Supplementary Information

Facile Construction of Non-Precious Iron nitride-Doped Carbon Nanofibers as Cathode Electrocatalysts for Proton Exchange Membrane Fuel Cells

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Experimental Section

Synthesis of Catalyst: For all the catalysts in this work, we have used commercially obtained carbon nanofiber (CNF) as the support material and iron acetate (FeAc) (Rankem), 1, 10-phenanthroline (phen) (Aldrich 99%) as the Fe and nitrogen precursors respectively. The surface area and average pore radius of the CNF are approximately 45 m^2/g and 16 Å respectively as evident from the N₂ sorption studies (Fig. S13). In a typical synthesis of iron nitride-doped CNF (FeN_xCNF), appropriate amount of CNF was dispersed in 50 ml of ethanol (Rankem 99.9%) by ultrasonication. An excess of phen was dissolved in 25 ml of ethanol and was allowed to fill the inner pore of CNF by magnetic stirring for about 30 min. Further the required amount of FeAc in ethanol was added drop by drop to phen in CNF mixture. The weight percentage of Fe was maintained about 0.5 %. The FeAc reacted with phen to form Fe [(phen) $_3$]²⁺ chelate complex which was confirmed from the color change from pale yellow to wine red. Subsequently, the chelate

complex solution was mechanically stirred for 24 h at room temperature to achieve better diffusion of iron chelate complex into the inner pore through the open ends of the CNF. The resulting mixture was placed in a beaker on an oven and the solvent was evaporated at 50 °C for about 3 h. The resulting solid material was placed in a quartz tube and pyrolysed in Ar atmosphere at 900 °C. The temperature ramp was 10 °C per minute till it reaches 900 °C and maintained at that temperature for 3 h with an Ar flow of 0.5 sccm. While heating, when the temperature reaches around 350 °C, greenish vapors came out via the outlet which indicates the decomposition of phen in the reaction mixture. This was allowed to cool to room temperature after pyrolysis with Ar flow. The pyrolysed product is then washed with ethanol, filtered (filter paper 0.2 μ m pore size, Rankem) to remove the chars of organic residues. The final product was dried at 100 °C for 2 h and preserved for further study. We have prepared a series of catalysts with same experimental conditions in which the weight percentage of Fe was varied from 1, 2 and 5 which are represented as FeN_xCNF1, FeN_xCNF2 and FeN_xCNF5 respectively along with the 0.5 wt% FeN_xCNF. The nitrogen-doped CNF (N-CNF) was also prepared by the same experimental procedure without the addition of Fe precursor. For comparison, we have also prepared a 10 wt% PtCNF catalyst, where Pt was decorated selectively on the inner wall of CNF, by an in-house developed polyol process.

Structural Characterization

The X-ray diffraction patterns (XRD) of the prepared catalysts were obtained by using PANalytical X'pert Pro instrument. All data were collected with the scan rate of 0.5° per min using Cu K α (1.5418 Å) radiation. The structure and morphology of the catalysts were characterized by using a High Resolution Transmission Electron

Microscope (HR-TEM) FEI model TECNAI G² F30 instrument operated at an accelerating voltage of 300 kV (Cs = 0.6 mm, resolution 1.7 Å). TEM samples were prepared by suspending the prepared catalysts in ethanol and then placing a drop of the suspension on a 200 mesh copper grid coated with carbon film (ICON Analytical), dried in vacuum for overnight, and loaded in electron microscope chamber. Energy dispersive X-ray analysis (EDX) measurements were performed on a scanning electron microscope (SEM) system (FEI, Model Quanta 200 3D) equipped with EDX attachment at an operating potential of 30 kV. X-ray photoelectron spectroscopy (XPS) was done on a VG Microtech Multilab ESCA 3000 spectrometer that was equipped with an Mg Ka X-ray source (hv = 1253.6 eV). Raman analysis of CNF, N-CNF and FeN_xCNF were performed on an HR 800 Raman spectrometer (Jobin Yvon, Horiba, France) using 632.8 nm green laser (NRS 1500 W) in order to obtain the effect of oxidation and reduction. Nitrogen adsorption-desorption experiments were conducted at 77 K using Quantachrome Quadrasorb automatic volumetric instrument. Ultra pure N2 (99.9995%) was purified further by using calcium aluminosilicate adsorbents to remove trace amounts of water and other impurities before introduction into the system. For measurements at 77 K, a standard low-temperature liquid nitrogen Dewar vessel was used. Before gas adsorption measurements, the sample was activated at room temperature (for 24 h) and 100 °C (for 36 h) under ultrahigh vacuum (10⁻⁸ mbar) overnight. About 50 mg of samples were loaded for gas adsorption, and the weight of each sample was recorded before and after out gassing to confirm complete removal of all guest molecules including the coordinated H₂O in CNF, N-CNF and FeN_xCNF.

Electrochemical studies

All electrochemical studies were performed on an Autolab PGSTAT 30 (Ecochemie) using conventional three electrode test cell received from Pine Instruments. Ag/AgCl (4M KCl) and Pt wire were used as reference and counter electrodes respectively. A glassy carbon (GC) electrode (5 mm diameter) embedded in Teflon was used as the working electrode, which was polished on a polishing cloth using 0.3 μ m alumina slurry followed by washing with water and acetone. The working electrode was prepared as follows: 5 mg of total catalyst was dispersed in 1 ml of ethanol in water (3:2) solution by sonication. 10 μ L from the prepared slurry was drop casted on the GC electrode with the help of micro syringe, followed by 3 μ L of 0.1 % Nafion[®] solution in ethanol was coated to get uniform layer and to protect the detachment of catalyst. This electrode was further dried in air for 3 h and was used as the working electrode. 0.5 M HClO₄ was used as the electrolyte for all the cyclic voltammetry (CV), chronoamperometric (CA) and rotating disc electrode (RDE) studies. All the CV experiments were carried out at a scan rate of 5 mV/s whereas all the RDE experiments were carried out at a scan rate of 10 mV/s. Chronoamperometric (CA) measurements where carried out by changing the initial potential from 0.7 V to a potential (0.16 V and 0.43 V for N-CNF and FeN_xCNF respectively) where the ORR catalytic activity was observed before and after lifetime studies by potential cycling. Oxygen and Argon were used to achieve Oxygen rich and Oxygen free environments respectively for the RDE experiments. The electrical conductivity measurements of CNF and nitrogen doped

composite catalysts were carried out in a four probe set-up by measuring the resistivity of the pellets made from the above samples at room temperature.

Results:





Fig. S1: Full range XPS survey of N-CNF and FeN_xCNF.

The elemental surface compositions of N-CNF and FeN_xCNF were evaluated using XPS. The full range XPS survey spectra of N-CNF and FeN_xCNF are shown in Fig. S1, where the presence of Carbon, Oxygen (O), Nitrogen (N) and Fe can be clearly seen in the wide spectra. The main peak at 284.3 eV responsible for sp^2 -carbon which indicates most of the carbons are in graphitic nature. The additional peak at 398 eV, 532 eV and 702 eV are corresponding to nitrogen, oxygen and Fe respectively. The peak for O arises mainly due to the adsorbed oxygen at the surface of CNF. In case of N-CNF there is a small peak for iron around 702 eV which may be due to metal impurity of CNF.





Fig. S2: EDX spectrum of (a) N-CNF (b) FeN_xCNF showing 4.79 % of nitrogen doping in the N-CNF and 3.93 % of nitrogen doing in the FeN_xCNF .

EDX Quantification of N-CNF

Elem Wt % At % K-Ratio Z A F C K 87.11 89.53 0.7406 1.0015 0.8489 1.0001 N K 4.79 4.22 0.0036 0.9941 0.0760 1.0001 O K 8.10 6.25 0.0090 0.9875 0.1129 1.0000 Total 100.00 100.00

EDX Quantification of FeN_xCNF

Elem	Wt %	At %	K-Ratio	Ζ	А	F	
C K	92.66	94.20	0.8403	1.0012	0.9057	1.0001	
N K	3.93	3.43	0.0028	0.9938	0.0719	1.0000	
O K	2.98	2.27	0.0032	0.9872	0.1084	1.0000	
FeK	0.42	0.09	0.0038	0.8520	1.0616	1.0000	
Total	100.00	100.00					





Fig. S3: Comparison of a) Fe 2p spectra of N-CNF and b) FeN_xCNF.

Since the impurity iron content is negligible in N-CNF, Fe 2p spectra could not be deconvoluted into sub peeks (shown in Figure S3a). The Fe 2p spectra of FeN_xCNF (Figure S3b) are deconvoluted into four peaks. The peak located at low binding energy 706.8 e V is assigned as Fe₁ corresponds to metallic iron or iron carbide (Fe 2p_{3/2}) indicating the presence of trace amount of iron carbide. The pair of peaks at 708.8 and 710.8 eV correspond to the ionic state of iron (Fe 2p_{1/2}) revealing that most of the iron is coordinated with the nitrogen atom.





Fig. S4: XRD patterns of CNF, N-CNF and FeN_xCNF.





Fig. S5: XRD patterns of various catalysts with different weight percentage of Fe.

The arrow indicates the growth of iron carbide (Fe₃C) with increased weight percentage of Fe in the catalyst. It seems only at percentages higher than that of FeN_xCNF 1, the iron carbide formation occurs as observed from the XRD patterns in Fig. S5.





Fig. S6: Raman spectra of CNF, N-CNF and FeN_xCNF.

Raman spectral analysis has been carried out in order to determine the structural changes or defects of the nitrogen-doped composite catalysts. There are two distinct peaks observed for the CNF as well as nitrogen-doped composite catalyst. The graphitic peak (G band) at 1565-1560 cm⁻¹ is due to E_{2g} vibrational mode of the C-C bond stretching and the disorder peak (D-band) at 1310-1330 cm⁻¹ is due to A_{1g} vibrational mode. The intensity ratio of the D-band and G-band, the I_D/I_G ratio estimates the degree of disorder of the carbon matrix and the higher ratio values signifies the more defects present in the carbon matrix. The I_D/I_G ratios of FeN_xCNF and N-CNF have been calculated from the Raman spectra and found to have values as 0.644 and 0.574

respectively, which is significantly higher than the I_D/I_G ratio of CNF (0.456) ensures higher defects present in the nitrogen-doped composite catalysts due to the effective nitrogen doping. This conclusion is well in agreement with the conclusions derived from XRD, XPS and HR-TEM analysis. Figure S7:



Fig. S7: (a) High-resolution TEM image of N-CNF (b) Highlighted portion of side wall of N-CNF.

Figure S8:



Fig. S8: (a) and (b) High-resolution TEM images of pristine CNF (the blue circle indicates the open tips of CNF (c) Pyrolysed FeN_xCNF before washing (d) after washing with ethanol.

The High-Resolution TEM images are shown in Fig. 8 (a) and (b), where the blue circle indicates the open end of CNF. The presence of organic residues (indicated by black arrows) can be seen clearly in the inner pore of pyrolised product of FeN_xCNF (Fig. S8c). After washing the catalyst with ethanol, these residues are completely eradicated from the catalyst (Fig. S8d). It reveals the formation of active site selectively in the inner pore of the FeN_xCNF . In both the case, there are some dark particles indicating the presence of metal (Fe) impurities in CNF.



Figure S9:

Fig. S9: Pore size distribution plot of (a) CNF (b) FeN_xCNF .

The surface area and pore size distribution of the nitrogen-doped composite catalysts and CNF are measured by nitrogen adsorption-desorption method. The surface area of the FeN_xCNF is smaller than the surface area of CNF, indicating occupancy of the active sites by the FeN_x moiety. The pore size distribution profile of bare CNF indicated distribution of pores possessing various size levels of few angstroms on the surface, possibly might have originated due to the stacking of slanting graphene layers with terminal edges. This stacking creates slit pores and edge sites mostly along the inner wall of the substrate. It is clearly visible from the figure that the peaks corresponding to each

pore size distribution decrease when the FeN_x moiety occupies the surface (FeN_xCNF), which supplements the conclusion that the geometric feature of the surface played a major role in anchoring the active sites. The surface area values of all the catalysts are tabulated in Table S1.

Catalyst	Surface Area (m ² /g)
CNF	45.09
N-CNF	58.33
FeN _x CNF	35.58

Table S1:



Figure S10:

Fig. S10: Electrochemical stability measurements of (a) N-CNF (b) FeN_xCNF by Cyclic Voltammetry in 0.5 M HClO₄ at a scan rate of 5 mV/s.



Figure S11:

Fig. S11: Chronoamperometry measurements of CNF, N-CNF (before and after durability measurements) and FeN_xCNF (before and after durability measurements).

Chronoamperometric (CA) measurements have been carried out to study the stability of the nitrogen-doped composite catalyst by changing the initial potential from 0.7 V to a potential 0.16 V and 0.43 V for N-CNF and FeN_xCNF respectively for 1000 s, where the system displayed maximum ORR activity. The experiment was performed both before and after lifetime studies by potential cycling. The CA studies show after initial fall in current by few micro amperes, the systems displayed more less stable performance. Potential cycle over a period of ~5 h did not induce significant change in the performance of both in the case of N-CNF and FeN_xCNF, indicating good electrochemical stability of the systems.

Conductivity measurements

The electrical conductivity of nitrogen doped composite catalysts and CNF have been calculated by measuring the resistivity of the catalysts using following equation.

$$K = 1/\rho$$
 ------(1)

$$\rho = \rho_0 / G_7 (W/S)$$
 ------ (2)

 $\rho_{o} = (V/I) 2\pi S$ ------(3)

Where,

K - Conductivity

 ρ – Resistivity

 ρ_o – Specific resistance

- W Thickness of the pellet
- S Distance between two probes
- G7-Correction factor

V - Voltage

I – Current.

The measured conductivity of CNF and nitrogen based composite catalysts is tabulated in Table S2.

Table: S2

Catalyst	Conductivity (Scm ⁻¹⁾
CNF	0.55
N-CNF	4.34
FeN _x CNF	29.42



Figure S12:

Fig. S12: Koutecky - Levich plots of CNF, N-CNF and FeN_xCNF obtained from RDE measurements in O_2 saturated 0.5 M HClO₄ at a potential of -0.23 V. Sweep rate: 10 mV/s.





Fig. S13: High-resolution TEM image of 10 wt% PtCNF showing uniform distribution of fine Pt nano particles along the inner wall of CNF.

Mechanism



Fig. S14: The Probable mechanism for ORR on the FeN_xCNF

The detailed mechanism of ORR on non- precious electrocatalysts is still unclear. Nevertheless, it can be proposed based on oxygen reduction on the heme protein.¹ Because the active site present in the heme protein (iron bound with four-nitrogen atoms) is almost similar to the active site, exist in the present work. Fig. S14 shows the probable mechanism of the ORR. In the first step O₂ molecule binds with Fe^{II}N₂C to from oxygenated Fe^{III}N₂C-OO. This species is protonated with one electron to form the hydroperoxo compound (Fe^{III}N₂C-OOH) in the second step. In the third step, second protonation associated with one electron reduction results in the fourth step, again protonation associated with one electron reduction results in the

formation of $Fe^{III}OHN_2C$ which in turn in the final step combines with a proton and electron to form H₂O and the original catalytic active sites.

References

(1) F. Jaouen and J. P. Dodelete, J. Phys. Chem. C, 2009, 113, 15422.