Fe-Doped Copolymer-Templated Nitrogen-Rich Carbon as a PGM-Free Fuel Cell Catalyst

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ABSTRACT: Platinum group metal-free (PGM-free) catalysts present a promising opportunity to make hydrogen fuel cells more affordable; however, issues with stability and electrochemical activity continue to hinder their application. Recent studies point to the availability of nitrogen and a controlled mesoporous structure as avenues of improvement. To address this need, copolymer-templated nitrogen-enriched carbon (CTNC) was used as the precursor to prepare PGM-free catalysts for the oxygen reduction reaction (ORR). By employing its rich nitrogen content and interconnected mesoporous structure, a significant amount of Fe–N–C-active sites were formed by coannealing CTNC with FeSO₄. The formed N/Fe co-doped nanocarbon (CTNC-Fe) catalyst exhibits good electrochemical activity with a half-wave potential of 0.781 V vs normal hydrogen electrode (NHE), a total surface area of 400 m²/g, and a power density of 180 mW/cm². The block copolymer (BCP) was made by



atom transfer radical polymerization (ATRP), which allows control and tunability of the block copolymer. This work opens new opportunities to improve the electrochemical activity and stability of PGM-free catalysts by controlled polymerization techniques that precisely tune the pore structure and maximize nitrogen content to improve the formation of active sites in the catalysts.

KEYWORDS: PGM-free, catalyst, hydrogen fuel cells, block copolymer, ATRP

INTRODUCTION

In the search for sustainable and clean energy sources, proton exchange membrane fuel cells (PEMFCs) have become one of the most promising alternatives. The oxygen reduction reaction (ORR) and hydrogen evolution reaction (HER) make it possible to surpass the Carnot efficiency limit of heat engines. Furthermore, hydrogen is a sustainable and non-polluting energy resource with a specific energy density (143 MJ/kg) that is 3 times that of hydrocarbon fuels such as natural gas (53.6 MJ/kg) and gasoline (46.4 MJ/kg) and can be used in both mobile and stationary power generation.^{1,2} However, one major drawback to PEMFCs is the sluggish kinetics of ORR, which require the use of noble metals such as platinum.¹ This limits their large-scale application as the cost of the catalyst is ~41% compared to the rest of the fuel cell pack.³

To address these issues, the development of platinum group metal-free (PGM-free) catalysts has been a subject of intense research over the past decade.^{4–12} These catalysts, also referred to as transition metal–nitrogen–carbon catalysts (M-N-C), are synthesized with inexpensive, abundant precursors and show excellent compatibility with PEMFCs.^{4–6} They are usually made from a mixture of transition metal salts and organic nitrogen-rich compounds, which when heat-treated at temperatures in the range of 600–1100 °C result in a graphitic

carbon with high porosity and surface area.⁵ The catalyst relies on heteroatom moieties in the graphitic surface composed of mainly nitrogen and transition metal atoms as the catalytic active sites.^{4–12} Moreover, it is generally agreed that atomically dispersed iron coordinated by nitrogen ligands is the most electrochemically active moiety in the catalyst, as it is capable of a full 4e⁻ reduction from oxygen to water in acidic conditions.¹³⁻¹⁶ However, some studies suggest the presence of a persistent hydroxide radical ligand on the MN₄-active site as a significant factor in increasing electrochemical activity of the active site, except when the metal ion is Co.¹⁷ The reaction pathway, eqs 1-5, has been tentatively agreed on as the ORR for MN₄-active sites (where * is the active site). Density functional theory calculations point to the fourth step being the potential determining step in the case of Fe as the metal component, though this is a continued topic of debate in the research community.¹⁷

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$$* + 4H^{+} + 4e^{-} + O_2 \rightarrow *OO + 4H^{+} + 4e^{-}$$
(1)

$$*OO + 4H^{+} + 4e^{-} \rightarrow *OOH + 3H^{+} + 3e^{-}$$
 (2)

$$*OOH + 3H^{+} + 3e^{-} \rightarrow *O + H_2O + 2H^{+} + 2e^{-}$$
 (3)

$$*O + H_2O + 2H^+ + 2e^- \rightarrow *OH + H_2O + H^+ + e^-$$
(4)

$$*OH + H_2O + H^+ + e^- \rightarrow * + 2H_2O$$
 (5)

M-N-C catalysts were first reported in 1964 when metalcontaining macrocyclic molecules such as porphyrin were first tested as catalysts for ORR.18 Additionally, this type of ORR catalysis has similarities to biochemical processes such as hemoglobin oxygen binding and cellular respiration performed by cytochrome c oxidase, thereby prompting some researchers to follow a biomimetic approach to develop new catalysts.¹⁹⁻²¹ However, synthesizing a catalyst that achieves the same ORR activity as platinum catalysts has remained a great challenge from both the electrochemical activity perspective and their stability.⁶ Many methods of synthesis have been developed recently, including varying the source of carbon, nitrogen, and transition metal, to continuously improve the catalyst performance.⁴⁻¹² There are three major types of processes that have been developed: (1) pyrolysis of metal organic frameworks (MOFs), (2) nitrogen and iron doping of high surface area carbon templates using transition metal salts and nitrogen-rich gases, solutions, and/or polymers, and (3) a mixture of nitrogen, carbon, and metal precursors with a volatilizing agent, which generates porous nitrogen and iron co-doped carbon structures after being heat-treated.⁴⁻¹² However, one issue is in their inability to reliably control the porous structure.⁴⁻¹² In the case of MOFs and precursor mixtures, the porous structures are generated by evaporation of zinc chloride, cyanamide, and other volatile agents.^{4,5} On the other hand, the use of hard templates can generate a controlled structure in carbon,²² but iron doping and the addition of salts tend to change the nanostructure of carbon, which makes it difficult to control the final structure of the catalyst.⁵ The lack of control over pore size can be an impediment for forming a high density of active sites, as their formation is greatly influenced by the size and structure of the pores.^{23–26}

To overcome this issue, block copolymers were used as templates for the synthesis of nanocarbons.^{27–30} In the case of A–B diblock copolymers, the thermodynamic incompatibility between blocks A and B drives A–B diblocks to self-organize via microphase separation to generate different morphologies.

Additionally, self-assembly of BCPs is low-cost, fast, and easily scalable along with modern synthetic chemistry, enabling tailoring of the structure and hence the properties of individual blocks and the assembly.³¹ To account for this, we employed a copolymer-templated nitrogen-rich nanocarbon (CTNC) as a base for a PGM-free catalyst, which was previously used as electrochemically active heteroatom-enriched mesoporous carbons.³²⁻³⁸ The polymer precursor, poly(acrylonitrile)-bpoly(n-butyl-acrylate) (PAN-b-PBA), was synthesized by copolymerization of acrylonitrile (AN) and n-butyl acrylate (BA) using atom transfer radical polymerization (ATRP).^{39–41} PAN acts as both a nitrogen and carbon precursor, and PBA is the sacrificial component that generates porosity after pyrolysis at temperatures above 600 °C.⁴² The well-defined nanostructure is generated by self-assembly driven by phase separation of the two immiscible polymer blocks,^{28,31} which is then fixed using the oxidative stabilization of PAN, as is implemented in carbon fiber manufacturing.^{33,43} Among various self-assembled morphologies, of particular interest to this work are bicontinuous gyroid-like morphologies,^{31,32} which assure the overall pore connectivity and accessibility required for improved electrochemical performance. This is a potentially new, advantageous approach to improving the electrochemical activity of PGM-free catalysts by "soft templates" rather than relying only on surface activation by compounds such as ZnCl₂ and KOH.⁴⁴⁻⁴⁶ ZIF/MOFs-derived PGM-free catalysts, on the other hand, though highly electrochemically active and made with a method that allows excellent control over particle size, have a narrow pore size range compared to CTNC as proven by efforts to tailor their morphology through use of nanofibers and silica templates.⁴

The method using CTNC is unlike other previously tested methods of reactive polymerizations, where monomers such as phenylenediamine, aniline, pyrrole, 3-methylthiophene, etc., are polymerized in a mixture of carbon black or nano-tubes.^{47–59} Although the presence of a volatile sacrificial component (PBA in this case) is similar to the case in reports using a reactive polymerization process,^{60–62} our work is more reminiscent of synthesis methods with no added carbon sources other than the nitrogen precursors.

Scheme 1 illustrates the process of preparing CTNC-Fe, an Fe–N–C catalyst using the BCP-derived carbon as a base. In addition, the nitrogen content of CTNC measured in previous work has been found to reach a maximum of 17 atom % at lower heat treatment temperatures of 600 °C, 33,35 determined by measurements using X-ray photoelectron spectroscopy (XPS). This rich nitrogen content could prove very beneficial

in the formation of $Fe-N_x$ -active sites in the presence of an iron precursor.

In this work, we utilized CTNC with a unique bicontinuous morphology as a precursor to producing N/Fe co-doped nanocarbons (CTNC-Fe) for PGM-free fuel cells. For the carbon to retain the mesoporous structure, the metal doping process was performed after thermal stabilization in air. Iron(II) sulfate was used as the metal component since iron has been previously found to be the most electrochemically active transition metal in this type of catalyst, and sulfate salts have been used as a precursor for Fe-N-C catalysts in several reports.^{26,48,62} The goal of this work is to determine whether CTNC could be applied to make a working Fe-N-C catalyst that retains its nanostructure. The proof-of-concept was supported by testing in a fuel cell assembly with hydrogen and oxygen flow at low-temperature fuel cell conditions. The morphology and elemental composition of the catalyst were also analyzed by different characterization methods.

EXPERIMENTAL SECTION

Materials. Azobisisobutyronitrile (AIBN), dimethylsulfoxide (DMSO), dimethylformamide (DMF) CuBr_2 , tris(2-pyridylmethyl)amine (TPMA), acrylonitrile (AN), bipyridine nitrate (BPN), *n*-butyl acrylate (BA), HCl, methanol, ultrapure water, FeSO₄·7H₂O, 0.5 M sulfuric acid aqueous solution, Nafion 5 wt % solution, and ultrapure water were used. All materials were obtained from Millipore Sigma. CuBr₂ was purified by stirring in glacial acetic acid, followed by washing with ether and dried overnight under vacuum. Monomers were passed through a basic alumina column prior to use.

Preparation of PAN-*b***-PBA Copolymers.** PAN₁₀₃ was synthesized by initiator for continuous activator regeneration (ICAR) ATRP using a previously reported technique.⁶³ In a typical procedure, 17 mg of AIBN (0.1 mmol, 0.1 equiv), 30 mL of DMSO and 3 mL of DMF were charged into a Schlenk flask and degassed with N₂ for 30 min. A stock solution of CuBr₂ and 3 mL of DMF was prepared and degassed for 10 min, then 9 mg (0.04 mmol, 0.04 equiv) of CuBr₂ and 36 mg (0.12 mmol, 0.12 equiv) of TPMA were added to the Schlenk flask. Briefly, 27 mL (415 mmol, 400 equiv) of degassed AN was added to the above flask, and finally 139 mg (1.0 mmol, 1 equiv) of BPN was added, and the polymerization was started by immersing the flask in an oil bath at 65 °C and conducted for 5 h to reach 26% conversion. The final polymer was isolated by precipitation resulting from the addition of the reaction mixture to methanol/water (4:1, v/v), and dried under vacuum at room temperature overnight.

 PAN_{103} -*b*-PBA₆₀ block copolymer (BCP) was synthesized by a supplemental activator and reducing agent atom transfer radical polymerization (SARA ATRP) developed previously.^{32,33} Using this approach, 5 g (0.9 mmol, 1 equiv.) of PAN-Br macroinitiator (Mn, NMR = 5600) was dissolved in 50 mL of DMF. The solution was then added to a 100 mL Schlenk flask containing 1.5 mg of CuBr₂ (0.0067 mmol, 0.0075 equiv) and 5.8 mg of TPMA (0.02 mmol, 0.0225 equiv) and bubbled with nitrogen for 20 min. Then, 19 mL of deoxygenated BA (134 mmol, 150 equiv) was carefully added under vigorous stirring to prevent PAN precipitation. Cu wire (8 cm length x 1 mm diameter), previously cleaned with HCl/MeOH solution (1:1, v/v), was added to start polymerization at room temperature. The reaction was stopped after 4.2 h, with the conversion reaching 40%. The resulting block copolymer was precipitated by adding the reaction solution to methanol/water (6:4, v/v), then it was filtered and dried under vacuum overnight.

Preparation of CTNC-Fe Čatalyst. PAN₁₀₃-*b*-PBA₆₀ BCP was stabilized in air at 280 °C for 1 h, and then it was ball-milled for 90 min. Then, 90 mg of ball-milled, stabilized BCP was mixed in 5 mL of ultrapure water with 18.0 mg of FeSO₄·7H₂O and was stirred for 12 h. The solution was then heated to 80 °C and stirred for an additional 2 h until water fully evaporated. The dry mixture was further dried for 4 h in air at 60 °C, and then it was heat-treated at 600 °C for 0.5 h in 50

mL/min N₂ flow. The resulting product was ground in an agate mortar for 10 min, then it was mixed into a 0.5 M H₂SO₄ solution at 80 °C and was stirred for 2 h. Afterward, it was extracted using a vacuum filter and then was thoroughly rinsed with ultrapure water followed by being dried in 60 °C air for 4 h. Finally, the product was heat-treated a second time in 100 mL/min N₂ flow at 900 °C for 3 h to complete the CTNC-Fe catalyst preparation. Pristine CTNC was made from stabilized BCP heat-treated at 600 °C for 30 min and then at 900 °C for 3 h under nitrogen flow.

Testing the Electrochemical Activity. Measurements of the electrochemical activity were captured using rotary disk electrode (RDE) potentiometry. An ink was prepared using 5 mg of the catalyst with 40 μ L of 5% Nafion solution in alcohol dissolved in 0.5 mL of *n*-propanol. The ink was sonicated in an ice bath for 1 h, and an aliquot of 17 μ L was cast onto the glassy carbon electrode for a 0.8 mg/cm² catalyst loading. A 0.5 M sulfuric acid solution at room temperature with a mercury/mercurous sulfate reference electrode and a graphite counter electrode was used. Cyclic voltammetry was implemented from 0 to 1 V (vs normal hydrogen electrode (NHE)) in 50 mV/s steps at 200 rpm in nitrogen flow, and chronoamperometry scans were captured at 50 mV/30 s steps at 900 rpm under oxygen flow.

Materials Characterization. The polymer solution monomer conversion rate was tested at different times during the polymerization process to ensure proper controlled/"living" radical polymerization using proton nuclear magnetic resonance (¹H NMR). Polymer molecular mass and distribution was tested using gel permeation chromatography (GPC) equipped with a Wyatt Optilab T-rEX refractive index (RI) detector, using DMF as the mobile phase. The carbon and nitrogen contents of the catalyst were found by volatilization of the catalyst and separately measuring the evaporated nitrogen and carbon products; this analysis was performed by Midwest Micro Lab and was used to accurately estimate the total amounts of N in the sample. Iron content was determined by energy dispersive spectroscopy (EDS) using a Quanta 600 scanning electron microscope. The nature of the bonding of heteroatoms in the carbon matrix was determined using X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD), and the surface area and pore size were measured using Brunauer-Emmett-Teller (BET) surface area analysis. Powder samples were first degassed at 120 $^\circ C$ for at least 4 h before N₂ sorption measurement. The micropores were analyzed using the *t*-plot method with the Halsey equation. The slope of the *t*plot was used to calculate the external SSA, while the micropore surface area (S_{micro}) was obtained from subtracting $S_{external}$ from S_{BET} . The mesoporous size distribution was obtained from Barett-Joyner-Halenda (BJH) method from the adsorption branch with KJS correction. Finally, the presence of mesopores was tested using a JEOL JEM 2000EX transmission electron microscope (TEM).

Fuel Cell Testing. The catalyst ink was prepared in a 9:1 isopropanol and water solvent mixture with an ionomer to catalyst ratio of 0.6:1 and a solvent to ionomer ratio of 59:1. The ink was sonicated in an ice bath for 2 h and then blade-coated onto a Freudenberg H23C6 gas diffusion layer with a loading of 4 mg/cm²; this served as the cathode. A commercially available 10% Pt/C gas diffusion electrode with a 0.3 mg_{Pt}/cm² loading was used for the anode. Both electrodes were hot-pressed onto a Nafion 212 membrane at a temperature of 130 °C and a pressure of 2.7 MPa to create the membrane electrode assembly (MEA).

The MEA was installed into commercial 5 cm² fuel cell hardware connected to a fuel cell stand for gas delivery and cell heating (Scribner Associates Inc., Southern Pines, NC). A BioLogic VSP potentiostat was used to perform the polarization tests to characterize the fuel cell's overall performance. The cell was conditioned by purging with nitrogen on both the anode and the cathode at 100% relative humidity, 80 °C temperature, and 50 kPa backpressure for 2 h. For cyclic voltammetry, the gas flow in the anode was switched to 200 mL/min, and for the polarization test, the cathode gas flow was switched to 1 L/min of oxygen, both with 100% relative humidity and 50 kPa backpressure. Each voltage step was held for 30 s and then averaged from the last 10 s of current readings during analysis.



Figure 1. (a) ¹H NMR spectrum and (b) GPC trace of PAN₁₀₃-*b*-PBA₆₀ block copolymer. PMMA calibration with DMF as the solvent was used to analyze the GPC curve, and d_{6} -DMSO was used for ¹H NMR.



Figure 2. TEM photographs of pristine CTNC and CTNC-Fe catalysts at different stages during synthesis. (a) Pristine CTNC (P-CTNC), (b) CTNC-Fe catalyst, (c) CTNC-Fe after first heat treatment at 600 °C, and (d) CTNC-Fe after acid treatment.

RESULTS AND DISCUSSION

Morphology and Porosity of the Catalyst. ATRP was utilized to prepare PAN-*b*-PBA BCP with <100 ppm Cu catalyst.⁶³ Figure 1a demonstrates that the composition of the BCP is PAN₁₀₃-*b*-PBA₆₀ by integration of peaks b and e. GPC trace (Figure 1b) shows a low molecular weight distribution $(M_w/M_n = 1.24)$, manifesting strong control over polymerization.

The pristine CTNC obtained from the stabilized block copolymer (Figure 2a) was characterized as an isotropic structure of interconnected pores and channels. The CTNC-Fe catalyst in Figure 2b (Figure S1 shows TEM images at lower magnification) shows that the interconnected pores were largely retained, and the mesoporous structure of the CTNC base was unaffected. Further analysis was performed throughout the synthesis of the catalyst: one, after the first heat treatment at 600 $^{\circ}$ C (Figure 2c) and another, after acid treatment (Figure 2d). Figure 2d shows less uniformity in the nanostructure, which is likely due to residues from the acid treatment clogging the porous structure.

This was corroborated by BET surface area analysis, which shows that CTNC-Fe after the acid treatment (CTNC-Fe-AT) had a surface area of approximately half of the completed CTNC-Fe catalyst (Table 1).

Figure S2 displays the BET N_2 adsorption-desorption isotherms and pore width distribution of different CTNC samples during the synthesis process. The CTNC-Fe appears to undergo surface activation due to the acid treatment and heat treatment at 900 °C since the mesoporous surface area remains almost completely unchanged (227 m²/g after the first Table 1. BET Surface Area Analysis Results for CTNC-Fe Catalyst After First Heat Treatment (CTNC-Fe-600), After Acid Treatment (CTNC-Fe-AT), and After Completion of the Synthesis Process (CTNC-Fe)^a

sample	total surfa area (m²/s	ce micropor g) (m²/g)	$me mesopore (m^2/g)$	average pore size (nm)
CTNC-Fe	395.8	164.7	231.1	8.10
CTNC-Fe-600	332.7	105.7	227.0	8.67
CTNC-Fe-AT	183.1	34.6	148.6	9.58
P-CTNC-600	392.7	158.9	233.8	9.36
P-CTNC	528.6	276.4	252.2	8.72
^a P-CTNC-600	is pristine	CTNC with	similar heat	treatment to

CTNC-Fe-600, and P-CTNC has similar heat treatment to CTNC-Fe.

heat treatment and 231.1 m^2/g after the second heat treatment). However, Fe-doping only had minor effects on the nitrogen sorption isotherms (Figure 3a and Table 1) and the pore size distribution (Figure 3b). In addition, the average pore size of the CTNC-Fe catalyst is approximately the same as P-CTNC at similar heat treatment conditions (Table 1), despite the total surface area of CTNC-Fe being ca. 25% less than that of P-CTNC.

As observed in Table 1, the difference in the surface area was mostly in the microporous region. This suggests that the addition of the iron precursor mainly affected the micropores, leaving the mesoporous region largely intact. The decrease in the surface area of micropores could potentially affect mass transport, leading to excessive overpotential in the performance of the catalyst. However, as seen in Table 1, the acid treatment has a surface activation effect without significantly affecting the mesoporous region (when comparing CTNC-Fe to CTNC-Fe-600). Therefore, it is likely that a controlled amount of surface activation could negate the reduction of surface area effects caused by the introduction of iron to CTNC.

Elemental Analysis and the Influence of Fe-Doping. The nitrogen and iron species present in CTNC-Fe were analyzed by high-resolution XPS (Figure 4). For the N 1s XPS signal (Figure 4a), three main peaks at 399 eV (25.7 atom %), 401.1 eV (48.8 atom %), and 403 eV (25.4 atom %) were observed. The peak at 403 eV can be identified as oxidized N^{54,60,6454,60,64} and the peak at 401.2 eV can either represent pyrrolic/quaternary N^{54,60} or graphitic N.⁶⁴ The peak with the binding energy of 399 eV was identified as either N–Fe

moeities^{49,52,64} or pyridinic N.^{53,54} According to the N 1s XPS spectra obtained from P-CTNC (Figure S3d), the pyridinic N peak for this material is 398.6 eV. Thus, the 399 eV peak in CTNC-Fe in Figure 4a is likely related to either N-Fe moieties, the Fe being coordinated by pyridinic N, or there is a mixture of N-Fe and pyridinic N. The same can be said for the pyrrolic/graphitic N peak as it manifests at 400.8 eV in P-CTNC (Figure S3d). The presence of Fe in CTNC-Fe increased the deconvoluted peak energy values of pyridinic N and pyrrolic/graphitic N \sim 0.4 eV, which means it is likely that N-Fe moieties are composed of not only pyridinic N but also graphitic and pyrrolic N.65 Furthermore, the atom percent of pyrrolic and graphitic N is almost double that of pyridinic N as seen in Table S1. Therefore, even if it was less energetically favorable for Fe to interact with graphitic and pyrrolic N to form FeN_x-active sites than it is with pyridinic N, the greater concentration of these N species would make up for it.

Fe 2p spectra showed four peaks at 710.8, 715.4, 724, and 729.3 eV upon deconvolution. The two lower peaks at 710.8 and 715.4 eV pertain to Fe $2p_{3/2}$. The binding energy of the main peak and satellite peak indicated that the catalyst contains both Fe²⁺ and Fe³⁺ with a larger fraction of Fe²⁺, as shown by the higher intensity of the lower energy peaks.^{46,61} The two higher binding energy peaks at 724 and 729.3 eV represent Fe $2p_{1/2}$, which represents a smaller fraction of Fe³⁺.⁴⁹ This mix of oxidation states is likely a result of the following processes. On one hand, the highly oxidative H₂SO₄ during the synthesis of CTNC-Fe could possibly oxidize Fe²⁺ to Fe³⁺. On the other hand, the N-rich graphitic carbon could provide a reducing environment to regenerate Fe²⁺ from the newly formed Fe³⁺ species.

The elemental composition was also analyzed by dispersive X-ray electron spectroscopy (EDS, Figure S4) and combustion-based elemental analysis. As seen in Table 2, less than 0.5 wt % iron in CTNC-Fe catalyst was detected according to XPS, whereas EDS showed a value of 12.04 wt % Fe in the catalyst. Considering that EDS has substantially greater penetration depth than XPS, this discrepancy would suggest that either most of the Fe is trapped in the carbon matrix or is too deep inside the mesoporous structure for the XPS signal to be detected. Figure 5 shows that there are many massive particles close to and above 10 μ m in diameter, which would indeed make it difficult for XPS to detect Fe. Furthermore, according to the EDS elemental analysis in Table 2, acid treatment significantly reduced the Fe content from 12.18 wt % in CTNC-Fe-600 to 7.17 wt % in CTNC-Fe-AT. Since the



Figure 3. BET surface area analysis results for CTNC-Fe catalyst and pristine CTNC (P-CTNC) heat-treated at similar conditions. (a) Nitrogen adsorption–desorption isotherms at –196 °C and (b) pore size distribution.



Figure 4. High-resolution XPS spectra of CTNC-Fe for (a) N 1s and (b) Fe 2p. The peak shape of Gaussian/Lorentzian convolution functions was used for the fitting, with a L/G mix ratio of 30% for all peaks.

Table 2. Elemental Composition of CTNC-Fe Catalyst	
Throughout the Synthesis Process and Pristine CTNC	

analysis type	sample	N (wt %)	Fe (wt %)	C (wt %)	S (wt %)
XPS	CTNC-Fe	4.2	< 0.5	95.8	0
	CTNC-Fe-600	10.8	< 0.5	89.2	0
	CTNC-Fe-AT	14.2	< 0.5	84.1	1.7
	P-CTNC	3.2	0	95.5	0
	P-CTNC-600	13.7	0	86.3	0
EDS	CTNC-Fe	1.4	12.04	83.5	1.45
	CTNC-Fe-600	7.11	12.18	76.23	1.95
	CTNC-Fe-AT	8.73	7.17	75.99	3.42
elemental	CTNC-Fe	5.3		82.6	
analysis	CTNC-Fe-600	16.5		63.6	
	CTNC-Fe-AT	16.1		62.6	

carbon content remained similar during the acid treatment, it can be inferred that \sim 40% of Fe initially included in the CTNC-Fe mixture during synthesis formed metallic Fe and other unstable species that were washed away by the acid treatment.

In addition, a comparison of N content between XPS and the results obtained by gasification elemental analysis shows that the nitrogen present in CTNC-Fe is not completely present in the surface of the catalyst. There is some noticeable, if not substantially significant, amount of nitrogen that remains trapped in the carbon matrix. To improve on this catalyst, the method of synthesis will need to be adjusted so that CTNC-Fe is able to retain more of the nitrogen content when heattreated at higher temperatures than 600 $^{\circ}\mathrm{C}$ and to affect N heteroatom migration from the bulk of the carbon to the surface.

Regarding S content, there was none detected by XPS except in the case of CTNC-Fe after acid treatment with sulfuric acid, which is attributed to remnants from the acid treatment (Figure S5). As observed with Fe, EDS analysis showed a significantly higher S content in the catalyst (Figure S4), which points to sulfur being either trapped in the carbon matrix at a depth outside the range of XPS or deep inside the mesoporous structure that cannot be accessed due to CTNC-Fe particle size. This is supported by the lower surface area value of CTNC-Fe-AT, the catalyst tested right after the acid treatments, which suggests that there are some trapped residues from the acid washing that remain before the final heat treatment at 900 °C. Since S content decreases after the final heat treatment, it is likely that these trapped residues were volatilized during the heat treatment.

Moreover, high-resolution XPS spectra for C 1s produced two deconvoluted peaks at 285.2 eV (84.0 atom %) and 288.7 eV (16.0 atom %), which can be attributed to a mixture of graphitic and amorphous carbon for the former, more likely graphitic according to Lesiak et al.,⁶⁶ and for more complex coordination involving Fe, N, and O for the latter. The value of graphitic carbon for CTNC-Fe was only slightly lower than pristine CTNC, as seen in Figure S6 and Table S2. Therefore, we conclude that the addition of an iron precursor, in this case FeSO₄, had little effect on the chemical structure of the carbon.



Figure 5. SEM photograph scans of the particle size and structure of (a) P-CTNC and (b) CTNC-Fe.

Addition of iron to CTNC also had a pronounced effect on the XRD patterns of CTNC-Fe (Figure 6) compared to



Figure 6. XRD profile of CTNC-Fe catalyst with labeled diffraction peaks for detecting π -stacking of nanographitic platelets (002) and assessing their lateral size (100).

pristine CTNC.³³ Although the Bragg peaks at 25, 44.3, and 82° (peaks associated with the presence of nanographitic structures commonly observed in pyrolytic carbons⁶⁷) are still present, the one at 25° almost completely disappeared. We observed additional peaks at 38.5, 65.3, and 78.3°, which are likely associated with iron oxide particles or other type of crystallites such as FeS or CFe_{15.1}.⁴⁹ Analysis of the basal plane crystallite sizes calculated from the width of the (100) peak using the Scherrer equation⁶⁸ produced a value of 4.6 nm for the carbon crystallite sizes.

Electrochemical Activity and Fuel Cell Performance. Although, to this point, only one type of CTNC (obtained from the PBA_{60} -*b*-PAN₁₀₃ copolymer) was tested, we have been able to design a synthesis process that produces CTNC-Fe catalyst with significant electrochemical activity (Figure 7). CTNC-Fe also served as a PGM-free catalyst for hydrogen fuel cells (Figure 8). The best sample obtained to date has achieved a half-wave potential of 0.781 V vs NHE with a limiting current density of ~3.5 mA/cm², as seen in Figure 7a. As with some of

the characterization techniques used, we measured the electrochemical activity of the catalyst at different steps of the synthesis process. The half-wave potential for CTNC-Fe-600 was 0.631 V vs NHE, which is likely related to the low heat treatment temperature (600 °C) that resulted in insufficient electrical conductivity. However, the half-wave potential increases to 0.706 V vs NHE after the acid treatment (CTNC-Fe-AT). It is uncertain what may cause this effect since the actual surface area decreases according to the BET results seen in Table 1. In addition, Figure 7b shows a similar capacitive surface area response as noted from the cyclic voltammetry curves showing negligible differences. Therefore, it is likely that the increase in electrochemical activity from CTNC-Fe-600 to CTNC-Fe-AT might be due to the increase in surface-exposed nitrogen, as shown by the XPS results in Table 2. Corrosion of the carbon by the acid treatment is likely the source of the increase in surface-exposed nitrogen, which is lost to volatilization after the final heat treatment at 900 °C. This behavior is inherent to CTNC materials, as observed by Zhong et al.³⁴

The open-circuit voltage for the fuel cell using pure oxygen flow reached 0.881 V. In terms of activity, the fuel cell was able to reach an activity of 17.9 mA/cm² (4.38 A/g) at a cell voltage of 0.8 V and 83.8 mA/cm² (20.85 A/g) at 0.7 V, in addition to maximum power densities of 180 mW/cm² with pure oxygen flow in the cathode (Figure 8a) and 105 mW/cm² with airflow (Figure 8b). This was achieved despite the large particle sizes shown in the SEM images from Figure 5, which produced an electrode thickness of 78.3 μ m, which is the likely cause of large ohmic overpotential issues. This is shown by the potentiostatic electrochemical impedance spectroscopy curve (Figure S7), which produced a high-frequency resistance (HFR) of 0.065 Ω due to contact resistance. This value is significantly higher than the expected 0.01 Ω proton conduction resistance of the Nafion 212 membrane. Furthermore, the apparent resistance of the fuel cell, obtained by calculating the slope of the IV curve in the linear (Ohmic) region, was 0.15 Ω , which is 3 times the measured HFR. High apparent ohmic resistances in PGM-free cathode fuel cell polarization curves are often due to a liquid water-saturated cathode in which the proton conduction across the flooded catalyst layer to the active zone at the hydrophobic MPL interface leads to a large ohmic loss that is not captured by EIS due to the electrode capacitance.69



Figure 7. Electrochemical activity results on ORR of the CTNC-Fe catalyst tested at different steps in the synthesis process. (a) Polarization curve of ORR in acidic environment obtained using chronoamperometry scans in oxygen-saturated 0.5 M H_2SO_4 solution at room temperature. (b) Cyclic voltammetry curve obtained in nitrogen-saturated 0.5 M H_2SO_4 solution at room temperature.



Figure 8. Results of fuel cell tests performed using a 4 mg/cm² CTNC-Fe cathode and a 0.3 mg/cm² anode at 80 °C, 100% relative humidity, and 50 kPa backpressure hydrogen in the anode and either (a) 100% relative humidity, 50 kPa backpressure oxygen or (b) 100% relative humidity, 50 kPa backpressure air in the anode.

Furthermore, as seen in Figure S8, the capacitive surface area of the electrode, according to the cyclic voltammetry curve of the fuel cell, showed a value of 238.7 m²/g. This is significantly lower than the surface area value obtained using BET and no doubt led a small fraction of macropore formation, which could be a cause of flooding.⁶⁹ Considering these fuel cell testing results, a key area of future work is the control of the catalyst aggregate size, with a smaller, more uniform distribution of catalyst aggregate sizes. Conversely, perhaps a different amount of ionomer and a CTNC-Fe catalyst-optimized method of electrode preparation would produce higher fuel cell performance. Future work will include experimentation with CTNC-Fe electrode composition, thickness, and assembling in MEA.

While the electrochemical activity of CTNC-Fe is not the highest when compared to other catalysts currently under development, its half-wave potential is higher than average.⁶⁹ In addition, CTNC-Fe is at an early stage of development compared to current top PGM-free catalysts. For example, the CM + PANI-Fe-C(Zn) catalyst mentioned in Table 2 in Beltrán et al.⁷⁰ has a half-wave potential of 0.83 V vs NHE as of 2017. However, at the beginning of its development in 2008, the half-wave potential was ~ 0.75 V vs NHE.⁷¹ Likewise, metal organic framework-derived PGM-free catalysts currently reach some of the highest electrochemical activities above 0.85 V vs NHE according to recent work;⁷² however, in 2010, when the catalyst was first reported,⁴ the catalyst had a half-wave potential of 0.77 vs NHE. On the other hand, commercial catalysts such as those based on silica templating,⁷³ have low half-wave potentials (around 0.7 V vs NHE) but have great stability and durability.⁷³ Therefore, CTNC-Fe is very well on its way as our group continues to experiment on it.

CONCLUSIONS

The PGM-free catalyst, CTNC-Fe, was synthesized by Fedoping a copolymer-templated nitrogen-rich carbon obtained from the copolymer PAN₁₀₃-*b*-PBA₆₀. The copolymer was the base of the catalyst, where the PAN phase was the source of carbon and nitrogen, and the PBA phase acted as a sacrificial component to generate a mesoporous structure. The nanostructure was controlled by the length and ratio of lengths of the polymer blocks to produce a bicontinuous morphology with an interconnected pore nanostructure. The morphology of the catalyst mesoporous structure was confirmed using BET surface area analysis and TEM, and the composition and presence of FeN_x were analyzed by use of EDS and XPS. RDE potentiometry was used to test the n^2)

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electrochemical activity of the catalyst in an acidic environment, and a fuel cell test with oxygen/air flows in the cathode and hydrogen gas flow in the anode was used to confirm its feasibility as an actual fuel cell catalyst. The catalyst achieved a 0.781 V vs NHE half-wave potential, and the fuel cell produced a maximum power of 180 mW/cm², which proved that the catalyst could perform ORR in a proton exchange membrane fuel cell. Further research on this topic is expected to continue improving on CTNC-Fe, as it has done to its present state. Possible areas of future improvement on CTNC-Fe catalyst are the issue of particle size, nitrogen retention at heat treatment temperatures over 600 °C, and increase in pore surface area either by chemical treatment surface activation or by manipulation of the polymer blocks to produce a more efficient pore structure. This last method specifically makes use of CTNC as a base for an Fe-N-C catalyst, a unique and novel undertaking not limited to affecting mass transport in fuel cell operation but also by the effects of pore structure on the formation of Fe–N moieties, which serve as catalytic active sites as theorized in previous works.^{74,75} By studying the effects of minor changes in pore size and structure afforded by the fine control and tunability of CTNC with the use of controlled/ living radical polymerization methods on the formation of active sites and electrochemical activity of CTNC-Fe, we aim to design a catalyst that may eventually reach the goal of matching and even surpassing the electrochemical activity of platinum group metal catalysts.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsaem.1c01769.

TEM scan photographs of CTNC-Fe during various stages of the synthesis process; BET surface area analysis results; high-resolution N 1s XPS spectra; nitrogen species amounts calculated from N 1s XPS spectra; EDS map of CTNC-Fe; XPS S 2p spectra; XPS C 1s spectra; XPS C 1s deconvoluted peaks analysis; fuel cell PEIS; fuel cell CV; and chronoamperometry raw data (PDF)

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Author Contributions

R.M.T. contributed the most to writing the manuscript, designing and synthesizing the catalyst, and testing all samples. M.S. contributed by the synthesis of the copolymer, performing TEM and BET operations, and analyzing XPS results. R.Y. contributed by the synthesis of copolymers and on the part of the manuscript about polymer synthesis. M.A. contributed by performing a fuel cell test.

Notes

The authors declare no competing financial interest.

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