 2 nm) introduce mass transport limitations at high flux [7]. Thus, it is of interest to identify how to combine the high ORR activity in microporous channels with larger, transport-friendly mesoporous microstructures. Herein, we examine the use of block copolymer (BCP) directed carbons with larger, well-defined mesostructures (mesopore size >20 nm) and micropores in the mesopore walls to address this question. We find that larger, well-defined mesoporous carbon structures...
based on co-continuous gyroid structures can achieve high volumetric ORR activity despite having larger pore sizes. Thus, this approach may serve as a route to high ORR activity for PGM-free catalysts.

Mesoporous N- and Fe-doped carbon synthesized via silica-based hard templates [8, 9] can yield tunable pore sizes up to 12 nm and shows ORR activity in acidic electrolytes [10]. However, this approach requires time-consuming steps to prepare the silica template and utilizes toxic hydrofluoric acid for the silica removal. While Pluronic BCPs can be used as structure-directing agents to simplify the synthesis, their low molar mass creates < 5 nm pore sizes, which are too small for our interest in examining the effect of larger mesopores [11–13]. Pyrolysis of Fe- and N-containing metal-organic frameworks in the presence of H2 can also yield modest mesoporosity, although the mesopore size (< 10 nm) remains small [14]. While there have been some reports on larger-pore, mesoporous doped carbon catalysts, most have been tested in alkaline electrolytes [15, 16], where it is unclear if the results can translate to acidic environments [17]. In a direction that departs from these earlier works, we examine the ORR performance in acidic media of ordered mesoporous carbon catalysts with large (>20 nm) pores synthesized using BCP self-assembly. Our result shows that mesostructured Fe-N-C electrocatalysts have high ORR activity, similar to microporous Fe-N-C electrocatalysts, thereby demonstrating a possible pathway to realizing high ORR activity at high current density, where pore accessibility plays a critical role in addition to the active-site density [18–20].

Our synthesis of double gyroid mesoporous carbon (G2P-MC) ORR catalysts doped with nitrogen and iron uses a one-pot, BCP self-assembly approach [21, 22], which is applicable to a range of materials [23, 24]. In this approach, the nanoscale structures and dimensions can be controlled by adjusting the block volume fractions, BCP molar mass, and BCP-additive ratio, based on considering bulk BCP phase diagrams [25]. We use phenol-formaldehyde resols ('resols') as carbon sources which selectively mix with the hydrophilic block of the BCP and can be crosslinked. The as-made material's structure is obtained by evaporation induced self-assembly. Upon subsequent heating in an inert atmosphere, the polymer template decomposes into volatile species, while the highly crosslinked resol is converted to fine-grained graphitic carbon. Thermal removal of the polymer template eliminates the hazardous and time-consuming post-synthesis step of silica removal in the silica templating approach. By providing highly periodic templates, the BCP-directed approach also improves the carbon filling fraction compared to typical microporous catalysts that do not pack as efficiently and as a result contain significant dead space. Because of this efficient packing, our G2P-MC materials have comparable specific surface areas (hundreds of m2 g−1) to microporous catalysts despite also having significant mesoporosity. We compare two methods of N incorporation, one via an additive incorporated during the self-assembly synthesis (N-G2P-MC) and another via heat treatment under ammonia (G2P-MC-NH3). In our ORR test in acidic electrolytes, we found that their ORR activities were similar even though N-G2P-MC had only half as much N as G2P-MC-NH3. We attribute this result to the preferred incorporation of the nitrogen moieties used in the self-assembly synthesis to the pyridinic and quaternary N sites. Finally, we further improve the ORR activity by including Fe during self-assembly (Fe-N-G2P-MC). This incorporation creates a PGM-free electrocatalyst with volumetric ORR activity competitive with purely microporous configurations, but with a mesoporous morphology, which helps enhance micropore accessibility.

2. Methods

2.1. Synthesis

Synthetic approaches for undoped gyroidal mesoporous carbons [26–28] were adapted to prepare mesostructured fine-grained graphitic carbon doped with N and Fe. The structure-directing agent used was an amphiphilic triblock terpolymer with two hydrophobic blocks and one hydrophilic block, specifically, poly(isoprene)-block-poly(styrene)-block-poly(ethylene oxide) (PI-b-PS-b-PEO, or simply ISO). The ISO terpolymer had an overall molar mass of 28.0 kg mol−1 with volume fractions of 10.5% polyisoprene, 34.1% polystyrene, 55.4% poly(ethylene oxide) and a dispersity of 1.11. The terpolymer was dissolved in a solution of tetrahydrofuran (THF) and chloroform (1:1 by mass), then an oligomeric phenol-formaldehyde resol ('resol') was added as the carbon precursor. The resol was synthesized by polymerizing phenol and formaldehyde under basic conditions [28].

Nitrogen was incorporated in two ways. In the first way, pyridine-containing additives were used (figure 1). Specifically, an N-containing oligomeric resol was synthesized from the polymerization of 3-hydroxypridine and formaldehyde under basic conditions using a similar procedure as for the carbon precursor. The pyridinic resol was then added with the phenolic resol to a terpolymer solution. The two resol solutions were added in three different ratios of phenolic to pyridinic resols to control the amount of N incorporated in the structure: 1-to-1, 2-to-3, and 3-to-7. Both resols hydrogen bond to the hydrophilic ethylene oxide block of the terpolymer through their hydroxyl groups (figure 1). In the second incorporation method, ammonia was used as a nitrogen source, introduced during a post-synthesis thermal treatment.
After stirring the polymer/additive solution overnight, hybrid monoliths were cast in a Teflon beaker and annealed at 50 °C in a THF and chloroform vapor atmosphere. Afterward, the monoliths were heated at 130 °C for 24 h to crosslink the resols and then pyrolyzed to decompose the polymer template and form fine-grained graphitic carbon. Undoped G\textsuperscript{D}MC was heated to 600 °C at 1 °C min\textsuperscript{-1}, then to 900 °C at 5 °C min\textsuperscript{-1} and held for 3 h under flowing N\textsubscript{2} (60 cm\textsuperscript{3} min\textsuperscript{-1} STP). To limit N rejection at high temperatures, N-G\textsuperscript{D}MC was only heated at 600 °C for 3 h (1 °C min\textsuperscript{-1} ramp) under flowing N\textsubscript{2} (60 cm\textsuperscript{3} min\textsuperscript{-1} STP). For samples with N dopants introduced from ammonia (G\textsuperscript{D}MC-NH\textsubscript{3}), the mesoporous carbon monoliths obtained from pure resols underwent an additional heating step in flowing NH\textsubscript{3} (60 cm\textsuperscript{3} min\textsuperscript{-1} STP). A series of heating times and temperatures were used to optimize the amount of N incorporated. The specific conditions include: 500 °C for 1 h, 680 °C for 1 h, or 820 °C for either 1 h or for 30 min.

Iron was introduced into the mesoporous structure using a similar method. Specifically, 5, 10, 15, 20-tetrakis(4-methoxyphenyl)-21H,23H-porphine iron(III) chloride was added to the oligomeric resols together with the ISO terpolymer dissolved in THF and chloroform. The sample was then annealed under a solvent-vapor atmosphere. Afterward, we used the same 900 °C heating protocol described above to promote Fe incorporation in the carbon. Several ratios of carbon-to-nitrogen-to-iron precursors were used: 50:50:1, 10:10:1, 5:5:1, and 5:5:2.

2.2. Characterization

Multiple structure and porosity characterization techniques, including small angle X-ray scattering (SAXS), scanning electron microscopy (SEM), and nitrogen sorption with Brunauer–Emmett–Teller (BET) analysis were used to characterize the synthesized samples. SEM images were collected using a TESCAN MIRA3 LM field-emission SEM at an accelerating voltage of 15 kV. All monoliths were coated with Au-Pd to increase conductivity. SAXS measurements were collected at the Cornell High Energy Synchrotron Source (CHESS) using a 11.3 keV incident beam and a Dectris Eiger 1 M detector. For N\textsubscript{2} sorption, all monoliths were crushed into a powder and degassed at 120 °C for 6 h under vacuum prior to measurement using a Micromeritics ASAP 2020 surface area and porosity analyzer at 77 K. Finally, the concentration and nature of the nitrogen species were investigated using X-ray photoelectron spectroscopy (XPS) on a Scienta Omicron ESCA-2SR with monochromatic Al K\textsubscript{α} X-rays (1486.6 eV) at an operating pressure of ∼1 × 10\textsuperscript{-9} Torr.

2.3. Electrochemical testing

Catalyst inks were prepared by dispersing crushed monoliths in an isopropanol/water mixture to 2 mg ml\textsuperscript{-1}. After adding Nafion binder to the ink and sonicating the solution, inks were dropcast onto glassy carbon rotating disk electrodes (RDEs) and allowed to dry under ambient conditions for a catalyst loading of 0.2 mg cm\textsuperscript{-2}. All measurements were conducted in a three-electrode electrochemical cell with 0.5 mol l\textsuperscript{-1} H\textsubscript{2}SO\textsubscript{4} as the supporting electrolyte, a platinum wire as the counter electrode, and an Ag/AgCl reference electrode. The reference electrode was calibrated against the reversible hydrogen electrode (RHE) scale by measuring the onset of hydrogen evolution/oxidation with a polycrystalline Pt disk. To characterize the ORR performance, cyclic voltammetry was used in O\textsubscript{2}-saturated 0.5 mol l\textsuperscript{-1} H\textsubscript{2}SO\textsubscript{4} at 10 mV s\textsuperscript{-1}. Koutecky-Levich analysis was used to calculate the kinetic current (I\textsubscript{k}) and the number of electrons transferred using the average of the forward and reverse polarization curves. The volumetric and gravimetric activity was reported by dividing I\textsubscript{k} by either the catalyst volume or mass, respectively.
3. Results and discussion

SAXS measurements for all four types of samples (figures 2(a) and S1 (available online at [https://stacks.iop.org/JPENERGY/3/015001/mmedia])) exhibited multiple higher order peaks with spacing consistent with the double gyroid morphology (Ia-3d, space group #230). The lattice parameter for G\textsuperscript{D}MC was 45.6 nm, while the doped samples had slightly increased lattice parameters. The lattice parameter was 49.9 nm for N-G\textsuperscript{D}MC (1.9% N by mass), 47.2 nm for G\textsuperscript{D}MC-NH\textsubscript{3} (3.5% N by mass), and 50.4 nm for Fe-N-G\textsuperscript{D}MC (1.6% Fe by mass). SEM images confirmed the double gyroid morphology of each material (figures 2(b), (c), (e), (f), S2 and S3), showing an interconnected network with narrowly dispersed pore sizes. Most images (figures 2(b), (c) and (e)) showed the characteristic double wavy pattern of a (211) plane of the double gyroid structure (figure 2(b), inset), likely due to its large cross sectional density fluctuations, which causes the monolith to fracture along that plane when prepared for imaging [29]. The image of Fe-N-G\textsuperscript{D}MC (1.6% Fe by mass) (figure 2(f)) shows a (100) plane of a double gyroid structure, in agreement with level-set simulations [30] (figure 2(f), inset). The materials’ nitrogen sorption results were characterized using BET analysis. The results showed type IV isotherms with H\textsubscript{1}-type hysteresis (figure S4), well-defined mesopores (pore sizes of 2 to 50 nm) and microporosity (< 2 nm) for all samples. The BET surface areas were 562 m\textsuperscript{2} g\textsuperscript{-1} for G\textsuperscript{D}MC, 594 m\textsuperscript{2} g\textsuperscript{-1} for N-G\textsuperscript{D}MC (1.9% N by mass), 869 m\textsuperscript{2} g\textsuperscript{-1} for G\textsuperscript{D}MC-NH\textsubscript{3} (3.5% N by mass), and 445 m\textsuperscript{2} g\textsuperscript{-1} for Fe-N-G\textsuperscript{D}MC (1.6% Fe by mass). The increased surface area for G\textsuperscript{D}MC-NH\textsubscript{3} is due to increased microporosity from the reaction of carbon with NH\textsubscript{3} to form volatile products [31].

Although the specific surface areas between samples varied with doping concentrations, the surface area values were similar among the various synthesis methods and comparable to the microporous N-C and Fe-N-C electrocatalysts reported in literature [2]. Barrett–Joyner–Halenda (BJH) analysis showed that the average mesopore size at the same doping concentrations was 20.0 nm for G\textsuperscript{D}MC, 21.6 nm for N-G\textsuperscript{D}MC, 21.2 nm for G\textsuperscript{D}MC-NH\textsubscript{3}, and 24.0 nm for Fe-N-G\textsuperscript{D}MC (figure 2(d)). These results are consistent with the SAXS and SEM results, demonstrating that the mesoporosity of the materials is maintained throughout the heating steps. A summary of the surface areas, pore sizes and pore volumes for each material is shown in table S1.

It has been established that the nitrogen concentration correlates with higher ORR activity [32]. We estimated the nitrogen concentration using XPS (figure 3) by integrating the XPS area of the N 1 s and C 1 s regions. The N mass fractions for the N-G\textsuperscript{D}MC catalysts prepared using different phenolic to pyridinic resol
concentrations of 1-to-1, 2-to-3, and 3-to-7, were 1.1%, 1.5%, and 1.9%. These numbers are lower than the starting N mass fractions, which are 8.3%, 12.0%, and 17.5%, respectively. The reduced N concentration indicates only partial nitrogen incorporation during the self-assembly and/or N removal during heating. For the G\textsuperscript{D}MC-NH\textsubscript{3} catalysts, we measured N mass fractions of 1.5% (500 °C/1 h), 2.3% (820 °C/1 h), 3.0% (680 °C/1 h), and 3.5% (820 °C/30 min).

Different nitrogen incorporation geometries can substantially impact electrochemical properties [5]. We differentiated between the different nitrogen groups using the following XPS binding energy fitting: pyridinic N (398.5 eV), pyrrolic N (400.1 eV), quaternary N (401.1 eV), and oxidic N (403.2 eV) [5]. Pyridinic N and quaternary N have been proposed to be the most active nitrogen sites for the ORR [5, 33]. XPS fitting showed that the N functionality in N-G\textsuperscript{D}MC is primarily quaternary (50.6%) and pyridinic (18.4%) N, while G\textsuperscript{D}MC-NH\textsubscript{3} had mostly pyrrolic N (50.7%) with some quaternary (17.9%) and pyridinic N (20.5%). From our analysis, if the parameters critical for the ORR are the pyridinic and quaternary N groups, we expected N-G\textsuperscript{D}MC to be the more active material at constant total N concentration.

For both N-G\textsuperscript{D}MC and G\textsuperscript{D}MC-NH\textsubscript{3}, the ORR activity was highest for the catalysts with the highest N content (figures 4(a), (b), S5 and S6). The number of electrons transferred (n) for the N-G\textsuperscript{D}MC and G\textsuperscript{D}MC-NH\textsubscript{3} catalysts was \(~2, indicating that the ORR followed the H\textsubscript{2}O\textsubscript{2} pathway (O\textsubscript{2} + 2 H\textsuperscript{+} + 2e\textsuperscript{−} \rightarrow H\textsubscript{2}O\textsubscript{2}). This observation is consistent with previous studies on mesoporous N-doped carbons synthesized via hard templating schemes [34–36], which attributed the H\textsubscript{2}O\textsubscript{2} vs. H\textsubscript{2}O selectivity to whether the electrocatalyst can subsequently reduce the formed H\textsubscript{2}O\textsubscript{2} before it escapes the catalyst layer. The Tafel slopes for the N-G\textsuperscript{D}MC (151–175 mV dec\textsuperscript{−1}) and G\textsuperscript{D}MC-NH\textsubscript{3} (144–187 mV dec\textsuperscript{−1}) catalysts were consistent with previous N-doped carbon H\textsubscript{2}O\textsubscript{2} production catalysts [36]. Interestingly, the ORR activity is higher for N-G\textsuperscript{D}MC compared to G\textsuperscript{D}MC-NH\textsubscript{3} at constant N concentration. For example, the most heavily doped N-G\textsuperscript{D}MC (1.9% N by mass) had approximately half the N concentration of the most heavily doped G\textsuperscript{D}MC-NH\textsubscript{3} (3.5% N by mass); yet, their ORR activities were comparable. Based on the distribution of nitrogen as determined using XPS, this activity trend suggested that the active sites for the studied catalysts likely included quaternary N, which N-G\textsuperscript{D}MC had in much higher concentration than G\textsuperscript{D}MC-NH\textsubscript{3}.

While the N-doped carbons were active towards the ORR in acidic environments, their activity was still substantially lower than state-of-the-art Fe-N-C catalysts and they could not catalyze H\textsubscript{2}O\textsubscript{2} reduction. To improve the activity and H\textsubscript{2}O selectivity, we introduced Fe to the synthesis (Fe-N-G\textsuperscript{D}MC). Based on the amount of Fe precursor used, we expected Fe mass fractions of 0.1%, 0.5%, 0.9%, and 1.6%. No discrete Fe clusters were observed using SEM, suggesting that most of the Fe was incorporated as active isolated Fe sites in the carbon network. We found that the activity of the Fe-N-G\textsuperscript{D}MC catalysts for the ORR in 0.5 mol l\textsuperscript{−1} H\textsubscript{2}SO\textsubscript{4} increased systematically with the Fe concentration (figure 4(c)), with the most active Fe-N-G\textsuperscript{D}MC catalyst (1.6% by mass) having an ORR mass activity of 1.92 A g\textsuperscript{−1} and an ORR volumetric activity of 1.09 A cm\textsuperscript{−3} at 0.75 V vs. RHE (figure 4(d)). This catalyst also selectively formed H\textsubscript{2}O (n \sim 4) and had a

Figure 3. N 1s X-ray Photoelectron Spectroscopy spectra for (a) N-G\textsuperscript{D}MC and (b) G\textsuperscript{D}MC-NH\textsubscript{3} showing relative fraction of each N doping position.
Figure 4. Polarization curves showing ORR activity of mesoporous carbons: (a) N-G^D^MC, (b) G^D^MC-NH_3, and (c) Fe-N-G^D^MC. (d) Tafel plot comparing ORR volumetric activity of N-G^D^MC (1.9% N by mass, red), G^D^MC-NH_3 (3.5% N by mass, blue), and Fe-N-G^D^MC (1.6% Fe by mass, green). All current densities were measured in O_2-saturated 0.5 mol l^{-1} H_2SO_4 at 10 mV s^{-1} using a rotating disk electrode at 1600 rpm.

Tafel slope of 57 mV dec^{-1}. The more lightly doped Fe-N-G^D^MC catalysts (0.1% to 0.9% by mass) produced a mixture of H_2O_2 and H_2O. Our observations indicated that the incorporation of additional Fe enhances H_2O_2 decomposition as well as the ORR activity. The Tafel slopes also increased to 87–130 mV dec^{-1} for the lightly doped Fe-N-G^D^MC samples.

While the peak Fe-N-G^D^MC activity was lower than the state-of-the-art values measured in a membrane electrode assembly [1–3], it is comparable to several reports on microporous doped carbon catalysts with similar Fe mass fractions (0%–1% Fe by mass) [37–39]. We did not optimize the Fe and N incorporation since the goal of this work is not to obtain the record Fe-N-C activity but rather to demonstrate that a mesoporous Fe-N-C catalyst can support ORR activity at the level of microporous Fe-N-C systems. Our work provides evidence that a Fe-N-C catalyst with substantially larger, mesoporous pore sizes can be combined with microporous side walls to yield an ORR activity that is competitive with traditional Fe-N-C catalysts that are solely microporous. We attribute our result to the high filling fraction in the mesoporous catalysts derived from BCP self-assembly, which allows more efficient internal surface area packing, enabling the use of larger pores. This improvement is evident in the ratio of mass to volumetric activity (1.76 vs. ∼2–3 in literature [7]), which suggests that a mesoporous structure with microporous mesopore walls allows high retention and utilization of the internal surface area, and delivers high ORR activity. Further studies to optimize the Fe and N incorporation and testing in PEMFCs are important next steps to understand the role of mesopores and identify whether the structure can enable better utilization at higher flux (current density).

4. Conclusion

We report the synthesis and characterization of mesoporous N-doped as well as Fe and N-doped carbon with large, uniform and co-continuous gyroidal mesopores as well as microporous pore walls using a one-pot BCP self-assembly approach. We evaluated the materials for the ORR in acidic environments and demonstrated that these Fe-N-C catalysts can provide comparable ORR volumetric activities to traditional
Fe-N-C systems that are purely microporous, despite our Fe-N-C catalysts having a morphology that is more conducive to efficient reactant mass transport. We attribute this result to the high filling fraction in the BCP-directed structures, whose regular pore size distribution allows high internal surface area but with a more readily accessible co-continuous pore morphology. We further relate the activity of our mesoporous catalysts to their synthesis conditions. Our observation reveals that chemically introducing a pyridine-based N precursor improves the ORR activity for a given doping concentration compared to directly heating the catalysts under NH3 due to a higher fraction of N at the active quaternary N positions. Fe addition provides additional improvement to the ORR activity and further improves the 4e− selectivity. Optimizing the Fe and N incorporation to reach higher ORR activity while maintaining the mesopore structure is an important next step to show the functionality of mesoporous Fe-N-C catalysts for PEMFC applications.

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