A comparison of N-containing Carbon Nano-structures (CN_x) and N-coordinated Iron-Carbon Catalysts (FeNC) for the Oxygen Reduction Reaction in Acidic Media

Deepika Singh¹, Juan Tian¹, Kuldeep Mantani¹, Jesaiah King¹, Jeffrey T. Miller², Umit S. Ozkan¹

¹ *Department of Chemical and Biomolecular Engineering, The Ohio State University, Columbus OH 43202*

² *Chemical Sciences and Engineering Division, Argonne National Laboratory, 9700 S. Cass Ave, Argonne, IL 60439*

Corresponding author:

Phone: 614-292-6623

Email: Ozkan.1@osu.edu

Abstract

In light of the debate about the role of the transition metal in non-precious metal catalysts (NPMCs), two different NPMCs, CN_x and FeNC, were compared for activity towards oxygen reduction in acidic media and characterized using various techniques, including X-ray photoelectron spectroscopy (XPS), X-ray absorption near edge spectroscopy (XANES), Extended X-ray absorption fine structure (EXAFS), Superconducting quantum interference device (SQUID) magnetometry, inductive-couple plasma optical emission spectrometry (ICP-OES) and temperature-programmed oxidation (TPO). The effect of acid washing as well as long-term exposure to fuel cell and half-cell environment on both catalysts was also studied. Although FeNC exhibited a much higher initial activity than CN_x , it was seen to degrade rapidly in both half-cell and fuel cell environments, while CN_x retained much of its initial activity. The results discussed are sought to clarify some of the ambiguity in the role of the transition metal in these two catalysts, and help establish that they are indeed two different materials with different active sites that catalyze ORR.

Key words: CN_x , FeNC, ORR, XANES, EXAFS, SQUID

Introduction

Increasing concern about CO₂ emissions, together with the limited availability of fossil fuels have provided a great impetus towards development of efficient energy conversion devices. Proton Exchange Membrane (PEM) fuel cells, that use hydrogen as a fuel and generate energy while producing water as the only by-product, are among such efficient energy conversion devices.

Commercial PEM fuel cells use platinum supported on carbon as the anode and cathode catalyst. The hydrogen oxidation reaction on the anode exhibits relatively fast reaction kinetics and, therefore, low loadings of platinum are sufficient to catalyze the reaction. However, the ORR is a kinetically slow reaction that requires high loadings of platinum on the cathode, thereby significantly increasing the cost of a PEM fuel cell[1]. The associated high cost and limited platinum availability have motivated research towards development of non-precious metal catalysts (NPMCs) for the ORR in PEM fuel cells[2].

The first NPMC for ORR was reported by Jasinski, almost 50 years ago. Cobalt macrocycles were used and found to be significantly active for ORR in alkaline media, albeit unstable[3]. Subsequently, Anson and co-workers analyzed the mechanism of ORR on cobalt porphyrin, and found it to be facilitated by the interaction of the oxygen molecule with the two cobalt atoms simultaneously[4, 5], but this too lost its activity over time. [6]. A few decades later, it was found that a heat-treatment step imparted stability to these macrocycles in acidic media, possibly through formation of isolated metallic sites coordinated by thermally-modified ligands that retained the inner metal-N₄ macrocyclic structure[7]. This hypothesis was counter-argued by

Yeager, who proposed that macrocycles such as heat-treated tetramethoxyphenylporphyrins (TMPP) do not require the presence of a transition metal center within the complex to be active for ORR (rather, the transition metal could be present as an impurity in carbon, or added separately), and that the heat-treatment destroys the metal-N₄ centers in these complexes[8]. Wiesener and co-workers proposed that the thermal treatment of N₄-chelates leads to the formation of active carbons with specific surface functional groups involving nitrogen that catalyze ORR without the contribution of the metal[9]. The metal seemed to be only mediating the formation of these active sites during heat treatment.[10] Eventually, the expensive macrocycles were replaced with simple nitrogen precursors (e.g. polyacrylonitrile (PAN)), a transition-metal salt and a carbon support that were combined together and heat-treated between 600-900°C to yield active and stable ORR catalysts[11]. The activity of these materials was attributed to pyridyl-type nitrogen bound to transition-metal ions, which then reduced oxygen via the peroxide decomposition route[11].

Dodelet and co-workers have conducted extensive research on transition-metal, carbon, nitrogen (Fe- or Co-N-C) type materials for the last two decades. In their initial studies on heat-treated PAN+ Co systems, they attributed activity to small metallic clusters up to 20 Å in diameter[12, 13]. They later revised this assertion, stating that there are two catalytic Fe sites co-existing in catalysts made out of Fe salts or Fe porphyrins, namely FeN₄/C and FeN₂/C[14].

Moreover, they pioneered the development of well-known Fe-N-C catalysts prepared by incorporation of nitrogen into a Fe acetate-carbon matrix facilitated by NH₃ treatment at T > 600°C[2, 15, 16]. Other noteworthy reports of NPMCs consist of supported and heat-treated cobalt or iron macrocycles that were etched in a strong acid or base to leach out the support, [17-24] which revealed partial decomposition of the macrocyclic ring, resulting in the formation of

carbon-nitrogen polymer-like materials[25]. There were several other reports of metal-nitrogen-containing polymers[26] and carbon catalysts made of cobalt-polypyrrole composite[27], or a polyaniline-iron-cobalt composite[28], all of which showed good activity and the last one showed notable stability.

Most of these Metal-N-C catalysts, except for the polymer-based ones developed by Zelenay's group[28] are prone to rapid deactivation under fuel cell conditions, with much speculation about the causes of their deactivation. One hypothesis for degradation was the dissolution of metallic species under acidic conditions that led to activity loss over prolonged fuel cell tests [29]. On the other hand, Gojkovic et al. observed that for heat-treated iron-porphyrin catalysts adsorbed on carbon[30, 31], metallic particles were encapsulated in a graphitic shell which protected iron dissolution in the acidic environment of rotating disk electrode (RDE) tests.

Another proposed degradation mechanism was H_2O_2 formation through the 2-electron reduction of oxygen, which would oxidize the nitrogen atoms bound to a central metal[32]. More recently, their activity loss has been attributed to the anion binding effect in the acidic PEM fuel cell environment of the protonated basic nitrogen functional groups on the surface[33].

In parallel to the work that proposed that the metal was a part of an active site, there has been a growing body of literature, suggesting nitrogen-doped carbons to have significant activity for ORR.[34, 35]. Maldonado and Stevenson were among the first to report the use of N-doped carbon nanofiber electrodes for oxygen reduction in alkaline media. According to them, the transition metal facilitates incorporation of stable nitrogen species into the graphitic matrix. Nitrogen doping increases the basicity of the attached graphitic carbon as a result of the lone

pair of the pyridinic-type species, which stabilizes the carbon against oxidation and facilitates oxygen reduction[36].

Ozkan and co-workers were among the first to report the use of nitrogen-doped carbon nanostructure (CN_x) catalysts for ORR in acidic media. These materials were prepared by acetonitrile decomposition at high temperatures on iron- or cobalt-impregnated supports (silica, magnesia, alumina or Vulcan carbon)[35, 37-39]. Once the CN_x catalysts were formed, the inactive oxide support and exposed metallic species were washed away by leaching with a strong acid or base. The catalyst left behind contained varying levels of pyridinic nitrogen and exhibited different morphologies such as stacked cups, stacked platelets, nano-onions, and cubes, depending on the support and transition metal used[40-44]. However, in all cases, the catalyst exhibiting higher activity for ORR also had significant edge-plane exposure, and as a result, higher pyridinic-N content. While the role of pyridinic N as the source of activity is still somewhat speculative, it was seen as a definite marker for high ORR activity as the catalysts containing higher fractions of pyridinic N demonstrated significantly high activity for ORR. Some transition metal was left behind in CN_x , but it was encased within a graphite shell, as observed by TEM, and was, therefore, inaccessible to oxygen molecules to facilitate ORR. Significant ORR activity was also observed for CN_x grown on pure alumina, without a transition metal[35]. Accordingly, these results agree with the findings of Stevenson and co-workers in postulating that the transition metal in the catalysts may facilitate the formation of catalytically active sites, but does not directly participate in catalyzing the reaction[36]. This was further affirmed by poisoning experiments, in which CN_x catalysts were shown not to poison with H_2S , CO and cyanide[45, 46]. Moreover, an increase in activity from H_2S treatment and a mere dilution effect upon introduction of CO was observed. Since Fe would easily be deactivated by

these known industrial poisons if it was part of the active center, these experiments rendered additional support to the hypothesis of a metal-free active site. More recently, the metal-phase of CN_x catalysts was characterized during the growth of CN_x with in situ X-ray Absorption Spectroscopy. It was observed that the transition metal underwent different transformations during the pyrolysis, depending on the growth substrate used, starting with metal acetate and resulting in predominantly metallic and some carbidic phases after pyrolysis and acid-washing [47].

Popov and co-workers studied different materials including heat-treated nitrated carbon and other nitrogen precursors that were acid-treated to remove metallic impurities[48-50]. ORR activity of nitrated carbons was attributed to carbon sites adjacent to N atoms. An increase in ORR activity was observed with higher pyridinic nitrogen concentrations, and a loss of activity of these catalysts in acidic medium was attributed to protonation of the pyridinic-N sites resulting in pyridinic-N-H sites that were inactive for ORR. Ikeda et al. provided further confirmation with experimental and computational studies that graphene-like edges possess activity for ORR due to the presence of a nearby graphitic-N atom.[51], without requiring a metal-centered site[52].

Since most of the CN_x materials contain some transition metal left in them from the pyrolysis step, the nature of the active site of these carbon-based catalysts has been a topic of debate for many researchers, especially the role of the transition metal[53]. Recent studies reported by Dai and his co-workers, however, dispelled any ambiguity by demonstrating that N-doped carbon materials, such as N-graphene, that were prepared without any metal, had very high ORR activity in alkaline media [54-59].

Based on these reports as well as their own work, Ozkan and co-workers suggested that the two type of catalysts denoted as CN_x and FeNC may indeed be different materials[45, 60]. Fe-N-C catalysts that are prepared by supporting a macrocycle on a carbon support and going through a heat-treatment step do have a metal center. Since there is no acid washing step in the preparation to leach out the metal, it is expected that a metal center still remains in these materials, although its exact nature may not yet be fully understood. CN_x , on the other hand, prepared by decomposition of a nitrogen-carbon source on a metal-impregnated support, undergoes an acid-digestion step to leach away any exposed metal; any remaining metal is encased in carbon and does not participate in ORR.

In this current work, we have attempted to distinguish between Fe-N-C and CN_x catalysts, in terms of their possible active sites and degradation mechanisms, by means of activity and extended durability tests in a fuel cell and half-cell. The catalysts have been characterized using X-ray photoelectron spectroscopy (XPS), X-ray absorption near edge spectroscopy (XANES), Extended X-ray absorption fine structure (EXAFS), Superconducting quantum interference device (SQUID) magnetometry, inductive-couple plasma optical emission spectrometry (ICP-OES) and temperature-programmed oxidation (TPO). The results show significant differences in the activity, stability and compositional characteristics of these materials, shedding light on their inherent differences in catalyzing ORR.

Experimental

Catalyst Synthesis

CN_x : The CN_x growth media were synthesized by incipient wetness impregnation of 2 wt% Fe on high surface area magnesia, using an aqueous solution of iron(II) acetate (Sigma Aldrich),

followed by drying overnight in an oven at 110 °C. One gram of this growth media was weighed into a quartz boat that was placed in a quartz tube in a high-temperature furnace. The calcination tube was purged with nitrogen flowing at 65 mL/min for 30 min before ramping the temperature at 10 °C/min to 900 °C, at which time acetonitrile-saturated nitrogen was streamed over the growth media for 2h. At the end of the 2h period, CN_x grown over the support was removed from the quartz tube and acid washed in 250 mL of 1M HCl for 1h. After the acid-wash, it was vacuum filtered, rinsed with 1 L DI water and dried overnight in an oven at 110 °C. Samples were also prepared by acid-leaching for a longer duration of 2 days and 1 week.

FeNC: FeNC catalyst precursor was prepared via a wet-impregnation technique by dissolving 1,10-phenanthroline (phen) in a 150-mL solution of 2:1 deionized water: ethanol (Fisher Scientific). Next, 31 mg iron(II) acetate was added to this solution, which was stirred until it attained a deep red color indicative of the formation of [Fe(phen)₃]²⁺ complex. Black Pearl 2000 (Cabot Corp.) was added to this solution such that a ratio of 50:50 phen:BP2000 was achieved. The mixture was stirred at 80 °C until about 50 mL remained. The solution was then placed overnight in a drying oven at 90 °C. The residue obtained after drying was ball-milled for 3h in a rotary ball-mill at 200 rpm. The resulting fine powder was then weighed into a quartz boat, which was placed at the end of a long quartz tube in a pyrolysis furnace, such that the quartz boat itself was outside the furnace. The furnace was heated to 1050 °C with argon gas flowing at 300 mL/min, and upon reaching the set-point, the quartz boat was inserted in the furnace by means of a magnet-containing glass-rod directed by an external horseshoe magnet. The catalyst was then treated in argon for 1h, and removed from the furnace upon completion of the treatment time. A portion of the catalyst was then subjected to a second heat treatment in NH₃ at 950 °C for 20 min, following the same procedure outlined above. For the acid-washed samples, the NH₃ treated

catalyst was leached in 1M HCl for 1h, 2 days or 1week following the same procedure adopted for acid washing of CN_x .

It should be noted that while comparing the two classes of catalyst, CN_x and FeNC, we are comparing them in their most active form, which is CN_x -washed in HCl for 1h and FeNC-unwashed. Hence for the sake of clarity, the nomenclature CN_x -washed/ unwashed and FeNC-washed/unwashed are used to compare the two catalysts and the effect of acid washing on them, unless otherwise specified.

Fuel Cell Activity and Stability Tests

Membrane Electrode Assemblies (MEAs) were prepared by the following method. Anode comprised of commercial 20 wt % Pt/C from E-TEK (Pt loading 0.5 mg/cm^2). The ink for the cathode catalyst was prepared by using 10 mg catalyst, 326 μL 5 wt% Nafion in an aliphatic alcohol solution, with an ethanol:deionized water ratio of 55:45. The ink was sonicated in an ice bath until the catalyst was well-dispersed. An aliquot of 71 μL was spread uniformly on a gas diffusion layer of carbon paper with surface area of 1.14 cm^2 , to achieve a catalyst loading of 1 mg/cm^2 . After drying, the electrodes were hot-pressed at 140°C with a Nafion 115 membrane in between them.

Fuel cell tests were performed using an Arbin Fuel Cell Test Stand at a cell temperature of 80°C , flow rates of O_2 and H_2 at $300 \text{ cm}^3/\text{min}$ with a back-pressure of 15 psig and dew-point temperature of 85°C . Polarization curves were obtained by scanning the cell potential from open circuit voltage (OCV) to 0V at a scan rate of 0.5 mV/s . For stability tests, the first polarization curve was recorded once the temperature and pressures reached a steady-state. The cell was then

held at a potential of 0.5V for 1h, before recording a second polarization curve. The cell was then held at 0.5V for 100h before recording the third polarization curve.

Rotating Ring Disk Electrode (RRDE) Activity and Accelerated Durability Tests (ADTs):

A rotating ring disk electrode was used to measure the electrochemical activity of the catalysts in a 0.5M H₂SO₄ solution. The catalyst ink was prepared by dispersing 10 mg of catalyst in 95 μ L of 5 wt% Nafion solution mixed with 350 μ L ethanol. The ink was sonicated in an ice bath until the catalyst was well-dispersed ($\geq$ 1h), at which time 9 μ L of the ink was pipetted onto a glassy carbon disk of area 0.2472 cm², resulting in a catalyst loading of 800 μ g/cm².

All measurements were performed in a 0.5M-H₂SO₄ solution with platinum counter electrode and Ag/AgCl reference electrode. RRDE measurements were performed by collecting CVs at the disk in a potential range of 1.2 to 0.0 V vs. NHE with scan rates of 10 mV/s at 1600rpm, while the ring was held at a constant potential of 1.2V vs. NHE. Cyclic Voltammetry was conducted in argon-saturated H₂SO₄ at 10 mV/s from 1.2 to 0.0V vs. NHE to subtract the capacitive current. The conversion from Ag/AgCl to NHE scale was made by measuring the potential difference between Ag/AgCl and a Pt foil in the same electrolyte saturated with hydrogen. ORR activity is reported as the onset potential, which is defined as the potential at which the current density in oxygen-saturated electrolyte is -0.1 mA/cm².

Selectivity (n) is determined as the number of electrons transferred per oxygen molecule at the disk by comparing the disk and ring currents during ORR activity tests. The reactions occurring during the complete and partial reduction of oxygen to water or H₂O₂ respectively, are as follows:

Selectivity was determined by comparing the ring and the disk current obtained in the O₂ saturated solution, by the following formulae:

$$n = \frac{4I_D}{I_D + \frac{I_R}{N}} \quad (3)$$

Where n = number of electrons transferred per oxygen molecule, I_D = disk current, I_R = ring current and N = collection efficiency of the ring (equal to 37% as specified by the manufacturer). An n value of 4 corresponds to a complete reduction of oxygen to water, whereas an n value of 2 is equivalent to a complete formation of hydrogen peroxide. The ring was held at 1.2V vs. NHE, at a potential where ORR current is negligible and oxidation of H₂O₂ to oxygen would be mass transfer limited.

In addition, selectivity values were also determined by measuring the current density at several rotation rates (1000, 1600 and 2500 rpm) using the Koutecky-Levich Equation[61]

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{B\omega^{\frac{1}{2}}} \quad (4)$$

$$B = 0.62nFC_{O_2}(D_{O_2})^{\frac{2}{3}}\nu^{-1/6} \quad (5)$$

Where j is the current density (A/cm²), j_k is the kinetically controlled current density, n = number of electrons transferred per molecule of oxygen, F is Faraday's constant, C_{O_2} is the O₂ concentration in the electrolyte (1.1e-6 mol/cm³)[62], D_{O_2} is the diffusion coefficient for molecular oxygen in 0.5M H₂SO₄ at 25°C (1.4 e-5cm²/s)[62], ν is the kinematic viscosity of the

0.5M H₂SO₄ solution (0.01 cm²/s)[63]. The angular rotation rate is represented as ω . The number of electrons transferred per oxygen molecule (n) can be determined from the slope of the linear relation $1/j$ and $1/\omega^{1/2}$. These plots were parallel at different potentials indicating that the reaction follows first order kinetics[64-66].

In order to ensure that there is no contamination due to the use of a platinum counter electrode, we have conducted control experiments using the same set-up, but with only the plain glassy carbon electrode. There was no ORR activity observed in that set-up, indicating that any current observed on the disk is due to the catalyst only.

Accelerated durability tests (ADTs) were performed in O₂-saturated H₂SO₄ solution by first collecting initial activity data as described above. The electrode was then cycled between 1.2V to 0.0V to 1.2V vs. NHE at 100 mV/s for several hundred cycles, with a hold at 1.2V for 5 seconds after each cycle. Activity data was collected after 100, 500 and 1000 cycles.

X-ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy was used to analyze the composition of the surface species present on the CN_x and FeNC catalysts. The samples were prepared according to the procedure outlined in the catalyst preparation section. A Kratos Ultra Axis spectrometer was used with a monochromated aluminum anode source operated at 12 kV and 10 mA. Collected data were corrected for charge shifting using standard C 1s binding energy of 284.5 eV. XPS Peak 4.1 software package was used for curve fitting. Spectra baselines were determined using Shirley-type background fitting. Spectra were deconvoluted using Lorentzian-Gaussian combination peaks.

Temperature Programmed Oxidation (TPO)

Temperature-programmed oxidation (TPO) experiments were performed using an Autochem 2010 under 10% O₂/He gas at a flowrate of 30 ccm. 30 milligrams of the catalyst was packed in a U-tube quartz reactor and held in a high-temperature furnace. The sample temperature was first allowed to equilibrate to 50 °C for 15 min, then the temperature was ramped to 850 °C at 5°C/min and held there for 20 min. The TPO product stream was fed to an MKS Cirrus benchtop residual gas analyzer with mass signals of 1-100 monitored throughout the experiment.

X-ray Absorption Fine Structure Spectroscopy

Spectra were collected for the Fe K-edge (7112 eV) at the bending magnet beamline (5BM-D) of the Dow-Northwestern-DuPont Collaborative Access Team (DND-CAT) of the Advanced Photon Source, Argonne National Laboratory. The measurements were made in transmission mode with the Si(111) monochromator detuned by 30% to eliminate the higher order harmonics in the beam. The samples were pelletized using a die of diameter 13 mm and held in a 6 sample-holder against Kapton tapes transparent to the X-ray beam. Spectra for all samples and standards were collected in the *ex situ* mode.

Inductive Coupled Plasma Optical Emission Spectrometry (ICP-OES)

Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) was performed on the samples for Fe analysis using a Perkin Elmer Optima 3000. Fe samples were diluted 2x with deionized water and data were acquired for wavelengths of 234, 238, 239 and 259 nm. Calibration standards equivalent to 0, 2, 10 and 20 ppm in the original samples were prepared.

The standards were prepared using single element standards purchased from High Purity Standards and diluted with 2% v/v ultrapure HCl in deionized water. Calibration blanks were 2% v/v ultrapure HCl in deionized water.

TEM

An FEI Tecnai F20 XT Transmission Electron Microscope operated at 200kV was used to characterize the morphology of the CN_x and FeNC catalysts. Catalysts were prepared for imaging by suspending the catalyst in ethanol and then depositing the suspension on a lacey formvar carbon supported on a 200 mesh copper TEM grid.

Superconducting Quantum Conducting Device (SQUID) Magnetometry

Magnetization was measured as a function of field using a Superconducting Quantum Interference Device (SQUID) magnetometer (Quantum Design MPMS XL) at 300 K. The applied field was varied from -30000 Oe to +30000 Oe and then back to -30000 Oe. A total of 100 data points were collected for each sample.

The data were then fitted to the Langevin function (Equation 6) and the values for saturation magnetization and average iron particle size (assuming a spherical shape) were determined.

$$\frac{M}{M_{sat}} = L\left(\frac{M_s V H}{k_B T}\right) \quad (6) \quad \text{where}$$

M is the magnetization (emu/g)

M_{sat} is the saturation magnetization (emu/g)

M_s is the spontaneous magnetization (emu/cm³)

V is the volume of particle (cm³)

H is the applied field (Oe)

K_b is the Boltzmann Constant ($cm^2gs^{-2}K^{-1}$)

T is the temperature (K)

$L(x) = coth(x) - \frac{1}{x}$ is the Langevin function for superparamagnetic particles.

Results and Discussion

Rotating Ring Disk Electrode Tests

The RRDE activity tests for FeNC (unwashed and washed) and CN_x (unwashed and washed) are shown in Figure 1(a) and (b). Between the two catalysts, FeNC is clearly more active than CN_x, with an onset potential of 0.87V (unwashed) versus the onset potential of CN_x, which is 0.78V (washed). The effect of acid washing is markedly different on the two catalysts. While CN_x shows a dramatic improvement in activity (Figure 1b) after acid washing, FeNC, on the other hand, shows a noticeable decrease in its activity, to an onset potential of 0.83V, for the washed catalyst. This trend is a first evidence of the inherent differences in the catalytic active sites of the catalysts. Acid washing possibly leaches away some of the Fe from the active Fe-N_x sites in FeNC, leading to an activity loss, while in the case of CN_x, the effect of acid washing is to eliminate the inactive iron species from the catalyst surface, along with the oxide support. After acid washing, CN_x, which does not have exposed iron species, and consists of carbon nanostructures with Fe embedded within the graphitic matrix, exhibits significantly higher ORR activity.

Selectivity (n) of the catalysts was evaluated using RRDE as well as Koutecky-Levich (K-L) plots. Figure 2 shows typical ring and disk current plots obtained in the RRDE experiments and the as well as a K-L graph for FeNC-unwashed sample. The “n” are presented in Table 1. All catalysts except unwashed CN_x showed selectivities over 95% (i.e., “n” values higher than 3.8).

The variation in the “n” values between those measured by the RRDE and calculated by K-L was 0.2 or less, except for the unwashed CN_x, in which the selectivity from K-L plots was lower than that obtained from RRDE. This is somewhat expected since CN_x-unwashed did not quite reach a limiting disk current plateau, as seen in Figure 1(b); a phenomenon observed in catalysts with very low ORR activity. Also as expected, the selectivity for unwashed CN_x was very low, since this sample contains large amounts of the oxide support as well as uncoordinated surface iron. Another important point to note was that the acid washing did not have much effect on the selectivity of FeNC catalyst, although it was absolutely essential for the CN_x catalysts.

Although the active forms of the catalysts had n values around 3.9, it should be noted however, that, in two independent studies[67, 68], it has been observed that the selectivity of both CN_x and FeNC catalysts is highly dependent on the catalyst loading. For both catalysts, the selectivity was seen to increase with increased loading levels, suggesting a mechanism proceeding via an H₂O₂ intermediate, where the H₂O₂ molecules may have sufficient time to undergo further reduction to water while diffusing out of a thicker catalyst layer.

Accelerated Durability Tests using RDE

Accelerated durability tests were also conducted on CN_x as well as FeNC. In these tests, the most active forms of the two catalysts, namely CN_x-washed and FeNC-unwashed, were used. Figure 3(a) shows performance losses by ADTs in FeNC-unwashed. We observed that, over FeNC, there was a continued deterioration of performance with repeated cycles. This may be due to dissolution of iron in the acidic medium. At the same time, carbon support in FeNC catalysts itself may also be susceptible to corrosion, as seen previously by other researchers, leading to a continued degradation in performance[69-72].

In contrast to FeNC, which showed a steady loss of activity with increasing cycles, CN_x demonstrated the highest activity loss during the first 100 cycles of repeated CVs (Figure 3b). It reached a pseudo-steady state thereafter, as there was no significant activity loss between cycles 100, 500 and 1000. As reported by Ozkan and co-workers previously[73], CN_x materials do not undergo carbon corrosion as severely as some other carbon supports, such as Vulcan carbon, and this could be an additional factor responsible for its prolonged stability.

Fuel Cell Activity and Stability Tests

iR-free polarization curves obtained before and after a 100-hour potential hold at 0.5V are shown in Figure 4(a) for CN_x and FeNC, with the log of the current density in the high-voltage region shown as an inset. While CN_x performed worse than FeNC, it exhibited better retention of initial activity over the full range of current. FeNC, on the other hand, showed a dramatic loss of activity, to the extent that, after the 100-h potential hold, the activities for the two catalysts got closer together compared to their initial activities. It is worth noting that although CN_x exhibited lower initial activity than FeNC catalysts, it also showed significantly less degradation over time.

We also compared activities of acid-washed and unwashed FeNC catalysts. Figure 4(b) shows polarization curves of FeNC with and without an acid-wash. Although, the unwashed FeNC catalyst possessed a higher initial activity, after the potential hold, it is apparent that both the catalysts deactivated to almost the same level. This is even more apparent in the inset which shows the kinetically controlled region. This observation is significant in showing that the activity loss due to acid washing is similar in magnitude to the activity loss suffered by the catalyst during the potential hold.

Although the mechanism of deactivation is not yet fully understood, a clear distinction that emerges between FeNC and CN_x catalysts is that CN_x has a higher degree of stability than FeNC. This also suggests that the activity loss in FeNC catalysts is directly linked to the Fe sites, and CN_x catalysts, in which iron does not play a catalytic role, is not affected by this mode of deactivation.

X-ray Photoelectron Spectroscopy

N 1s: XPS spectra of the CN_x and FeNC catalysts in the N 1s region revealed differences in the distribution of their N species (Table 2 and Figure 5). The N 1s region was deconvoluted into three different nitrogen species, identified as pyridinic N (398.0-398.9 eV)[74, 75], quarternary-N (401-402 eV)[74, 76], and oxygenated pyridinic-N groups (N⁺-O⁻) at binding energies higher than 402 eV[39, 43, 44].

N 1s spectra for CN_x (unwashed and washed) and FeNC (unwashed and washed) are shown in Figures 5 (a-b) and Figure 5(c-d), respectively, and the distribution of different N species are tabulated in Table 2. It should be noted that at binding energies of ~399.2 eV, pyridinic-N attached to Fe species have been reported[77]. However, there is some discrepancy in the species attributed to this binding energy, making exact assignments difficult. Ganesan et al. have assigned BE of 399.7 eV to iron-pyridinic-N [78], whereas Palaniselvam et al. have reported Fe-N species in the range of 397.3-397.5 eV [79].

The fraction of N in pyridinic form was the same in CN_x catalyst before and after washing, suggesting that washing, which leaches out the oxide support and the exposed metal, does not affect the nitrogen species. The calculation of absolute N content for unwashed CN_x was not done because of the presence of the oxide support (MgO).

In the case of FeNC (Figure 5(c-d)), there was a significant increase in the pyridinic-N content, from 25% to 36%, after washing. The total nitrogen content of FeNC-unwashed and washed catalysts were 1.9% and 2.5% respectively, resulting in an absolute pyridinic N content of 0.47 and 0.9 atomic %. A possible explanation for this increase could be that Fe-species that were coordinated to edge-nitrogen species on two graphite planes were washed away, leaving behind more exposed edge-nitrogen and subsequently increasing the percentage of pyridinic nitrogen in FeNC.

The presence of pyridinic-N in Me-N_x type materials has given rise to two hypotheses in literature about the mechanism of deactivation of these catalysts. Popov and co-workers propose that the protonation of pyridinic nitrogen groups in the acidic fuel cell environment, leads to a decrease in activity of these catalysts over time[80]. This is harder to detect in XPS due to overlap in binding energy with quaternary nitrogen[81]. Whereas in a recent study by Dodelet's group, it was suggested that the basic nitrogen (pyridinic) groups (next to the coordinated Fe active sites) that can be protonated in an acidic fuel cell environment, act as a pathway for quick transfer of protons to the Fe-active site, thus significantly improving the turnover frequency for these composite sites[33, 53]. They further suggest that protonated NH⁺ group may be neutralized by the presence of an anion (sulfonate group of the proton exchange membrane), which leads to the long-term activity loss.

We have seen in this study that the higher pyridinic nitrogen content for both acid-washed FeNC catalysts and CN_x catalysts does not necessarily translate to lower stability. In fact, these catalysts showed higher stability than unwashed FeNC. Hence, one hypothesis that could explain this phenomenon is that protonation of pyridinic nitrogen or its anion binding does cause activity degradation, but is not the only source of activity loss. It is possible, however, that the unwashed

FeNC catalysts exhibit a loss in activity over time due to a coupled effect of the iron from the active sites being leached out, in addition to protonation effects/ and-or anion binding of the already-protonated pyridinic nitrogen.

The effect of acid-washing of FeNC could also be two-fold: gain of pyridinic-N species, at the expense of some Fe active sites that are leached out in the process. While the loss of Fe active sites may be leading to reduced activity, this effect might be counter-balanced with the gain in pyridinic-N species which could be contributing to activity. It is difficult to decouple the effect of the iron and nitrogen and the changes therein brought about by extended durability tests or acid-washing, especially since the surface iron sites are low in concentration and harder to analyze using surface spectroscopic techniques.

Temperature Programmed Oxidation (TPO)

Temperature-programmed oxidation was conducted on all CN_x and FeNC samples in 10% O_2/He . A Cirrus mass-spectrometer (MS) was used to record m/z signals of 28 (CO), 30 (NO), 44 (CO_2) and 46 (NO_2) which are reported here. Figure 6 shows the comparison of TPO profiles for FeNC and CN_x respectively for (a) and (b) unwashed, (c) and (d) washed for 1h (e) and (f) washed for 1week.

It is known that iron catalyzes the oxidation of carbon. As a result, the onset of oxidation temperature is nearly identical for both FeNC and CN_x unwashed catalysts (Figure 6(a) and (b), due to the presence of surface iron in both. After acid washing for one hour, there was a small increase in the oxidation onset temperature for FeNC (Figure 6(c), while for CN_x , the onset of oxidation temperature increased by $\sim 100^\circ\text{C}$ FeNC (Figure 6d). This is likely due to the leaching

away of the surface iron, that was present on CN_x before acid washing. After washing, there is no surface iron left on CN_x to catalyze the oxidation reaction.

There was no significant difference between the oxidation temperatures of CN_x or FeNC catalysts acid washed for 1 hour or 1 week. CN_x appears to be more resistant to oxidation than FeNC catalysts, with or without acid washing, but the difference becomes much more pronounced as the oxidation onset temperature for washed CN_x (1h or 1week) was consistently above that of washed FeNC (1h or 1week) by about 100°C . One of the causes for this may be due to the presence of carbon support in FeNC catalysts, which is more susceptible to oxidation than the carbon nanostructures in CN_x catalysts that are left behind after the support MgO itself is washed away.

It was also observed that there was significantly more NO formation ($m/z = 30$) over the CN_x catalysts than FeNC catalysts, indicating a higher concentration of nitrogen in these catalysts. Another feature of the NO profiles was that, the nitrogen species seemed to evolve at a higher temperature ($\sim 550^\circ\text{C}$) for CN_x acid washed for 1 week (Figure 6f), suggesting the possibility of edge sites with pyridinic N corroding with increased durations of acid washing and leaving behind a larger fraction of the quaternary nitrogen, which would require a bulk oxidation of the graphitic structure.

X-ray Absorption Near Edge Spectroscopy (XANES)

XANES spectra were collected ex situ for different CN_x and FeNC catalysts, along with references such as iron foil, iron(II) oxide and iron carbide. For the unwashed CN_x (Figure 7a), the Fe- K edge spectrum showed the sample to be more oxidized, possibly due to oxidation of the surface iron species upon exposure to atmosphere even if they were reduced to metallic Fe

during pyrolysis. Also, as seen in our previous studies of the carbon growth process using in situ XANES and EXAFS[47], oxygen contribution from the MgO support may be another factor leading to a higher oxidation state of the transition metal in the unwashed sample. For acid-washed CN_x (Figure 7b), the features corresponding to the oxide disappeared while the XANES energies showed similarities to the iron carbide as well as the iron foil standard.

In Figure 7 (c) and (d), the Fe-K edge XANES spectra of FeNC-unwashed and washed respectively, are shown. There is not a significant difference between the two spectra, both showing similarities to iron carbide, indicating that washing did not change nature of the Fe species. It should be noted that, although the heat-treated and acid-washed FeNC catalysts showed near-edge features similar to iron carbide, the presence of iron nitride in these catalysts cannot be discounted; indeed its presence is highly likely. Due to the inherent limitation of the technique to distinguish the second scatterers, especially if they are lighter elements such as carbon, nitrogen or sulfur, it is hard to distinguish between iron carbide or nitrides.

Extended-X-ray Absorption Spectroscopy (EXAFS)

Since analysis of the XANES spectra showed minor differences in the state of iron, the FT-magnitudes of the catalysts were compared with standards. The uncorrected values are presented in Figure 8. FT-magnitudes of CN_x -unwashed is shown with iron carbide and iron oxide references in Figure 8a. There were two peaks observed, one at a value of 2.7 Å and a smaller peak at about 1.7 Å. This spectrum compares very well with the iron oxide reference, and the two peaks are possibly Fe-O and Fe-O-Fe, respectively. For CN_x -washed, there is a large peak indicative of Fe-Fe bonds in metallic Fe at the value of ~2.1 Å (Figure 8b). However, there was a shoulder at ~1.5 Å that is evidence of iron carbide. This is in agreement with our previously

reported results from Mossbauer spectroscopy, in which presence of Fe oxide species were observed in the unwashed samples, whereas after acid washing, co-existence of a cementite-type Fe carbide phase was seen together with metallic γ -Fe, encased in the carbon structure[42].

The shoulder that is seen at about 1.5 Å in the iron carbide reference is present in the spectra of FeNC catalysts, both washed and unwashed, together with a Fe-Fe peak at 2.1 Å (Figure 8c and d). These features could be attributed to metallic Fe along with either a Fe-C_x or an Fe-N_x bond.

With XANES and EXAFS, although specific differences between Fe-C_x or Fe-N_x bonds are harder to discern, a significant difference between the effect of acid-washing on CN_x and FeNC emerges. In CN_x before acid-washing, Fe appears to exist as Fe²⁺ in an oxidized state. This is expected due to the presence of exposed iron species getting oxidized upon contact with air after pyrolysis, as well as due to oxygen contribution from the MgO support. After acid-washing, all of the oxidized Fe species is leached away, and what is left behind is mostly carbidic or metallic Fe encased in the carbon nanostructures. This difference is evident from both the XANES and EXAFS spectra of CN_x (washed and unwashed).

However, in the case of FeNC, the Fe species present in the catalyst already exist in the form of a Fe-N coordination in the unwashed FeNC. And although acid-washing leaches away a part of the Fe species, the remaining Fe in the catalyst still continue to exist in the same coordination state. This translates to the observed similarities in the XANES and EXAFS spectra of FeNC, both washed and unwashed.

ICP-OES and TEM

ICP-OES experiments were performed for both CN_x- and FeNC catalysts that were kept in 250 mL of 1M HCl solution for 48h, and aliquots of the acidic mixture were pipetted out at intervals

after 1h and 48h. The solutions were analyzed using ICP-OES for Fe content. The Fe content as well as the percentage of iron leached out from the initial iron content of the catalysts are tabulated in Table 3. The results show that 77% of the iron in CN_x leached out within the first hour, indicating that a significant amount of Fe in these samples is exposed after the pyrolysis step and it can be leached out easily. The total concentration of iron leached out from CN_x was also much greater than that of FeNC, (77% for CN_x versus 24% for FeNC after the first hour). It should be noted that CN_x -unwashed sample contains an oxide support. So during the acid washing, the oxide support is also leached out together with Fe which is not encased in carbon. That is why the absolute percentages in washed CN_x sample are somewhat higher than the unwashed sample. Another important observation is that, in the case of CN_x , most acid leaching took place within the first 1h of being immersed in the acid solution, and there was little change in iron concentration after that. For FeNC however, iron leaching continued with time, changing from 24% to 35% between 1h and 48h. These observations are consistent with the assertion that any iron left in CN_x after acid washing is encased in carbon and not readily accessible. TEM images taken over CN_x show iron particles encased in nanostructures while FeNC shows Fe to be on the surface (Figure 9).

These results are also significant in showing that, although most of the iron in CN_x catalysts leaches out during the 1-hour washing process, which is a routine step in the preparation procedure, these materials become substantially more active after washing. This observation provides further support to the assertion that Fe left in these materials is not part of the active site. FeNC catalysts, however, show significant activity loss as more and more Fe is lost through leaching. Also, the loss of activity continues, as does the loss of iron, with additional time in the acidic medium. This observation lends support to an active site model where Fe is an integral

part of the active center. It is important to note that we do not claim that acid-washing of FeNC catalysts renders them similar to CN_x . Acid-washing of FeNC leads to loss of Fe atoms that were previously coordinated to nitrogen sites. This possibly results in creation of pyridinic N sites, existing at the graphitic edge planes, as seen by the rise in pyridinic N concentration in XPS for FeNC-washed catalyst. However, after an hour of acid-washing there still exists 76% of the original Fe within the catalyst. Hence, the contribution of activity from both types of active sites is highly likely in the washed FeNC catalyst.

SQUID Magnetometry

Figure 10 shows the magnetization as a function of field at 300K for CN_x and FeNC (washed and unwashed). The data suggests a superparamagnetic behavior for all samples as evident from the negligible hysteresis in the curves. The values of saturation magnetization for various samples as observed in Figure 10 and reported in Table 4 reveal interesting trends. Firstly, acid-washing led to an increase in the saturation magnetization for CN_x sample while it showed the opposite effect for FeNC catalyst.

In our analysis of the characterization of iron-phases in acid-washed CN_x from Mossbauer Spectroscopy, it was seen that majority of the iron in the catalyst is either Fe^0 or Fe_3C [42], which is confirmed by the high saturation magnetization values of CN_x obtained from SQUID. Furthermore, after acid-washing, the diamagnetic contribution from the support (magnesia) as well as its dilution effect are eliminated, thereby leading to an increase in the saturation magnetization for acid-washed CN_x . On the other hand, in FeNC, acid-washing leaches away some surface iron species, consequently acid-washed FeNC has a lower saturation magnetization

than unwashed catalyst. This observation suggests that acid-washed FeNC contains a relatively lower fraction of iron in zero-valent state compared with the unwashed catalyst.

The values of particle diameters of iron for various samples were estimated by fitting Langevin function (Equation 6) to the data and were found to be in the range of 3.5-4.8 nm (reported in Table 4). These values are lower than the critical diameter for iron, below which superparamagnetic behavior is exhibited[82]. It must be noted that the iron particle sizes reported in these calculations are lower than the particle size observed in TEM; an observation also made by other researchers. This is attributed to the presence of an amorphous, magnetically “dead” layer surrounding the crystalline magnetic core which is not detected in magnetic measurements [83-85].

Conclusions

The results discussed in this article bring to light several differences between FeNC and CN_x materials for ORR. The first prominent difference between CN_x and FeNC was seen in their activity and stability towards ORR. CN_x was less active than FeNC, albeit more stable. CN_x underwent slower degradation in fuel cell stability tests and in ADTs, and attained stability faster while FeNC showed continued activity loss.

Effect of acid washing was strikingly different for both types of catalysts. CN_x gained significant ORR activity after acid washing, and just the reverse was seen in the case of FeNC. Acid-washed FeNC demonstrated a lower initial activity than unwashed catalyst, but after the 100-hour potential hold, there was no difference in activity between the former and latter. This suggests that the activity loss observed due to acid washing may occur through a similar process to the deactivation that takes place during a potential hold in the fuel cell environment. It was also

observed that after a potential hold of 100 hours, CN_x and FeNC catalysts converged to similar activity levels.

A significant insight from ICP-OES experiments was most of the iron in CN_x is leached readily during acid washing and further exposure to acid does not change its iron content. In FeNC, on the other hand, the loss of iron through leaching continues as long as the catalyst is immersed in the acid solution. This result supports the assertion that iron left in CN_x catalyst is encased in carbon and is not accessible while iron in FeNC is more readily accessible.

The causes for loss of activity are somewhat speculative, but a cumulative effect of iron leaching and either the protonation of pyridinic groups or their anion binding may be responsible for losses seen in FeNC catalysts, while iron leaching does not seem to affect ORR activity in CN_x negatively. Whether the pyridinic-N groups in CN_x undergo transformation in the fuel cell or half-cell environment is still unknown, but considering that both the catalysts showed different stability behavior, it is likely that their degradation mechanism is quite different.

XPS results indicated that pyridinic nitrogen was present in both CN_x and FeNC catalysts. CN_x catalysts exhibited a higher pyridinic-nitrogen content. Since pyridinic-nitrogen content was greater in CN_x , if protonation or anion binding of pyridinic nitrogen was the only cause of deterioration of the stability for both these catalysts, it cannot explain the greater stability of CN_x . Hence, there is clearly another degradation mechanism involved for FeNC. Another interesting finding from XPS was that the acid-washed FeNC catalysts exhibited higher pyridinic-nitrogen content than unwashed FeNC. This could be attributed to some of the iron centers leaching out, leaving behind exposed edge nitrogen sites. CN_x was also seen to be more resistant to oxidation than FeNC from TPO experiments.

EXAFS and XANES revealed significant differences in the effect of acid-washing on CN_x and FeNC. In CN_x , the oxidized Fe species exposed to air after pyrolysis were removed upon washing with acid, with only carbide-like or metallic Fe left behind encased within carbon. Whereas in FeNC, although the acid-washing leached out a part of Fe from the FeNC matrix, the iron left behind still existed in a similar coordination, with or without the washing.

SQUID results indicated major differences in the magnetic properties of CN_x and FeNC, with CN_x having the higher saturation magnetization after acid-washing, while FeNC showed the opposite trend. This behavior is attributed to the diamagnetic contribution of oxide-species originating from the MgO support in CN_x before acid-washing, which lower its overall saturation magnetization in the unwashed state. Whereas in the case of FeNC, acid-washing leads to a loss of surface Fe species, lowering its saturation magnetization in the acid-washed sample.

With the results discussed above, we have established that CN_x and FeNC materials are indeed two different classes of NPMC catalysts, with different activities and deactivation behavior towards ORR in acidic media, and evidently different active sites. While iron certainly plays an active role in catalyzing ORR for FeNC, its presence in CN_x does not manifest itself with higher ORR activity. We believe the findings reported in this article will shed some light on the ambiguity of the role of the transition metal on the active sites of these two materials.

Acknowledgements

We gratefully acknowledge the financial support by the U. S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-FG02-07ER15896. Portions of this work were performed at the DuPont-Northwestern-Dow Collaborative Access Team

(DND-CAT) located at Sector 5 of the Advanced Photon Source (APS). DND-CAT is supported by E.I. DuPont de Nemours & Co., The Dow Chemical Company and Northwestern University. Use of the APS, an Office of Science User Facility operated for the U.S. Department of Energy (DOE) Office of Science by Argonne National Laboratory, was supported by the U.S. DOE under Contract No. DE-AC02-06CH11357.

References

- [1] H.A. Gasteiger, S.S. Kocha, B. Sompalli, F.T. Wagner, Review - Activity benchmarks and requirements for Pt, Pt-alloy, and non-Pt oxygen reduction catalysts for PEMFCs, *Appl. Catal. B-Environ.*, 56 (2005) 9-35.
- [2] H.A. Gasteiger, N.M. Markovic, Just a dream - or future reality?, *Science*, 324 (2009) 48-49.
- [3] R. Jasinski, Cobalt phthalocyanine as a fuel cell cathode, *J. Electrochem. Soc.*, 112 (1965) 526-528.
- [4] R.R. Durand, C.S. Bencosme, J.P. Collman, F.C. Anson, Mechanistic aspects of the catalytic reduction of dioxygen by cofacial metalloporphyrins, *J. Am. Chem. Soc.*, 105 (1983) 2710-2718.
- [5] J.P. Collman, P. Denisovich, Y. Konai, M. Marrocco, C. Koval, F. Anson, Electrode catalysis of the four-electron reduction of oxygen to water by dicobalt face-to-face porphyrins, *J. Am. Chem. Soc.*, 103 (1980) 6027.
- [6] J.H. Zagal, Metallophthalocyanines as catalysts in electrochemical reactions, *Coordin. Chem. Rev.*, 119 (1992) 89-136.
- [7] J.A.R. van Veen, J.F. van Baar, K.J. Kroese, Effect of heat treatment on the performance of carbon-supported transition-metal chelates in the electrochemical reduction of oxygen, *Chem. Soc., Faraday Trans. I*, 77 (1981) 2827.
- [8] E. Yeager, Electrocatalysts for O₂ reduction, *Electrochim. Acta*, 29 (1984) 1527-1537.
- [9] K. Wiesener, N₄-chelates as electrocatalysts for cathodic oxygen reduction, *Electrochim. Acta*, 31 (1986) 1073-1078.
- [10] R. Franke, D. Ohms, K. Wiesener, Investigation of the influence of thermal treatment on the properties of carbon materials modified by N₄-chelates for the reduction of oxygen in acidic media, *J. Electroanal. Chem.*, 260 (1989) 63-73.
- [11] S. Gupta, D. Tryk, I. Bae, W. Aldred, E. Yeager, Heat-treated polyacrylonitrile-based catalysts for oxygen electroreduction, *J. Appl. Electrochem.*, 19 (1989) 19.
- [12] M.C. Martins Alves, J.P. Dodelet, D. Guay, M. Ladouceur, G. Tourillon, Origin of the electrocatalytic properties for O₂ reduction of some heat-treated polyacrylonitrile and phthalocyanine cobalt compounds adsorbed on carbon black as probed by electrochemistry and X-ray Adsorption Spectroscopy, *J. Phys. Chem.*, 96 (1992) 10898-10905.
- [13] M. Ladouceur, G. Lalande, D. Guay, J.P. Dodelet, L. Dignard-Bailey, M.L. Trudeau, R. Schulz, Pyrolyzed cobalt phthalocyanine as electrocatalyst for oxygen reduction, *J. Electrochem. Soc.*, 140 (1993) 1974-1981.

- [14] M. Lefevre, J.P. Dodelet, P. Bertrand, Molecular oxygen reduction in PEM fuel cells: Evidence for the simultaneous presence of two active sites in Fe-based catalysts, *J. Phys. Chem. B*, 106 (2002) 8705-8713.
- [15] F. Jaouen, M. Lefevre, J.-P. Dodelet, M. Cai, Heat-treated Fe/N/C catalysts for O₂ electroreduction: Are active sites hosted in micropores?, *J. Phys. Chem. B*, 110 (2006) 5553-5558.
- [16] F. Jaouen, J. Herranz, M. Lefevre, J.-P. Dodelet, U.I. Kramm, I. Herrmann, P. Bogdanoff, J. Maruyama, T. Nagaoka, A. Garsuch, J.R. Dahn, T.S. Olson, S. Pylypenko, P. Atanassov, E.A. Ustinov, Cross-laboratory experimental study of non-noble-metal electrocatalysts for the oxygen reduction reaction, *ACS Applied Materials & Interfaces*, 1 (2009) 1623-1639.
- [17] T.S. Olson, B. Blizanac, B. Piela, J.R. Davey, P. Zelenay, P. Atanassov, Electrochemical evaluation of porous non-platinum oxygen reduction catalysts for polymer electrolyte fuel cells, *Fuel Cells*, 5 (2009) 547-553.
- [18] T.S. Olson, S. Pylypenko, J. Fulghum, P. Atanassov, Bifunctional oxygen reduction reaction mechanism on non-platinum catalysts derived from pyrolyzed porphyrins, *J. Electrochem. Soc.*, 157 (2010) B54-B63.
- [19] I. Herrmann, U.I. Kramm, S. Fiechter, P. Bogdanoff, Oxalate supported pyrolysis of CoTMPP as electrocatalysts for the oxygen reduction reaction, *Electrochim. Acta*, 54 (2009) 4275-4287.
- [20] U.I. Koslowski, I. Abs-Wurmbach, S. Fiechter, P. Bogdanoff, Nature of the catalytic centers of porphyrin-based electrocatalysts for the ORR: A correlation of kinetic current density with site density of Fe-N₄ centers, *J. Phys. Chem. C*, 112 (2008) 15356-15366.
- [21] N.P. Subramanian, S.P. Kumaraguru, H. Colon-Mercado, H. Kim, B.N. Popov, T. Black, D.A. Chen, Studies on Co-based catalysts supported on modified carbon substrates for PEMFC cathodes, *J. Power Sources*, 157 (2006) 56-63.
- [22] Z. Chen, D. Higgins, A. Yu, L. Zhang, J. Zhang, A review on non-precious metal electrocatalysts for PEM fuel cells, *Energy and Environmental Science*, 4 (2011) 3167.
- [23] L. Zhang, K. Lee, C.W.B. Bezerra, J. Zhang, J. Zhang, Fe loading of a carbon-supported Fe-N electrocatalyst and its effect on the oxygen reduction reaction, *Electrochim. Acta*, 54 (2009) 6631-6636.
- [24] F. Jaouen, E. Proietti, M. Lefevre, R. Chenitz, J.P. Dodelet, H.T. Chung, C.M. Johnston, P. Zelenay, Recent advances in non-precious metal catalysis for oxygen-reduction reaction in polymer electrolyte fuel cells, *Energy and Environmental Science*, 4 (2011) 114-130.
- [25] K. Artyushkova, S. Levendosky, P. Atanassov, J. Fulghum, XPS structural studies of nano-composite non-platinum electrocatalysts for polymer electrolyte fuel cells, *Top. Catal.*, 46 (2007) 263-275.
- [26] S.-Y. Huang, P. Ganesan, B.N. Popov, Development of conducting polypyrrole as corrosion-resistant catalyst support for polymer electrolyte membrane fuel cell (PEMFC) application, *Appl. Catal. B-Environ.*, 93 (2009) 75-81.
- [27] R. Bashyam, P. Zelenay, A class of non-precious metal composite catalysts for fuel cells, *Nature*, 443 (2006) 63-66.
- [28] G. Wu, K.L. More, C.M. Johnston, P. Zelenay, High-performance electrocatalysts for oxygen reduction derived from polyaniline, iron, and cobalt, *Science*, 332 (2011) 443-447.
- [29] M. Lefevre, J.P. Dodelet, P. Bertrand, O₂ reduction in PEM fuel cells: Activity and active site structural information for catalysts obtained by the pyrolysis at high temperatures of Fe precursors, *J. Phys. Chem. B*, 104 (2000) 11238.
- [30] S.L. Gojkovic, S. Gupta, R.F. Savinell, Heat-Treated iron(III) tetramethoxyphenyl porphyrin supported on high-area carbon as an electrocatalyst for oxygen reduction I. Characterization of the electrocatalyst, *J. Electrochem. Soc.*, 145 (1998) 3493-3499.
- [31] S.L. Gojkovic, S. Gupta, R.F. Savinell, Heat-treated iron(III) tetramethoxyphenyl porphyrin chloride supported on high-area carbon as an electrocatalyst for oxygen reduction: Part III. Detection of hydrogen-peroxide during oxygen reduction, *Electrochim. Acta*, 45 (1999) 889-897.

- [32] H. Schulenburg, S. Stankov, V. Schuenemann, J. Radnik, I. Dorbandt, S. Fiechter, P. Bogdanoff, H. Tributsch, Catalysts for the oxygen reduction from heat-treated iron(III) tetramethoxyphenylporphyrin chloride: structure and stability of active sites, *J. Phys. Chem. B*, 107 (2003) 9034-9041.
- [33] J. Herranz, F. Jaouen, M. Lefevre, K.I. Ulrike, E. Proietti, J.P. Dodelet, P. Bogdanoff, S. Fiechter, I. Abs-Wurmbach, P. Bertrand, T.M. Arruda, S. Mukerjee, Unveiling N-protonation and anion-binding effects on Fe/N/C catalysts for O₂ reduction in proton-exchange-membrane fuel cells, *J. Phys. Chem. C*, 115 (2011) 16087-16097.
- [34] S. Maldonado, K.J. Stevenson, Direct preparation of carbon nanofiber electrodes via pyrolysis of iron(II) phthalocyanine: electrocatalytic aspects for oxygen reduction, *J. Phys. Chem. B*, 108 (2004) 11375-11383.
- [35] P.H. Matter, U.S. Ozkan, Non-metal catalysts for dioxygen reduction in an acidic electrolyte, *Catal. Lett.*, 109 (2006) 115-123.
- [36] S. Maldonado, K.J. Stevenson, Influence of nitrogen doping on oxygen reduction electrocatalysis at carbon nanofiber electrodes, *J. Phys. Chem. B*, 109 (2005) 4707-4716.
- [37] P.H. Matter, E. Wang, M. Arias, E.J. Biddinger, U.S. Ozkan, Oxygen reduction reaction catalysts prepared from acetonitrile pyrolysis over alumina supported metal particles, *J. Phys. Chem. B*, 110 (2006) 18374-18384.
- [38] P.H. Matter, E. Wang, U.S. Ozkan, Preparation of nanostructured nitrogen-containing carbon catalysts for the oxygen reduction reaction from SiO₂ and MgO supported metal particles, *J. Catal.*, 243 (2006) 395-403.
- [39] P.H. Matter, L. Zhang, U.S. Ozkan, The role of nanostructure in nitrogen-containing carbon catalysts for the oxygen reduction reaction, *J. Catal.*, 239 (2006) 83-96.
- [40] P.H. Matter, E.J. Biddinger, U.S. Ozkan, Non-precious metal oxygen reduction catalysts for PEM fuel cells, in: J.J. Spivey (Ed.) *Catalysis*, The Royal Society of Chemistry, Cambridge, UK, 2007, pp. 338-361.
- [41] P.H. Matter, E. Wang, M. Arias, E.J. Biddinger, U.S. Ozkan, Oxygen reduction reaction activity and surface properties of nanostructured nitrogen-containing carbon, *J. Mol. Catal.*, 264 (2007) 73-81.
- [42] P.H. Matter, E. Wang, J.-M.M. Millet, U.S. Ozkan, Characterization of the iron phase in CN_x-based oxygen reduction reaction catalysts, *J. Phys. Chem. C*, 111 (2007) 1444-1450.
- [43] E.J. Biddinger, D. von Deak, U.S. Ozkan, Nitrogen-containing carbon nanostructures as oxygen-reduction catalysts, *Top. Catal.*, 52 (2009) 1566-1574.
- [44] E.J. Biddinger, U.S. Ozkan, Role of graphitic edge-plane exposure in carbon nanostructures for oxygen reduction reaction, *J. Phys. Chem. C*, 114 (2010) 15306-15314.
- [45] D. von Deak, D. Singh, J.C. King, U.S. Ozkan, Use of carbon monoxide and cyanide to probe the active sites on nitrogen-doped carbon catalysts for oxygen reduction, *Appl. Catal. B-Environ.*, 113-114 (2011) 126-133.
- [46] D. von Deak, D. Singh, E.J. Biddinger, J.C. King, B. Bayram, J.T. Miller, U.S. Ozkan, Investigation of sulfur poisoning of CN_x oxygen reduction catalysts for PEM fuel cells, *J. Catal.*, 285 (2012) 145-151.
- [47] D. Singh, I.I. Soykal, J. Tian, D. Von Deak, J.C. King, J.T. Miller, U.S. Ozkan, In situ characterization of the growth of CN_x carbon nanostructures as oxygen reduction reaction catalysts, *J. Catal.*, 304 (2013) 100-111.
- [48] N.P. Subramanian, X. Li, V. Nallathambi, S.P. Kumaraguru, H. Colon-Mercado, G. Wu, J.-W. Lee, B.N. Popov, Nitrogen-modified carbon-based catalysts for oxygen reduction reaction in polymer electrolyte membrane fuel cells, *J. Power Sources*, 188 (2009) 38-44.
- [49] R.A. Sidik, A.B. Anderson, N.P. Subramanian, S.P. Kumaraguru, B.N. Popov, O₂ reduction on graphite and nitrogen-doped graphite: experiment and theory, *J. Phys. Chem. B*, 110 (2006) 1787-1793.
- [50] X. Li, G. Liu, B.N. Popov, Activity and stability of non-precious metal catalysts for oxygen reduction in acid and alkaline electrolytes, *J. Power Sources*, 195 (2010) 6373-6378.

- [51] S.M. Lyth, Y. Nabaie, S. Moriya, S. Kuroki, M.-a. Kakimoto, J.-i. Ozaki, S. Miyata, Carbon nitride as a nonprecious catalyst for electrochemical oxygen reduction, *J. Phys. Chem. C*, 113 (2009) 20148-20151.
- [52] J.-i. Ozaki, K. Nozawa, K. Yamada, Y. Uchiyama, Y. Yoshimoto, A. Furuichi, T. Yokoyama, A. Oya, L.J. Brown, J.D. Cashion, Structures, physicochemical properties and oxygen reduction activities of carbons derived from ferrocene-poly(furfuryl alcohol) mixtures, *J. Appl. Electrochem.*, 36 (2006) 239-247.
- [53] J.P. Dodelet, The controversial role of the metal in Fe- or Co-based electrocatalysts for the oxygen reduction reaction in acid medium, in: M. Shao (Ed.) *Electrocatalysis in Fuel Cells A Non- and Low-Platinum Approach*, 2013, pp. 271-338.
- [54] K. Gong, F. Du, Z. Xia, M. Durstock, L. Dai, Nitrogen-doped carbon nanotube arrays with high electrocatalytic activity for oxygen reduction, *Science*, 323 (2009) 760-764.
- [55] L. Qu, L. Yong, J.-B. Baek, L. Dai, Nitrogen-doped graphene as efficient metal free electrocatalyst for oxygen reduction in fuel cells, *ACS Nano*, 4 (2010) 1321-1326.
- [56] S. Wang, D. Yu, L. Dai, D.W. Chang, J.-B. Baek, Polyelectrolyte-Functionalized Graphene as Metal-Free Electrocatalysts for Oxygen Reduction, *ACS Nano*, 5 (2011) 6202-6209.
- [57] Z. Chen, D. Higgins, H. Tao, R.S. Hsu, Z. Chen, Highly active nitrogen-doped carbon nanotubes for oxygen reduction reaction in fuel cell applications, *J. Phys. Chem. C*, 113 (2009) 21008-21013.
- [58] Z. Chen, D. Higgins, Z. Chen, Nitrogen doped carbon nanotubes and their impact on the oxygen reduction reaction in fuel cells, *Carbon*, 48 (2010) 3057-3065.
- [59] D. Higgins, Z. Chen, Nitrogen doped carbon nanotube thin films as efficient oxygen reduction catalyst for alkaline anion exchange membrane fuel cell, *ECS Transactions*, 28 (2010) 63-68.
- [60] D. Singh, J.C. King, U. Ozkan, Modified carbon materials as O₂ reduction reaction electrocatalysts in acid PEM fuel cells, in: Z. Chen, J.P. Dodelet, J. Zhang (Eds.) *Non-Noble Metal Fuel Cell Catalysts*, Wiley-VCH, 2013.
- [61] A.J. Bard, L.R. Faulkner, *Electrochemical methods: fundamentals and applications*, John Wiley and Sons Ltd, New York, 2001.
- [62] K.-L. Hsueh, E.R. Gonzalez, S. Srinivasan, Electrolyte effects on oxygen reduction kinetics at platinum: A rotating ring-disc electrode analysis, *Electrochim. Acta*, 28 (1983) 691-697.
- [63] G. Baysinger, L.I. Berger, R.N. Goldberg, H.V. Kehiaian, K. Kuchitsu, G. Rosenblatt, D.L. Roth, D. Zwilling, *CRC Handbook of Chemistry and Physics*, 74 ed., CRC Press, Boca Raton FL, 2005.
- [64] R. Baker, D.P. Wilkinson, J. Zhang, Electrocatalytic activity and stability of substituted iron phthalocyanines towards oxygen reduction evaluated at different temperatures, *Electrochim. Acta*, 53 (2008) 6906-6919.
- [65] S.L. Gojkovic, S.K. Zecevic, R.F. Savinell, O₂ reduction on an ink-type rotating disk electrode using Pt supported on high-area carbons, *J. Electrochem. Soc.*, 145 (1998) 3713-3720.
- [66] E.J. Biddinger, D.S. Knapke, D. von Deak, U.S. Ozkan, Effect of sulfur as a growth promoter for CN_x nanostructures as PEM and DMFC ORR catalysts, *Appl. Catal. B-Environ.*, 96 (2010) 72-82.
- [67] A. Bonakdarpour, M. Lefevre, R. Yang, F. Jaouen, T. Dahn, J.-P. Dodelet, J.R. Dahn, Impact of loading in RRDE experiments on Fe-N-C catalysts: Two- or four-electron oxygen reduction?, *Electrochem. Solid-State Lett.*, 11 (2008) B105-B108.
- [68] E.J. Biddinger, D. von Deak, D. Singh, H. Marsh, B. Tan, D.S. Knapke, U.S. Ozkan, Examination of catalyst loading effects on the selectivity of CN_x and Pt/VC ORR catalysts using RRDE, *J. Electrochem. Soc.*, 158 (2011) B402-B409.
- [69] A.P. Young, J. Stumper, E. Gyenge, Characterizing the structural degradation in a PEMFC cathode catalyst layer: Carbon corrosion, *J. Electrochem. Soc.*, 156 (2009) B913-B922.
- [70] L. Li, Y. Xing, Electrochemical durability of carbon nanotubes in noncatalyzed and catalyzed oxidations, *J. Electrochem. Soc.*, 153 (2006) A1823-A1828.

- [71] Y. Shao, G. Yin, J. Zhang, Y. Gao, Comparative investigation of the resistance to electrochemical oxidation of carbon black and carbon nanotubes in aqueous sulfuric acid solution, *Electrochim. Acta*, 51 (2006) 5853-5857.
- [72] L. Li, Y. Xing, Electrochemical durability of carbon nanotubes at 80°C, *J. Power Sources*, 178 (2008) 75-79.
- [73] D. von Deak, E.J. Biddinger, U.S. Ozkan, Carbon corrosion characteristics of CN_x nanostructures in acidic media and implications for ORR performance, *J. Appl. Electrochem.*, 41 (2011) 757-763.
- [74] J.R. Pels, F. Kapteijn, J.A. Moulijn, Q. Zhu, K.M. Thomas, Evolution of nitrogen functionalities in carbonaceous materials during pyrolysis, *Carbon*, 33 (1995) 1641-1653.
- [75] F. Jaouen, S. Marcotte, J.-P. Dodelet, G. Lindbergh, Oxygen reduction catalysts for polymer electrolyte fuel cells from the pyrolysis of iron acetate adsorbed on various carbon supports, *J. Phys. Chem. B*, 107 (2003) 1376-1386.
- [76] F. Kapteijn, J.A. Moulijn, S. Matzner, H.-P. Boehm, The development of nitrogen functionality in model chars during gasification in CO₂ and O₂, *Carbon*, 37 (1999) 1143-1150.
- [77] S. Pylypenko, S. Mukherjee, T.S. Olson, P. Atanassov, Non-platinum oxygen reduction electrocatalysts based on pyrolyzed transition metal macrocycles, *Electrochim. Acta*, 53 (2008) 7875-7883.
- [78] S. Ganesan, N. Leonard, S.C. Barton, Impact of transition metal on nitrogen retention and activity of iron–nitrogen–carbon oxygen reduction catalysts, *Phys. Chem. Chem. Phys.*, 16 (2014) 4576.
- [79] T. Palaniselvam, R. Kannan, S. Kurungot, Facile construction of non-precious iron nitride-doped carbon nanofibers as cathode electrocatalysts for proton exchange membrane fuel cells, *Chem. Commun.*, 47 (2011) 2910.
- [80] G. Liu, X. Li, P. Ganesan, B.N. Popov, Studies of oxygen reduction reaction active sites and stability of nitrogen-modified carbon composite catalysts for PEM fuel cells, *Electrochim. Acta*, 55 (2010) 2853-2858.
- [81] G. Liu, X. Li, J.-W. Lee, B.N. Popov, A review of the development of nitrogen-modified carbon-based catalysts for oxygen reduction at USC, *Catalysis Science and Technology*, 1 (2011) 207-217.
- [82] D.L. Leslie-Pelecky, R.D. Rieke, Magnetic Properties of Nanostructured Materials, *Chem. Mater.*, 8 (1996) 1770-1783.
- [83] M. Boudart, A. Delbouille, J.A. Dumesic, S. Khammouma, H. Topsøe, Surface, catalytic and magnetic properties of small iron particles: I. Preparation and characterization of samples, *J. Catal.*, 37 (1975) 486-502.
- [84] S.H. Mahmood, Magnetic anisotropy in fine magnetic particles, *Journal of Magnetism and Magnetic Materials*, 118 (1993) 359-364.
- [85] D.K. Kim, Y. Zhang, W. Voit, K.V. Rao, M. Muhammed, Synthesis and characterization of surfactant-coated superparamagnetic monodispersed iron oxide nanoparticles, *Journal of Magnetism and Magnetic Materials*, 225 (2001) 30-36.

List of Figures

Figure 1. Comparison of ORR RRDE results for unwashed and acid washed catalysts at 1600 rpm in 0.5M H₂SO₄ oxygen-saturated solution. (a) FeNC and (b) CN_x

Figure 2. (a) RRDE graphs showing ring and disk currents and (b) Koutecky-Levich plot for FeNC-unwashed sample

Figure 3. Accelerated durability tests on the two most active catalysts. (a) FeNC-unwashed and (b) CN_x-washed

Figure 4. Fuel-cell polarization curves for (a) FeNC-unwashed and CN_x-washed (b) FeNC-unwashed and FeNC-washed before (solid lines) and after (dashed lines) 100h potential hold at 0.5V

Figure 5. N 1s XPS spectra of CN_x (a) unwashed (b) washed and FeNC (c) unwashed (d) washed

Figure 6. Comparison of TPO profiles of FeNC and CN_x catalysts acid washed for different durations of time. (a) and (b) unwashed, (c) and (d) washed for 1h, (e) and (f) washed for 1week

Figure 7. Fe-K edge XANES spectra of a) CN_x-unwashed, b) CN_x-washed, c) FeNC-unwashed, d) FeNC-washed. Reference spectra for Fe carbide, FeO, and Fe foil are included for comparison.

Figure 8. FT-Magnitudes of Fe-K edge of a) CN_x-unwashed, b) CN_x-washed, c) FeNC-unwashed, d) FeNC-washed. Reference spectra for Fe carbide, FeO, and Fe foil are included for comparison.

Figure 9. TEM images of (a) CN_x (washed) and (b) FeNC (unwashed)

Figure 10. Magnetization as a function of field at 300 K

Table 1. Selectivity values at 0.5V for CN_x and FeNC

Sample	Number of electrons transferred (n) per molecule of O ₂	
	RRDE	K-L
FeNC-unwashed	3.9	3.8
FeNC-washed	4.0	3.9
CN _x -unwashed	3.0	2.4
CN _x washed	3.8	4.0

Table 2. XPS N 1s content for FeNC and CN_x catalysts.

Sample	Pyridinic-N (398.0-398.9 eV)	Quarternary (401-402 eV)	Pyridinic N ⁺ -O ⁻ (eV) (402-405 eV)
Percentage distribution (%)			
FeNC-unwashed	25	57	18
FeNC-washed	36	48	16
CN _x -unwashed	27	66	7
CN _x -washed	27	51	22

Table 3. Weight percentage of iron in the unwashed and washed samples and the weight percentage of iron leached out in acid as determined by ICP-MS. Acid washing was continued for 1 hour or 48 hours.

Sample	wt% iron in the sample	wt% iron leached out relative to the amount present before acid washing
FeNC-unwashed	1.6	-
FeNC-washed-1h	1.2	24
FeNC-washed-48h	1.0	35
CN _x -unwashed	2.4	-
CN _x -washed-1h	2.5	77
CN _x -washed-48h	2.5	78

Table 4. Saturation magnetization and iron particle diameter for various samples estimated by fitting Langevin function to magnetization vs. field data

Sample	M_{sat} (emu/g of catalyst)	d (nm)
FeNC-unwashed	1.0	4.8
FeNC-washed	0.20	4.4
CN _x -unwashed	1.4	3.5
CN _x -washed	3.0	4.1

Figure 1. Comparison of ORR RRDE results for unwashed and acid washed catalysts at 1600 rpm in 0.5M H₂SO₄ oxygen-saturated solution. (a) FeNC and (b) CN_x

Figure 2. (a) RRDE graphs showing ring and disk currents and (b) Koutecky-Levich plot for FeNC-unwashed sample

Figure 3. Accelerated durability tests on the two most active catalysts. (a) FeNC-unwashed and (b) CN_x -washed

Figure 4. Fuel-cell polarization curves for (a) FeNC-unwashed and CN_x-washed (b) FeNC-unwashed and FeNC-washed before (solid lines) and after (dashed lines) 100h potential hold at 0.5V. iR-free cell voltage vs log of current density plots at high voltage region are shown as insets.

Figure 5. N 1s XPS spectra of CNx (a) unwashed (b) washed and FeNC (c) unwashed (d) washed

Figure 6. Comparison of TPO profiles of FeNC and CN_x catalysts acid washed for different durations of time. (a) and (b) unwashed, (c) and (d) washed for 1h, (e) and (f) washed for 1 week

Figure 7. Fe-K edge XANES spectra of a) CN_x -unwashed, b) CN_x -washed, c) FeNC-unwashed, d) FeNC-washed. Reference spectra for Fe carbide, FeO, and Fe foil are included for comparison.

Figure 8. FT-Magnitudes of Fe-K edge of a) CN_x -unwashed, b) CN_x -washed, c) FeNC-unwashed, d) FeNC-washed. Reference spectra for Fe carbide, FeO, and Fe foil are included for comparison.

Figure 9. TEM images of (a) CN_x (washed) and (b) FeNC (unwashed)

Figure 10. Magnetization as a function of field at 300 K