

UNDERSTANDING THE ROLE OF MAGNETIC SPECIES IN NONPRECIOUS METAL
OXYGEN REDUCTION ELECTROCATALYSTS

BY

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DISSERTATION

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ABSTRACT

Development and implementation of renewable energy storage and production to replace traditional fossil fuels is a requirement to combat climate change. While many different technologies are promising, many need further understanding of the components to lead to wide implementation. Electrocatalysts are of particular interest to enable the conversion of chemicals into energy. The first chapter of this dissertation describes the challenges faced in the implementation of fuel cells and efforts taken to address those challenges. The next 4 chapters describe the efforts taken to understand the speciation of Fe- and Co-based oxygen reduction reaction (ORR) catalysts.

An approach towards energy production uses fuel cells in place of existing combustion-based power production. In a fuel cell, H_2 is oxidized at the anode while O_2 is reduced at the cathode. Conversion of H_2 and O_2 to H_2O require appropriate catalysts to facilitate the oxidation/reduction reactions. In both cases, precious metals (including Pt and its alloys) can serve as a catalyst, however the low availability and subsequently high cost of Pt poses problems for widespread implementation. The search for an economically viable, highly active, ORR catalyst has led to intense research on nonprecious metal (NPM) ORR catalysts.

Chapter 2 of this dissertation describes the experimental methods used to produce the data in the following chapters. Chapter 3 describes the investigation of an Fe-based ORR catalyst utilizing traditional characterization methods such as x-ray photoelectron spectroscopy and Mössbauer spectroscopy as well as an underutilized technique, SQUID magnetometry. The SQUID magnetometry can inform the amount of superparamagnetic/ferromagnetic Fe species in the catalyst. The results from this

analysis disagree with the Mössbauer spectroscopy analysis which does not indicate the presence of any superparamagnetic/ferromagnetic Fe species. Additionally, a small molecule probe is used to better understand the role of C in the Fe-based NPM catalyst. This probe indicates that C is playing a significant role in the catalyst ORR activity.

Chapter 4 investigates Co-based catalysts using similar techniques as used in chapter 4. Based on the results from the SQUID magnetometry data we are able to synthesize a catalyst that contains 100% superparamagnetic Co species in order to compare the activity toward the ORR to another catalyst containing nearly 100% paramagnetic Co species.

Chapter 5 investigates the role of high temperature reductive gas treatments on the activity and characterization of Fe-based NPM ORR catalysts. NH_3 and H_2 high temperature gas treatments improve catalyst activity as compared to the untreated catalyst. 120 min of NH_3 treatment yields the most active ORR catalyst, which contains nearly 100% superparamagnetic Fe species. This indicates that both paramagnetic and superparamagnetic Fe species are active for the ORR.

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Chapter 1 Introduction

1. Importance of NPM ORR Catalysts

Our world is on seeing the results of ever-worsening climate change. Climate change is already leading to increased temperatures, more frequent and stronger weather events, fires, droughts, forced migrations, and poverty.¹ A necessary mitigation to combat these changes is to lower our CO₂ Production much of which stems from our current energy infrastructure.² Indeed, a concerted research effort to transition away from traditional power sources has already begun in the United States – starting with the first Energy Earth Shot.³

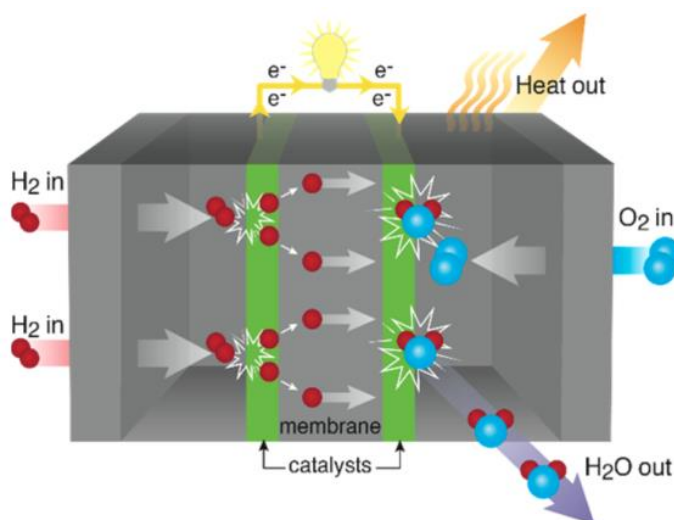


Figure 1.1. General schematic of a PEM fuel cell.

One promising approach towards low carbon energy production is the use of fuel cells in place of existing combustion-based power production. The benefits of this approach are two-fold as electrolytic fuel cells avoid the production of CO₂ during operation, while simultaneously achieving higher efficiencies than

combustion engines operating on the Carnot cycle.⁴ Indeed, polymer electrolyte membrane (PEM) fuel cells are being considered as a viable alternative for powering transportation, with several examples already on the road.^{2, 5} In a fuel cell, a fuel (typically H₂) is oxidized at the anode, while another species, typically O₂, is reduced at the cathode. A schematic of a fuel cell can be found in Fig. 1.1.⁶ Both the cathode and anode sides of

the fuel cell require an appropriate catalyst to facilitate the oxidation/reduction reactions. In both cases, precious metals (including Pt and its alloys) can serve as a catalyst, however the low availability and subsequently high cost of Pt poses problems for widespread utilization (Fig. 1.2).⁶⁻⁷ Additionally, while Pt works well for H₂ oxidation, it exhibits higher overpotentials and worse stability as a catalyst for the oxygen reduction reaction.⁸ In particular, overpotentials as high as 300 mV in acidic media are common.⁹ The combination of this poor activity and high cost makes the search for an economically viable, highly active ORR catalyst imperative to the widespread deployment of fuel cell systems.

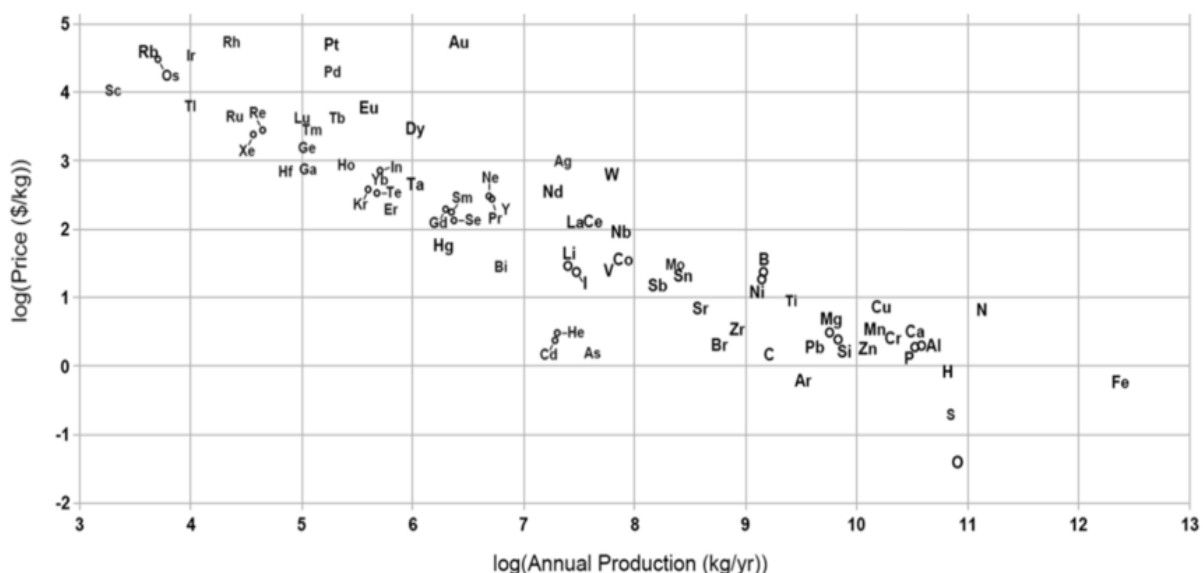


Figure 1.2. Plot of cost vs. production for elements.

2. Synthesis of NPM ORR Catalysts

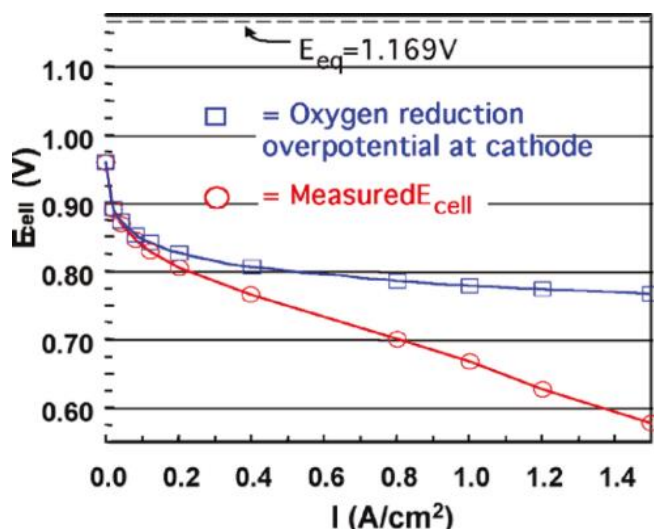


Figure 1.3. Measured current vs. potential for a typical Pt-based ORR catalyst. Dashed line is comparison with theoretical potential for ORR.

Nonprecious metal (NPM) catalysts based on Fe or Co are promising replacements for Pt because of their high activity (Fig. 1.3) and inexpensive production costs (Fig. 1.2).^{6, 10} NPM ORR catalysts were first reported by Jasinski over 50 years ago,¹¹ and have been the subject of almost continual development since then. A typical NPM ORR catalyst preparation

features pyrolysis of precursors (traditionally composed of a mixture of C, Fe and/or Co, and N containing moieties) at high (900-1100 °C) temperatures followed by a series of post processing steps involving gas exposure, washings, and additional pyrolysis.¹² A schematic of a general synthesis procedure can be found in Fig. 1.4.

A huge variety of different precursors have been studied for the synthesis of NPM catalysts include porphyrins, phthalocyanines,¹³ different Fe and Co salts,¹² a variety of

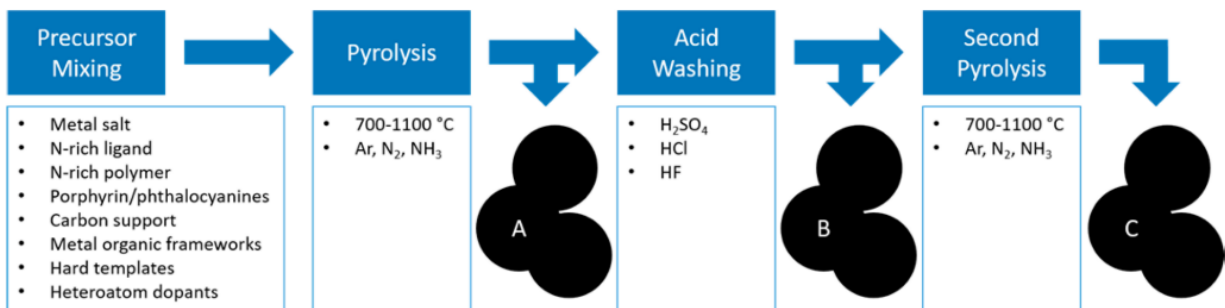


Figure 1.4. Description of typical step in NPM ORR catalyst synthesis.

N-containing materials,¹⁴ and different carbon hosts. Two N-containing materials seeing recent use include metal organic frameworks (MOFs)¹⁵ and polymers.¹⁶⁻¹⁷ Fe-containing catalysts synthesized from these precursors exhibit some of the highest stabilities and activities available.

3. Active Site Characterization

Due to the high temperature pyrolysis necessary to produce active NPM catalysts, the primary active sites which facilitate ORR remain unclear. Further development of NPM ORR catalysts requires a detailed understanding of such active sites. There have been substantial efforts directed at understanding speciation of Fe-based ORR pyrolyzed catalysts^{16, 18-24} with FeN_4 ^{23, 25}, Fe_xN^{26} , Fe_3C^{27} , $\text{Fe}(0)^{16-17}$, and C_xN_y ¹⁴ commonly featured as the proposed redox active moieties.

In addition to the study of specific active sites, many groups have also investigated other transition metals, including Co, which could serve as alternatives to Fe-based NPM catalysts. Co-based catalysts do not catalyze the Fenton reaction which is known to produce radical species that contribute to catalyst degradation.²⁸⁻²⁹ Multiple active materials for Co-based catalysts have been proposed including CoN_4 sites,^{28, 30-31} Co_3O_4 ,³²⁻³³ CoO , and Co nanoparticles.^{10, 34} A persistent issue is the apparent heterogeneity of the as prepared NPM material. Synthetic methods have been employed to make a more homogenous catalyst.^{16, 23, 35} It is difficult, however, to determine the absolute quantities of different species in the catalyst; particularly Fe and Co species which are often present in 1-5% quantities.³⁶ Characterization techniques such as Mössbauer spectroscopy, X-ray photoelectron spectroscopy (XPS), X-ray absorption spectroscopy (XAS), transmission electron microscopy (TEM) and X-ray diffraction (XRD)

provide speciation information about catalyst materials however, substantial disagreement exists in the literature regarding the relationship of the characterization results to the catalyst activity.^{16-17, 19, 24, 28, 30, 37-44}

Two less common NPM ORR catalysts characterization techniques are low temperature electron paramagnetic resonance (EPR)⁴⁵ and superconducting quantum interference device (SQUID) magnetometry.⁴⁶ SQUID magnetometry has been used to study similar Fe-based ORR catalysts by the Ozkan group,⁴⁷⁻⁴⁹ and in studying Co-based ORR catalysts.^{30, 50} Magnetometry can determine the relative amount of paramagnetic and non-paramagnetic species in a sample, while EPR can report on the chemical environment surrounding oxidized, paramagnetic species.⁵¹

In addition to analytical methods many publications use chemical methods (specifically perturbations to the synthesis of NPM ORR catalysts) to correlate structural motifs to the observed catalytic activity of their materials. One of the most common approaches to achieve such chemical modification is to modify the gas environment used during the pyrolysis steps, which has been shown to impact both the structure and activity of candidate materials.^{42, 52} As a concrete example, It is well known that NH₃-treatment at high temperatures can yield improved activity for Fe-based NPM ORR catalysts.^{20, 23, 49,}

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Several groups have leveraged this improved activity to discuss the structural characteristics impacting the activity of Fe NPM catalysts. In particular, Zitolo et al. reported increased basicity of the N groups on the catalyst surface and Kramm et al. reported increases in the catalyst surface area as well as an increase in FeN₄-like species (determined by Mössbauer spectroscopy).⁵² Changes in Fe speciation to Fe⁰ and iron

nitrides (determined by XRD) have also been reported.⁵²⁻⁵³ H₂ heat treatments can also been used in the synthesis of non-precious metal, Fe-based, ORR catalysts.^{16, 42, 54} These treatments have been correlated to increased Fe⁰ nanoparticles and FeN₄ sites.

In addition to these synthetic efforts, post-synthetic modifications have also been used to study the correlation between active site structure and catalyst function.^{13, 42, 55} For example, NO was used *in situ* to poison active sites in NPM ORR catalysts.²⁴ The procedure involves NO/NO₂⁻ exposure while the catalyst is at open circuit potential (OCP) and leads to significant catalyst deactivation. The on-electrode poisoning protocol, however, inhibits post-poisoning characterization because of the relatively small amount of material available although some results obtained from nuclear resonance vibrational spectroscopy (NRVS) showed changes in the bonding environment of the Fe following NO exposure.⁵⁶

Chapter 2 Experimental Methods

1. Catalyst Preparation

All chemicals were obtained from Sigma Aldrich (St. Louis, MO) and used without further purification. Ar (99.999%) and H₂ (99.99%) gases were purchased from Airgas (Randor, PA). NH₃ anhydrous (99.99%) was purchased from Matheson Tri-Gas (Basking Ridge, NJ).

ZIF-8 Preparation

ZIF-8 was prepared following a published method.⁵⁷ 2.933 g of zinc nitrate was dissolved in 200 mL of methanol. In a separate flask, 6.489 g of 2-methylimidazole was also dissolved in 200 mL of methanol. The zinc nitrate solution was rapidly poured into the 2-methylimidazole solution, the solution was stirred for 2 h, and then centrifuged. The methanol was decanted and the resulting solid was washed with methanol, centrifuged, and decanted. The resulting solid was dried at 40 °C overnight and then crushed to form a white powder. The powder x-ray diffraction spectrum was consistent with that reported previously.⁵⁸

Fe_{0.5}-950 Preparation

Fe_{0.5}-950 was prepared following a previously published method.²³ 1.18 g of ZIF-8, 0.0234 g iron acetate, and 0.295 g 1,10-phenanthroline were dried at 90 °C overnight, followed by mixing in an alumina ball mill container. Ball milling was done for a total of 10.5 hr broken into 2 hr chunks with 15 min breaks in between. The resulting pink powder was pyrolyzed in a tube furnace (Lindberg/MPH, Riverside, MI) in a ceramic boat under Ar gas flow. Gas flow rates in this and subsequent preparations were typically 1000 cc/min. The temperature was ramped at ~35 °C/min until 1050 °C was reached and held

constant for 1 h. The catalyst was then allowed to cool to room temperature under Ar gas flow, then heated at a ramp rate of ~ 30 $^{\circ}\text{C}/\text{min}$ to 950 $^{\circ}\text{C}$ under Ar flow and then the gas flow was switched to NH_3 for 5 min. After this treatment, the gas flow was switched back to Ar and the sample cooled to room temperature. Typical Fe content was 1 wt.%. The Brunauer-Emmett-Teller (BET) surface area was 960 ± 123 m^2/g . Representative gas isotherm from which BET surface area was calculated is shown in Figure 2.1.

Preparation of PANIFeC Catalyst

PANIFeC was prepared by following a published method.¹⁶ 500 mL of 2 M HCl, 2.5 mL aniline, and 10 g FeCl_3 were combined in a round bottom flask. The flask was placed in an ice bath and the solution was stirred. 5 g of ammonium persulfate was added and the resulting mixture was stirred for 2 h. 600 mg of carbon black (Ketjen Black EC-600JD, AkzoNobel Chicago, IL) was crushed with a mortar and pestle, added to the mixture and stirred for 48 h at room temperature. The solution was then evaporated under N_2 gas flow at 90 $^{\circ}\text{C}$ until all the solvent was removed. The resulting solid was ground in

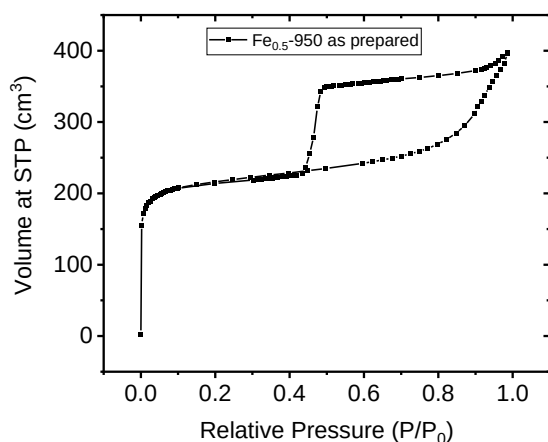


Figure 2.1. Representative N_2 gas adsorption isotherm for $\text{Fe}_{0.5}$ -950 as prepared.

a mortar and pestle and placed in a ceramic boat, then pyrolyzed under N_2 flow with a temperature ramp rate of ~ 30 $^{\circ}\text{C}/\text{min}$ until a temperature of 900 $^{\circ}\text{C}$ was reached. After 2 h at this temperature, the powder was allowed to cool under N_2 . The powder was then suspended in

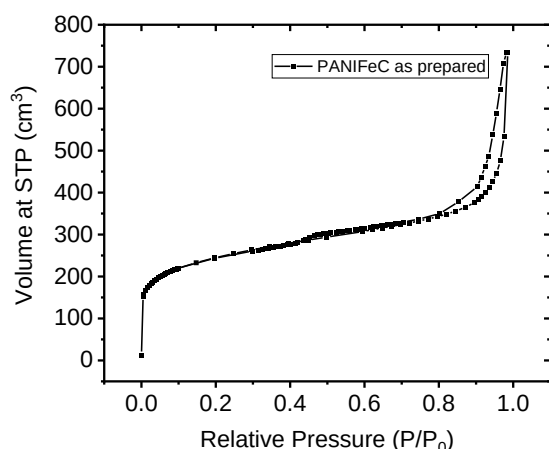


Figure 2.2. Representative N₂ gas adsorption isotherm for PANIFeC as prepared.

0.5 M H₂SO₄ with stirring at 60 °C overnight to remove excess Fe. The powder was recovered by using vacuum filtration, dried at 90 °C, and repyrolyzed at 900 °C for 1 h following the ramp protocol described above. Typical Fe content was 1 wt.%. The BET surface area was 997 ± 105 m²/g. Representative gas isotherm from

which BET surface area was calculated is shown in Figure 2.2.

Preparation of FePc Catalyst on XC72 carbon Support

Iron phthalocyanine (FePc) was purchased from Strem Chemicals in Newburyport, MA. FePc on XC72 was prepared by following a published method.³⁹ 0.12 g of FePc was dissolved in 10 mL of concentrated H₂SO₄ and stirred for 5 min. Then, 0.5 g of Vulcan XC72 (Fuel Cell Store, College Station, TX) was added and stirred for 10 min. Then the mixture was poured over 250 mL of cold 18Ω Milli-Q purified water. The powder was recovered by vacuum filtration through a 0.22 μm-pore nylon membrane (GVS Life Sciences). The powder was dried in a 90 °C oven under vacuum for at least 5 h.

CoNC Catalyst Preparation

A cobalt, nitrogen, carbon (CoNC) based catalyst was prepared by using a previously published method.²⁸ Briefly, Co(NO₃)₂·6H₂O, and Zn(NO₃)₂·6H₂O were dissolved in 50 mL of methanol. In a separate flask 2-methylimidazole was dissolved in 100 mL of methanol. The two solutions were poured together rapidly and stirred at room

temperature for 5 min. Then the mixture was stirred at 60 °C under reflux for 30 min. The resulting solution was centrifuged and decanted and washed once with methanol. The solution was then washed with ethanol, centrifuged and decanted. The remaining solid was dried under vacuum at 80 °C for 5 h. The resultant powder is a purple metal organic framework (MOF). 2-methylimidazole forms a MOF both with Zn and Co (ZIF-8 and ZIF-67, respectively). This MOF likely has both Zn and Co metal centers.⁵⁹ The dry solid was crushed to a powder and pyrolyzed in an alumina boat in a quartz tube at 900 °C for 3 h under flowing N₂. Gas flow rates in this and subsequent preparations were 1000 cc/min. The temperature was ramped at ~30 °C/min until 900 °C was reached and held constant for 3 h. The catalyst was then allowed to cool to room temperature under N₂ gas flow. This material is the CoNC as-prepared sample. CoNC was acid washed by mixing 50 mg of catalyst with 6 M HCl and stirred at 60 °C overnight. This material is the CoNC acid washed sample.

Preparation of CoNC modified with cetyltrimethyl ammonium bromide (CoNC-CTAB)

CoNC -CTAB was prepared by using a previously published method as a guideline.²⁸ Briefly, Co(NO₃)₂·6H₂O, and Zn(NO₃)₂·6H₂O were dissolved in 50 mL of methanol. In a separate flask 2-methylimidazole was dissolved in 100 mL of methanol. Two grams of CTAB and 50 mL of methanol were added to the first flask. The 2-methylimidazole solution was added slowly (over the course of 5 min) to the first flask and stirred at room temperature for 5 min. Then the mixture was stirred at 60 °C under reflux for 30 min. The resulting solution was centrifuged and decanted and washed once with methanol. The solution was then washed with ethanol, centrifuged and decanted. The remaining solid was dried under vacuum at 80 °C for 5 h. The resultant powder is a purple

MOF. This material is the CoNC-CTAB as-prepared sample. CoNC-CTAB was acid washed by mixing 50 mg of catalyst with 6 M HCl and stirred at 60 °C overnight. This material is the acid-washed sample of CoNC-CTAB.

Preparation of Co NPs supported on carbon black (XC-72) catalyst

Co NPs on XC-72 catalyst was prepared by first mixing 0.291 g of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 3.061 g of CTAB in a flask containing 200 mL of methanol. The flask was stirred for 5 min and then 10 mL of 0.1 M NaOH was added. The solution was heated at 60 °C under reflux for 3 h. The solution was then centrifuged and dried at 90 °C overnight. The resulting material was ground in a mortar and pestle with 0.0356 g of XC-72 carbon black (Cabot). The powder was then pyrolyzed at 900 °C for 3 h; identical pyrolysis procedure as compared to the CoNC-CTAB synthesis.

FeNC Preparation

FeNC-Ar was prepared following a previously published method.²³ 1.18 g of ZIF-8, 0.0234 g iron acetate, and 0.295 g 1,10-phenanthroline were dried at 90 °C overnight, followed by mixing in an alumina ball mill container. The material was ball milled for a total 10.5 h in 2 h blocks with 15 min breaks. The resulting pink powder was pyrolyzed in a ceramic boat in a tube furnace (Lindberg/MPH, Riverside, MI) under 1000 cc/min Ar gas flow. The temperature was ramped at ~35 °C/min until 1050 °C was reached and held for 1 h. The catalyst was then allowed to cool to room temperature under Ar gas flow.

The FeNC-Ar material was used as the starting material for subsequent gas treatments. In these preparations, we use a nomenclature FeNC-X-Y where X is the gas treatment used and Y is the length of time in minutes. The second heat treatment involved heating ca. 200 mg of FeNC-Ar in a ceramic boat under Ar gas (1000 cc/min) to 950 °C

at a ramp rate of ~ 35 $^{\circ}\text{C}/\text{min}$. Then, the gas flow was switched to either H_2 or NH_3 and held at 950 $^{\circ}\text{C}$ for the stated time. The catalyst was then allowed to cool to room temperature under Ar gas flow.

2. Catalyst modification Procedure

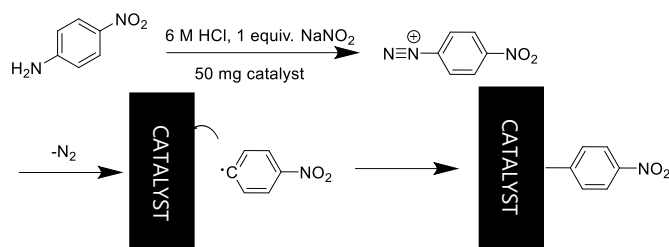


Figure 2.3. Modification procedure for the carbon-based modification.

$\text{Fe}_{0.5}\text{-950}$ and PANIFeC catalysts were modified by using click chemistry described previously and shown schematically in Fig. 2.3.⁵⁷ 50 mg of catalyst, 1.2 mmol 4-nitroaniline, 1.2

mmol sodium nitrite, 7.5 mL 18 Ω Milli-Q purified water, and 7.5 mL of concentrated HCl were added to a round bottom flask and the mixture was stirred overnight. The powder was recovered by vacuum filtration through a 0.22 μm -pore nylon membrane (GVS Life Sciences). The powder was washed with water until clear, followed by washing with methanol until clear. The powder was dried in a 90 $^{\circ}\text{C}$ oven under vacuum for at least 5 h. ‘Control’ measurements were performed on materials made following the above procedure without the addition of 4-nitroaniline to the reaction mixture.

3. Electrochemical Experiments

All electrochemical measurements were performed in a three-compartment electrochemical cell using a 760D Electrochemical Workstation (CH Instruments, Austin, TX) and a MSR rotator (Pine Instruments, Durham, NC). The counter electrode was a carbon rod and the reference electrode was a ‘leakless’ Ag/AgCl electrode (eDAQ, Colorado Springs, CO). All potentials were converted to RHE by measuring the open-

circuit potential of a flamed Pt wire electrode in H₂ gas-saturated electrolyte immediately preceding measurements. The cell was sparged with O₂ or Ar prior to measurements.

Catalyst ink for the Fe_{0.5}-950, PANIFeC, and Co-based materials was prepared by combining 5 mg of catalyst, 175 μ L of ethanol, and 47.5 μ L of Nafion (Sigma Aldrich) with planetary mixing. 5 μ L of catalyst ink were cast on polished glassy carbon electrodes.

Catalyst ink for the FeNC-X-Y materials was prepared by sonicating 5 mg of catalyst, 220 μ L of ethanol, 220 μ L of Milli-Q H₂O, and 45 μ L of Nafion for 5 min. 20 μ L of catalyst ink were cast by using a micropipette on a polished glassy carbon RRDE (rotating ring disk electrode) in 10 μ L increments. The cast was dried under a N₂ gas stream.

RRDE measurements were used to determine the number of transferred electrons during ORR by measuring the current from oxidation of H₂O₂ at a Pt ring. The Pt ring of the RRDE was polished prior to experiments by cycling the ring between -0.8 and 1.7 V vs. Ag/AgCl in 0.1 M HNO₃. Current ratios from reduction of K₃Fe(CN)₆ at the disk and oxidation at the ring was used to calibrate the collection efficiency.

Staircase voltammetry was conducted between relevant voltages, using 0.01 V step increments, 0.0167 s sampling width, and a 30 s step period. Values reported reflect the results of at least three independent measurements. The %H₂O₂ produced was determined using the RRDE with a Pt ring. The Pt ring was held at 1.2 V while ORR was performed at the disk to oxidize H₂O₂ to H₂O. The limiting current was measured at 0.2 V for all catalysts. The E_{1/2} for all catalysts was determined from the voltage at which the current reached half the limiting current for each individual SCV.

Cyclic voltammetry (CV) was conducted at a scan rate of 10mV/s, between relevant voltages, under O₂ and Ar saturated electrolyte at 1600, 1225, 900, and 400 rpm.

CVs were used to calculate the potential dependent kinetic current, i_k (A), values using the Koutecky-Levich equation (Eq. 2.1).⁶⁰ In Eq. 2.1 i is the observed current and ω is the rotation rate. The B term is defined in Eq. 2.2 where n is the number of transferred electrons, F (C/mol) is the Faraday constant, D (cm²/s) is the diffusion coefficient, ν (cm²/s) is the kinematic viscosity, and C (mol/cm³) is the analyte concentration. Values reported reflect the results of at least three independent measurements.

$$\frac{1}{i} = \frac{1}{B\omega^{1/2}} + \frac{1}{i_k} \quad (2.1)$$

$$B = .204nFAD^{2/3}\nu^{-1/6}C \quad (2.2)$$

The j_k (mA/mg catalyst) was determined using the mass loading of the catalyst on the RDE (0.21 mg). The j_k values were plotted against potential to determine the Tafel slope. Tafel slopes were determined between 0.9 V and 0.8 V.

For RRDE (rotating ring disk electrode), the Pt ring was polished by cycling the ring between -0.5 and 1.9 V vs. Ag/AgCl in 0.1 M HNO₃. All potentials were converted to RHE by measuring the open-circuit potential of a flamed Pt wire electrode in H₂ gas-saturated electrolyte immediately following measurements. Staircase voltammetry was conducted between relevant voltages, using 0.01 V step increments, 0.0167 s sampling width, and a 30 s step period. All electrochemical values reported reflect the results of at least three independent measurements.

4. Physical Characterization

Brunauer-Emmett-Teller (BET) surface area analysis was determined from N₂ physisorption data collected with a Quantachrome 2200e instrument. First the samples were heated to 150 °C under vacuum to remove trapped gases overnight. Then a gas adsorption isotherm was collected and BET theory was used to calculate surface area.

XPS was performed using a Kratos AXIS Ultra spectrometer with a monochromatic Al K α (1486.6 eV) X-ray source. All binding energies were referenced to graphitic carbon at 284.5 eV. X-ray diffraction (XRD) was collected using a Bruker D8 Advance XRD system. Reference XRD spectra were calculated from crystallographic information files using VESTA. Mössbauer spectra were recorded from a SEE Co. (Science Engineering & Education Co., MN) spectrometer (Johns Hopkins) in constant acceleration mode in a transmission geometry. All spectra reported were recorded at 300 K in the absence of a magnetic field. Isomer shifts were calibrated relative to the centroid of the spectrum of a metallic foil of α -Fe at room temperature. Samples were prepared in custom Delrin cups (10.0 mm $\times$ 12.4 mm outer diameter), sealed with tight-fitting Delrin inserts (5.0 mm $\times$ 11.0 mm outer diameter). Mössbauer spectroscopy measurements were also performed in part at Knox College and fit using proprietary software. The MossA program was used to determine the final fits to the Mössbauer data.⁶¹ SQUID (superconducting quantum interference device) magnetometry was collected at 300 K by using a Magnetic Property Measurement System (Quantum Design) with the sample placed in a plastic sample holder and inserted into a brass rod. The magnetic field was swept between -10000 and 10000 Oe and the magnetization of the sample was measured in emu. The magnetization was converted to emu/g Fe using the mass of sample in the sample holder and the wt.%Fe of the sample. The wt.% Fe of each sample was determined using ICP-OES (Perkin Elmer, Optima 8300) and the wt.% N was determined using CHN Analysis (Exeter Analytical, CE 440). EPR spectra were recorded at 5 K in ethanol solution on a Varian E-line 12' Century Series X-band CW spectrometer. Fits to the EPR spectra were obtained

by using the EasySpin program.⁶² Transmission electron microscopy (TEM) was performed on JEOL 2010 LaB6 with an accelerating voltage of 200 kV.

5. Calculations

Calculation 1

The rate constant k_f was calculated using a Koutecky-Levich analysis (Eq 2.1, 2.2, 2.3):

$$i_k = F A k_f C_{O_2} e^{\frac{-\alpha F (E - E_0)}{RT}} \quad (2.3)$$

Where k_f is the rate constant, α is the transfer coefficient (assumed to be 0.5), E is the potential that the kinetic analysis is performed at, E_0 is the equilibrium potential, R is the gas constant and T is temperature.

Calculation 2

We determined the number of Co atoms present in a single electrode cast for the catalysts using the ICP-OES data (Table 4.2) and the mass of catalyst on the electrode. We assume that all Co atoms present in the cast are active.

From the SQUID magnetometry measurements of the Co NPs + XC72 catalyst (Fig. 4.23) we can determine the volume of the Co nanoparticles by a Langevin function ($\mathcal{L}$) fit given by Equation 2.4:^{48, 63-64}

$$\frac{M}{M_{sat}} = \mathcal{L}\left(\frac{M_s V H}{k_B T}\right) \quad (2.4)$$

where M is equal to the magnetization, M_{sat} is equal to the saturation magnetization, M_s is equal to the spontaneous magnetization determined for Co⁰ (1335 emu/cm³), V is equal to the volume of a particle, H is equal to the applied magnetic field, k_B is the Boltzmann constant, and T is the temperature. The average number of atoms in a single Co

nanoparticle was calculated by determining the value of V for each sample and assuming spherical Co particles. The volume of each particle allowed us to calculate the number of Co atoms present per particle. Based on ICP-OES data and percentage of non-paramagnetic Co (Table 4.2) and the mass of catalyst cast on the electrode we can determine the total number of particles. Based on the diameter of a Co atom, we can calculate the number of atoms that would be on the surface of the particle.

Chapter 3 Characterization of Non-Precious Metal Oxygen Reduction Reaction Catalysts Using Magnetometry

1. Introduction

Two techniques seeing less usage in NPM ORR catalysts characterization are low temperature electron paramagnetic resonance (EPR)⁴⁵ and SQUID magnetometry.⁴⁶ SQUID magnetometry has been used to study similar Fe-based ORR catalysts by the Ozkan group,⁴⁸⁻⁴⁹ and in studying Co-based ORR catalysts.^{30, 50} Magnetometry can determine the relative amount of paramagnetic and non-paramagnetic species in a sample, while EPR can report on the Fe(III) environment in oxidized samples.⁵¹ Table 3.1 provides the expected Mössbauer, magnetometry, and EPR response from species suggested to be present in NPM ORR catalysts.

Table 3.1. Expected measurement responses for different Fe species.

Fe species	Mössbauer Response	EPR Response	Magnetometry Behavior
Fe (0) (superparamagnetic)	Singlet ¹⁶	Broad Feature ⁶⁵	Sigmoidal ⁶³
Fe(0) (ferromagnetic)	Sextet ¹⁸	Broad Feature ⁶⁵	Sigmoidal and hysteretic ⁶⁶
Fe(III)N ₄ O ₂	Doublet ⁶⁷	g=6, g=2 (g=4.3 possible for strained porphyrins) ^{45, 68}	Linear ⁴⁶
Fe ₃ O ₄	Sextet ⁶⁹	Broad Feature ⁶⁵	Sigmoidal and hysteretic ⁷⁰
Fe ₂ N	Doublet ²³	N/A	Linear ⁴⁶
Fe ₃ N	Sextet ⁷¹	Broad Feature ⁶⁵	Sigmoidal and hysteretic ⁷¹
Fe ₃ C	Sextet ¹⁶	Broad Feature ⁶⁵	Sigmoidal and hysteretic ⁷²

We also considered a new way to perturb the catalyst surface to understand how changes to the catalyst would affect presentation of the catalyst in characterization and in activity. Recently, NO was used *in situ* to poison active sites in NPM ORR catalysts.²⁴ The procedure involves NO/NO₂⁻ exposure while the catalyst is at OCP and leads to significant catalyst deactivation. The on-electrode poisoning protocol, however, inhibits post-poisoning characterization because of the relatively small amount of material available. Among techniques utilized, nuclear resonance vibrational spectroscopy (NRVS) showed changes in the bonding environment of the Fe following NO exposure.⁵⁶

A method with which to modify carbonaceous materials such as our catalysts, involves 'click' attachment of a ligand to the carbon surface.^{57, 73} Carbon modification sees use in creating electrodes that exhibit higher rates of small molecule detection⁷⁴ and can trap proteins and enzymes.⁷⁵ A typical procedure involves generation of a diazonium cation through oxidation of an aryl amine.⁵⁷ Exposure of the diazonium cation to the carbon leads to coverage with the small molecule of choice. The modification is performed prior to catalyst entrainment on the electrode and thus can be interrogated using physical techniques prior to use.

In this chapter we utilize SQUID magnetometry to distinguish the relative amounts of paramagnetic and non-paramagnetic Fe species present in the catalyst. In addition, we utilize click chemistry modification of NPM materials prepared using MOF and polyaniline precursors to perturb the catalyst surface and record changes in characterization.

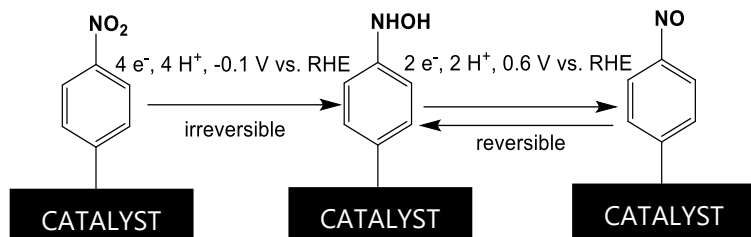


Figure 3.1. Electrochemical conversion of surface-attached 4-nitrobenzene to 4-nitrosobenzene. Conversion potentials are shown.

2. Catalyst Modification

The two catalysts studied here Fe_{0.5}-950 and PANIFeC were modified using click chemistry. The NO₂ moiety of the attached nitrobenzene provides

an electroactive species used to quantify the coverage of the molecule on the surface. As shown in Fig. 3.2, a potential hold at -0.1 V vs. RHE converts the NO₂ group via an irreversible, 4-e⁻, 4-H⁺ process to a NHOH group. The NHOH group can undergo a reversible, 2-e⁻, 2-H⁺ oxidation to NO.⁷⁵ Figure 3.1A shows CVs obtained at different scan rates following attachment of 4-nitroaniline to the surface of the PANIFeC catalyst and a potential hold at -0.1 V vs. RHE. CVs for the modified Fe_{0.5}-950 material were the same (Figure 3.3). CVs of the as prepared PANIFeC and Fe_{0.5}-950 samples show no evidence

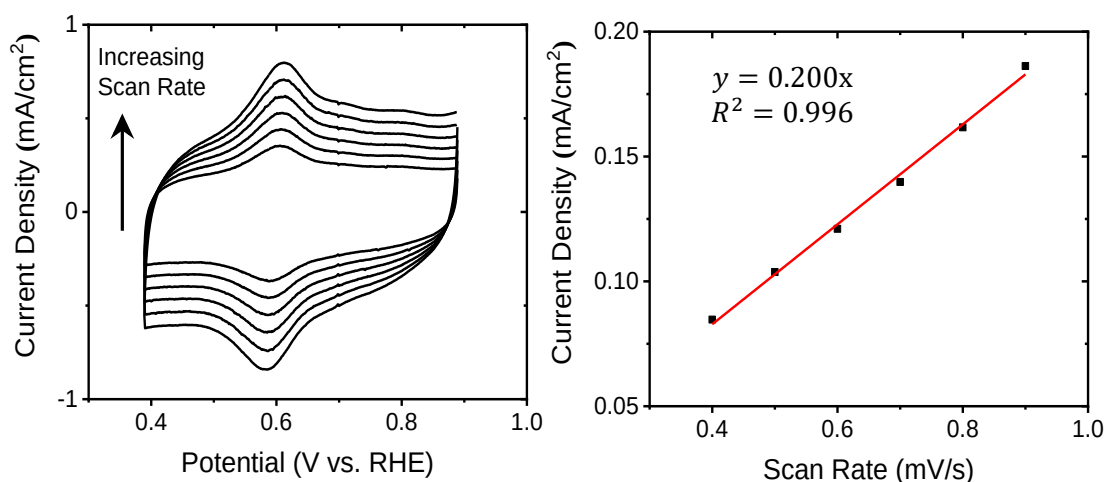


Figure 3.2. (A) Representative cyclic voltammograms of a modified PANIFeC catalyst at scan rates 0.4-0.9 mV/s, in 0.1 M HClO₄, under argon, after 400 sec potential hold at -0.1 V versus RHE. (B) Linear regression of average peak anodic current vs. scan rate.

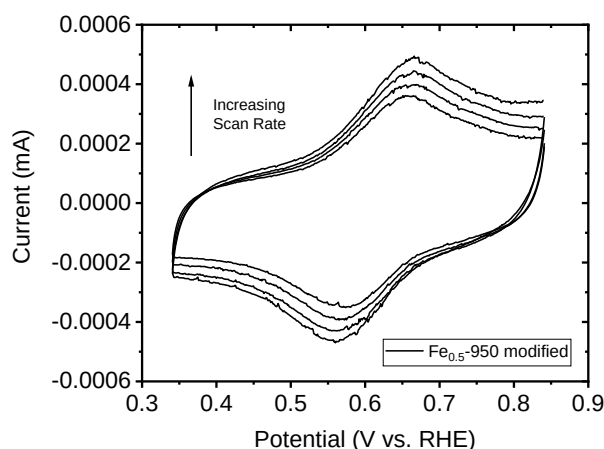


Figure 3.3. Representative cyclic voltammograms of a modified Fe_{0.5}-950 catalyst at scan rates 0.7-1 mV/s, in 0.1 M HClO₄, under argon, after 400 sec potential hold at -0.1 V versus RHE.

of the NO/NHOH couple (Figure 3.4).

The CVs show a single redox peak at 0.58 V vs. RHE associated with the NO/NHOH couple. Fig. 3.1B shows a plot of the peak height vs. scan rate. The linear relationship with scan rate confirms that the redox couple is surface confined.⁶⁰ The peak current can also be related to the number of moles of 4-nitrobenzene via Equation

3.1.⁶⁰

$$i_p/A = \frac{n^2 F^2 v \Gamma^*}{4RT} \quad (3.1)$$

Where i_p is the peak current, n is the number of electrons (2), F is Faraday's constant, v

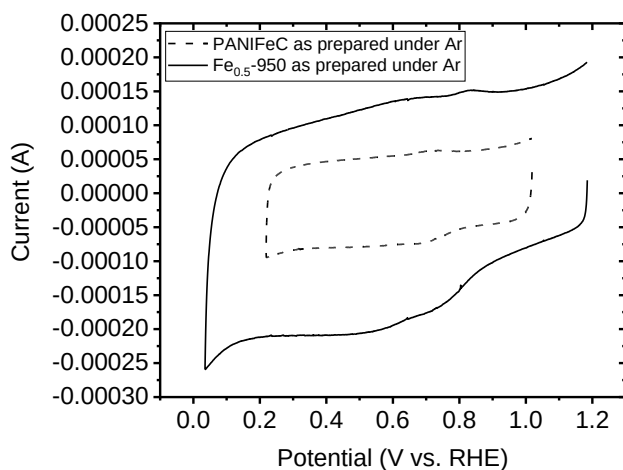


Figure 3.4. Representative cyclic voltammograms of Fe_{0.5}-950 and PANIFeC as prepared catalyst at 10 mV/s, in 0.1 M HClO₄, under argon, after 400 sec potential hold at -0.1 V versus RHE.

is the scan rate, A is determined from the BET surface area of the material and the catalyst mass deposited on the electrode, Γ^* is the surface concentration of active species, R is the gas constant and T is the temperature. The surface concentration of 4-nitrobenzene is determined to be $8 \pm 4 \times 10^9$ molecules of 4-nitrobenzene/cm²

for the Fe_{0.5}-950 material and $8 \pm 3 \times 10^9$ molecules of 4-nitrobenzene/cm² for the PANIFeC material.

There are other methods available to calculate the surface coverage of 4-nitrobenzene. If we use the geometric area as opposed to the BET surface area, we obtain a surface coverage of 1.8×10^{16} molecules of 4-nitrobenzene/cm², which is non-physical. A third way to calculate the coverage would be by using an XPS-based method.⁷³ Here, we use the ratio of oxidized N to C-C XPS peak area and obtain a coverage of 4×10^{14} molecule of 4-nitrobenzene/cm², consistent with results reported for bare carbon (1.5×10^{14} molecules of 4-nitrobenzene/cm²) also estimated from XPS data.⁷³ It is likely that the actual coverage is between 4×10^{14} molecules of 4-nitrobenzene/cm², which only examines XPS-addressable molecules and 8×10^9 molecules of 4-nitrobenzene/cm² which likely includes electrochemically unaddressable (but BET addressed) carbon. Using the XPS calculation may also be inaccurate due to some reduction of the NO₂ species on the 4-nitrobenzene as reported in our paper, which would lower the calculated coverage. In the following sections we will address the differences in characterization and activity with modification.

3. Mössbauer Spectroscopy

Mössbauer spectroscopy is typically used to understand Fe speciation in different catalyst preparations. Figures 3.5 and 3.6 show the room-temperature Mössbauer obtained from the as prepared Fe_{0.5}-950 and PANIFeC materials, respectively. Fits to the data (Table 3.2) are shown as solid lines in Figs. 3.5 and 3.6. Mössbauer spectroscopy fits the Fe_{0.5}-950 sample indicate the presence of only FeN₄-type Fe species. The

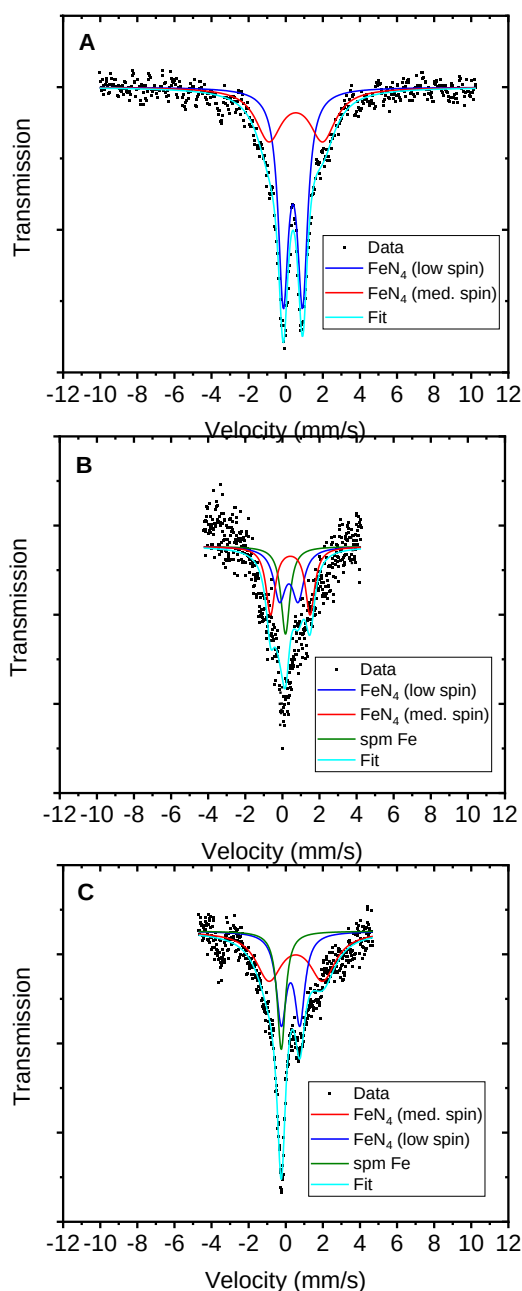


Figure 3.5. Mössbauer spectrum of (A) $\text{Fe}_{0.5}\text{-950}$ as prepared, (B) $\text{Fe}_{0.5}\text{-950}$ control, and (C) $\text{Fe}_{0.5}\text{-950}$ modified.

the control protocol. Similar spectra were obtained following the modification protocol as well. These Mössbauer spectra are different from that obtained from the as prepared sample in that there is now a new feature near $\delta=0$ (green line). This feature is typically

spectrum for PANIFeC exhibits a ferromagnetic component (Fe_3S_4), a doublet component (FeN_4 low spin) and a singlet component (superparamagnetic (spm) Fe). While the relative magnitude of these components varies with specific preparations and measurements, their presence has been seen in prior reports. These fittings are consistent with previous reports.^{16, 18, 23} Interestingly, while ferromagnetic species are evident in the PANIFeC Mössbauer spectrum (Fe_3S_4 , Fig. 3.6), there are no ferromagnetic species evident in the $\text{Fe}_{0.5}\text{-950}$ spectrum (Fig. 3.5).

Fig. 3.5b reports the Mössbauer spectrum and associated fits obtained from $\text{Fe}_{0.5}\text{-950}$ samples subjected to

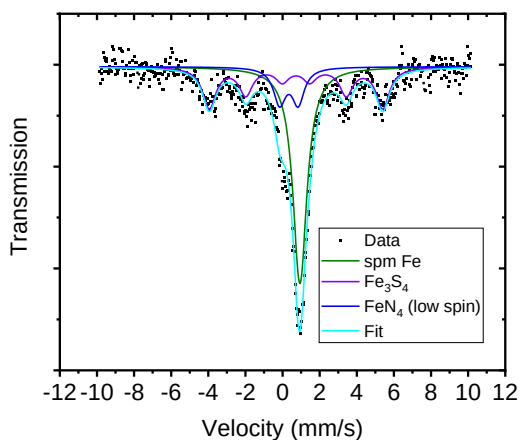


Figure 3.6. Mössbauer spectrum of PANiFeC as prepared.

associated with the presence of superparamagnetic Fe species. Thus, the acid washing associated with the control protocol leads to a substantively altered Mössbauer spectrum. Interestingly, this change in Mössbauer is not associated with a change in ORR activity in this sample.

Table 3.2. Fitting parameters for Mössbauer data. (Figs. 3.5, 3.6).

Component	$\delta_{iso}/\text{mm s}^{-1}$	$\Delta E_Q/\text{mm s}^{-1}$	Half-width Hyperfine Field H_0/T	fwhm/ mm s^{-1}	Ref.
FeN ₄ (low spin)	0.38/0.38/.26/0.40	1.0	N/A	0.65/0.60/.65/0.68	²³
FeN ₄ (med. spin)	0.54	2.8/2.9	N/A	1.7/1.7	²³
Fe ₃ S ₄	0.68	N/A	30.4	1.1	¹⁸
spm Fe	0.97/-0.24/0.47	N/A	N/A	0.84/0.53/0.50	¹⁸

4. Superconducting Quantum Interference Device (SQUID) Magnetometry

SQUID magnetometry is a technique which reports on magnetization response to an applied field.⁷⁶ Figure 3.7 shows the change in magnetization of each material (normalized to total Fe percentage as determined by ICP-OES (Table 3.3)) as a function of an external magnetic field at 300 K. The plots in Fig. 3.7 all show the presence of hysteretic behavior around zero applied magnetic field. The presence of this hysteretic response is associated with the presence of ferromagnetism in the samples. The

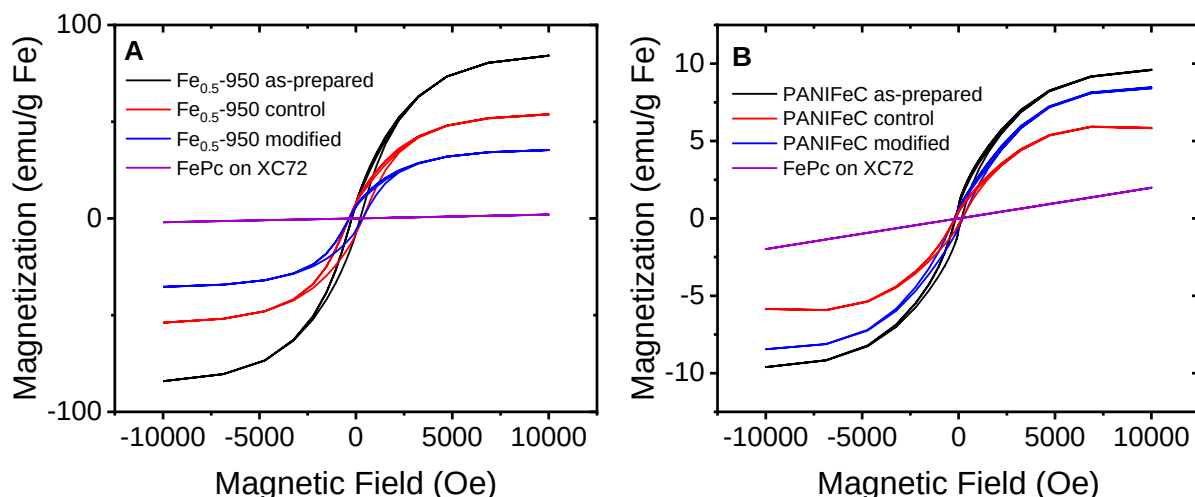


Figure 3.7. The effect of magnetization under an applied magnetic field for all materials of Fe_{0.5}-950 (A) and PANiFeC (B). The purple line is for FePc on XC72 for contrast.

sigmoidal shape and hysteretic behavior of the magnetization plot indicates the presence of superparamagnetic and/or ferromagnetic materials.⁶³⁻⁶⁴ This magnetization response is similar to what has been reported for similar Fe-based ORR catalysts.^{14, 48-49} Indeed TEM images of polyaniline- and ZIF-8-based catalysts exhibit what can be attributed to Fe particles.^{16, 77}

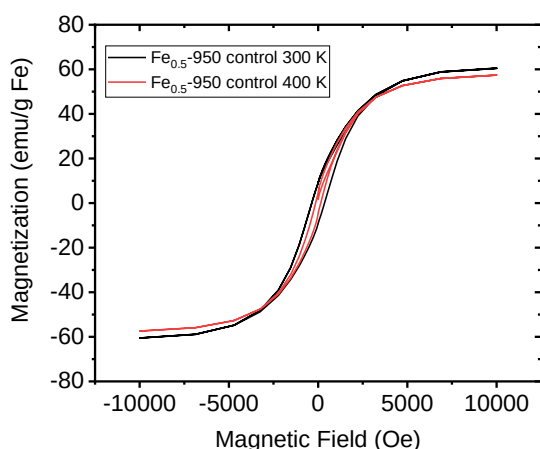


Figure 3.8. The effect of magnetization under an applied magnetic field for Fe_{0.5}-950 at 300 K and 400 K.

hysteretic behavior and saturation magnetization and behave like a paramagnet. In contrast, superparamagnetic materials will retain their saturation magnetization behavior.⁴⁶ The Curie temperature for Fe₃C is 480 K,⁷⁸ while that for other Fe species such as Fe₂O₃ or Fe(0) is much higher at 1043 K and 948 K, respectively.⁷⁹ While a 1000 K heat treatment will likely alter the as prepared catalyst, the catalysts should be stable with a 400 K treatment. From Fig. 3.8, 3.9 we see that both materials lose part or all of

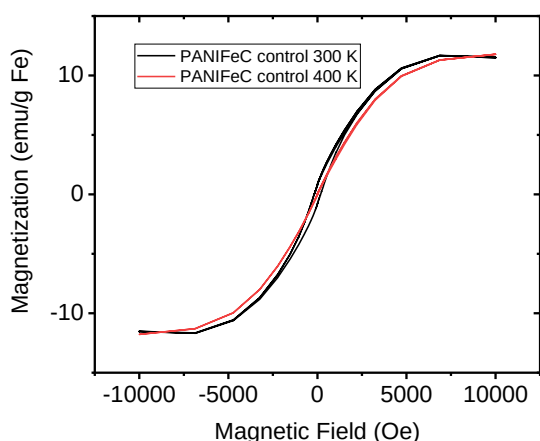


Figure 3.9. The effect of magnetization under an applied magnetic field for PANIFeC at 300 K and 400 K.

To better distinguish between ferromagnetic and superparamagnetic components we measured the magnetization response for the Fe_{0.5}-950 control material (Fig. 3.8) and the PANIFeC control material (Fig. 3.9) at 400 K. Above the Curie temperature of a ferromagnetic material the magnetization response will lose its

their hysteresis upon heating but retain the sigmoidal saturation magnetization. This result suggests that the magnetic materials in the catalysts are largely superparamagnetic.

From the plots in Fig. 3.7 we can determine the average domain size of

the magnetic component by a Langevin function ($\mathcal{L}$) fit given by Equation 2.4.⁶³⁻⁶⁴ Average domain diameter was calculated by determining the value of V for each sample and assuming spherical Fe particles. The average domain sizes, reported in Table 3.3, are consistent with the presence of superparamagnetic particles.

Fig. 3.10 shows temperature dependent magnetization obtained from the catalyst materials. The figure shows that while the overall magnetization decreases for the Fe_{0.5}-

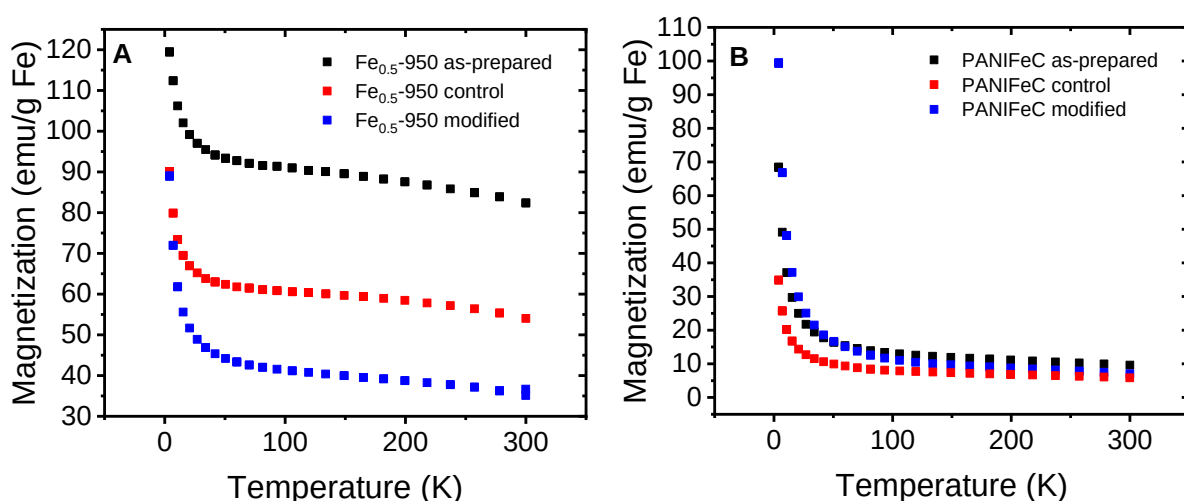


Figure 3.10. Temperature dependent magnetization of all catalyst materials.

950 material as a function of the modification procedure, such a decrease is not observed for the PANIFeC.

The temperature dependent magnetization data provides a μ_{eff} for each material by using equation 3.2⁷⁶:

$$\mu_{eff} = \sqrt{8\chi_M T} \quad (3.2)$$

Here, $\chi_M T$ is determined from the slope of a linear χ_M vs. $1/T$. The calculated μ_{eff} is summarized in Table 3.3. The total μ_{eff} of the Fe in all materials is the same within error.

Table 3.3. Parameters calculated for all materials from magnetization data.

Material	μ_{eff} (Bohr Magnetons)	wt% Total Fe	% non paramagnetic Fe	Domain radius (nm)
Fe _{0.5} -950 as prepared	2.4±0.1	1.2±0.6	40±2	1.9±0.3
Fe _{0.5} -950 control	2.7±0.08	0.8±0.1	10±10	1.90±0.09
Fe _{0.5} -950 modified	3.0±0.9	1.1±0.6	40±30	1.85±0.09
PANiFeC as prepared	2.3±0.8	2±2	3±2	1.6±0.1
PANiFeC control	2.4±0.5	0.5±0.2	3±3	1.6±0.2
PANiFeC modified	3±1	1±1	3±1	1.55±0.08

In order to estimate the percentage of metallic Fe in these samples relative total Fe, we compare the average M_{sat} of all materials to the M_{sat} of bulk iron (217 emu/g).⁶³ Inspection of Fig. 3.7 shows that the Fe_{0.5}-950 samples exhibit nearly an order of magnitude greater M_{sat} relative to the PANiFeC. This means that the PANiFeC has proportionally less non-paramagnetic Fe relative to the Fe in the Fe_{0.5}-950 samples. The fraction is summarized in Table 3.3. It is certainly possible that the non-paramagnetic component does not consist exclusively of bulk Fe but rather is a mixture of Fe₂O₃ (M_{sat} = 76 emu/g),⁸⁰ Fe₃N (M_{sat} = 80 emu/g),⁸¹ or Fe₃C (M_{sat} = 83 emu/g).⁷² Since the M_{sat} values for these species are smaller than that of bulk Fe, the amount of non-paramagnetic Fe in the samples would be larger than that reported in Table 3.3. Thus, the amounts reported there should be considered a lower bound for the amount of non-paramagnetic Fe in the samples. We note the modified Fe_{0.5}-950 sample exhibits a larger error in the calculated percentage of non-paramagnetic Fe. This error could be associated with partial oxidation of the non-paramagnetic Fe during the HCl acid wash.

5. Electron Paramagnetic Resonance (EPR) Spectroscopy

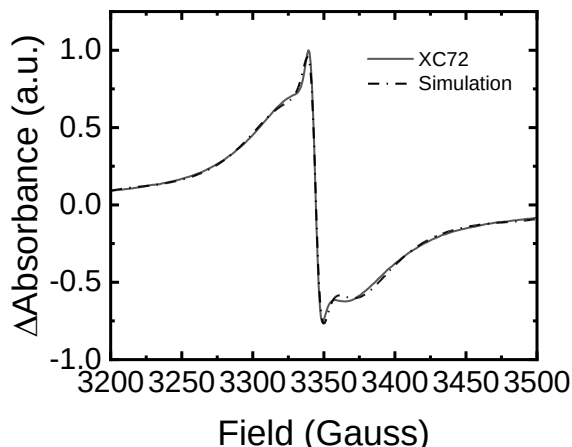


Figure 3.11. EPR spectrum of XC72 in ethanol at 5K.

The spectrum also shows $g = 4.30$ and $g = 2.01$ signals. The $g = 4.30$ signal is consistent with other reports for materials of this type.^{51, 82} EPR obtained from XC72 without pyrolysis (Fig. 3.11) exhibits two EPR signals, one broad and one narrow, at $g = 2.01$, consistent with prior reports.⁸³⁻⁸⁴ The $\text{Fe}_{0.5}\text{-950}$ control (Fig. 3.13B) exhibits decreased presence of broad features consistent with a decreased amount of ferromagnetic material due to the acid washing. The spectrum also shows $g = 4.30$ and $g = 2.01$ signals. A small

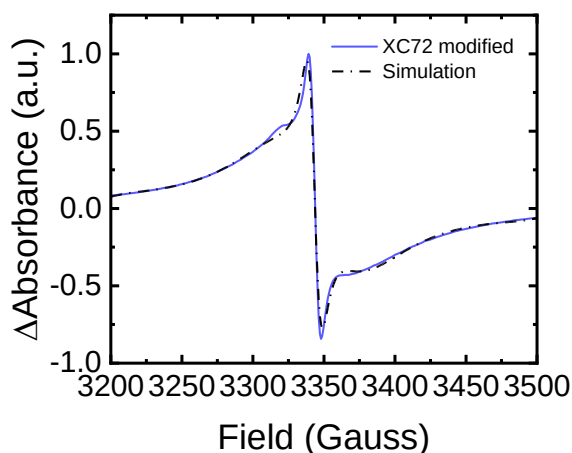


Figure 3.12. EPR spectrum of XC72 modified in ethanol at 5K.

EPR spectroscopy was used to understand the unpaired (paramagnetic) spins present in the $\text{Fe}_{0.5}\text{-950}$ and PANIFeC materials. Spectra were taken for samples dissolved in ethanol and maintained at 5 K. $\text{Fe}_{0.5}\text{-950}$ as prepared (Fig. 3.13A) exhibits broad features consistent with presence of ferromagnetic

feature at $g = 6$ is also seen. The inset to Fig. 3.13B shows a blowup of the $g = 2$ region, along with a fit to the EPR. $\text{Fe}_{0.5}\text{-950}$ modified (Fig. 3.13C) exhibits $g =$

4.30 and $g = 2.01$ signals, again with the small $g = 6$ signal. In contrast to the as prepared and control samples, however, there is a change in the signal shape around the $g = 2.01$

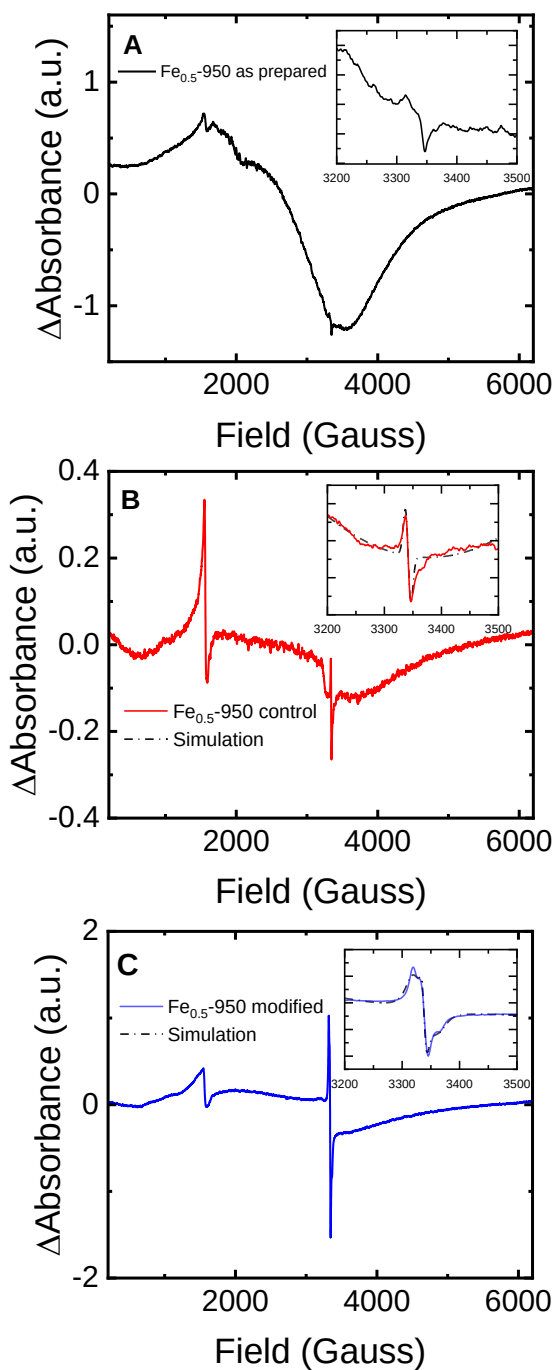


Figure 3.13. EPR of $\text{Fe}_{0.5}\text{-950}$ as prepared (A), control (B), and modified (C). Insets contain simulation fits.

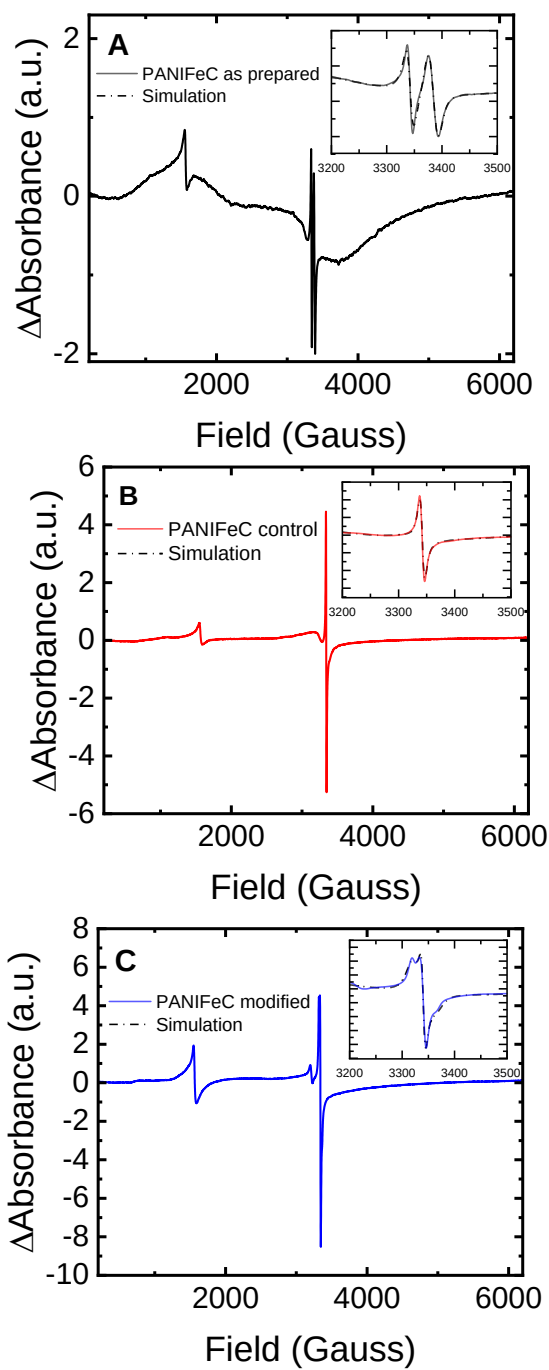


Figure 3.14. EPR of PANiFeC as prepared (A), control (B), and modified (C). Insets contain simulation fits.

signal. The signal is no longer isotropic but axial. A summary of the simulation parameters can be found in Table 3.4.

Table 3.4. Simulation parameters for EPR spectra.

^aLine width peak-to-peak (Gaussian, Lorentzian Broadening) (Gauss).

^bWeighting of g_{iso} with respect to g_1/g_2

Sample	g_1	g_2	LWPP ^a	Hyperfine Couplings (MHz)	g_{iso}	LWPP ^a	Weight ^b
Fe _{0.5} -950 control	N/A	N/A	N/A	N/A	2.01	10	N/A
Fe _{0.5} -950 modified	2.02	2.00	14, 15	22	2.02	6, 6	0.1
PANiFeC as prepared	1.99	N/A	7, 10	34	2.01	0, 14	0.9
PANiFeC control	2.02	N/A	40, 25	18	2.01	1, 9	0.9
PANiFeC modified	2.02	2.00	10, 15	32	2.01	3, 8	0.2
XC72	2.01	N/A	1, 10	N/A	2.01	20, 48	23.0
XC72 modified	2.01	N/A	0, 10	N/A	2.01	18, 59	18.5
FePc on XC72	2.01	N/A	1, 10	6	2.01	45, 100	50.5
FePc on XC72 modified	2.02	2.00	7, 5	73	2.02 / 2.01	48, 88/1, 6	10.5/.1

The EPR spectra for the PANiFeC materials (Fig. 3.14A, B, C) are similar to the Fe_{0.5}-950 materials. The PANiFeC as prepared material (Fig. 3.14A) exhibits an additional signal at $g = 1.99$ which is not present in the PANiFeC control spectrum (Fig. 3.14B). The PANiFeC modified EPR spectrum (Fig. 3.14C) exhibits the same axial $g = 2.01$ signal as the Fe_{0.5}-950 modified material as well as an additional $g = 2.09$ signal. This observation suggests that the modification procedure is affecting the paramagnetic Fe center of the catalyst.

6. XPS

XPS is a commonly used technique to evaluate the nitrogen speciation of the catalysts. Figures 3.15 and 3.16 show the N 1s XPS spectra for the as prepared, control, and

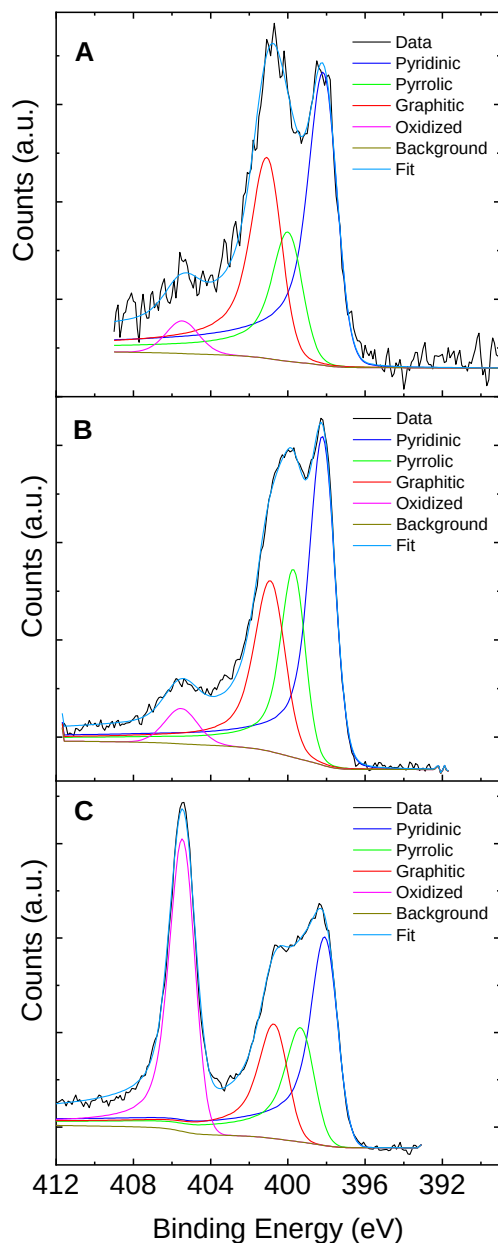


Figure 3.15. N 1s X-ray photoelectron spectroscopy of Fe_{0.5}-950 as prepared (A), control (B), and modified (C).

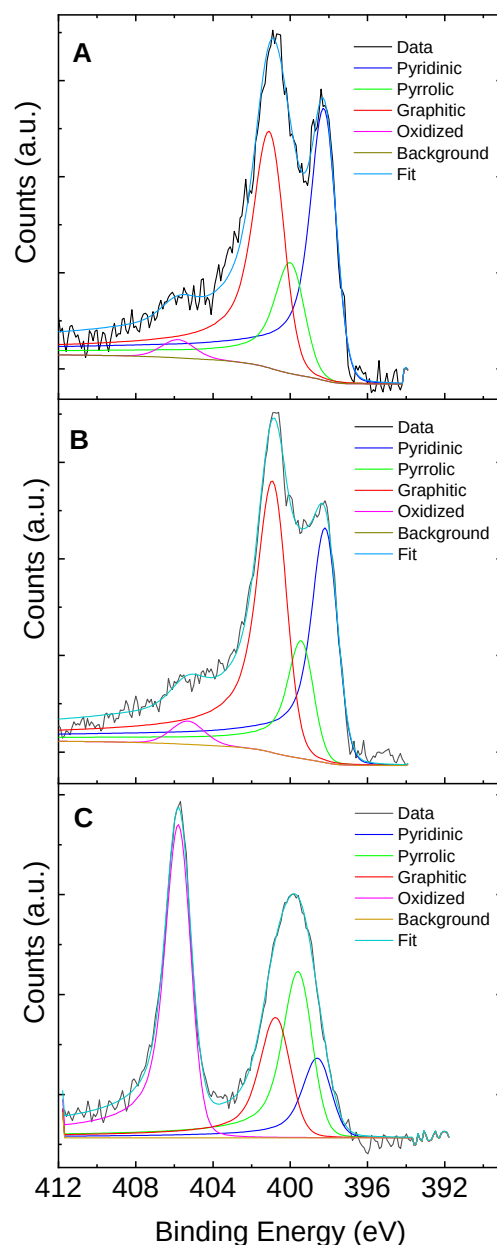


Figure 3.16. N 1s X-ray photoelectron spectroscopy of PANIFeC as prepared (A), control (B), and modified (C).

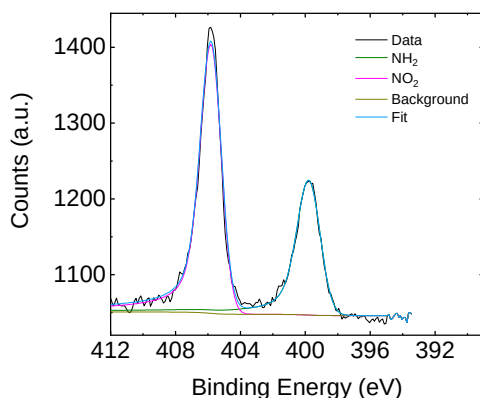


Figure 3.17. N1s XPS of modified XC72.

and modified $\text{Fe}_{0.5}\text{-950}$ and PANIFeC catalysts, respectively. Fig. 3.15A shows XPS obtained from the as prepared $\text{Fe}_{0.5}\text{-950}$ sample. The XPS exhibits four peaks at 398, 400, 401, and 405 eV.⁸⁵ Fig. 3.15B shows the XPS obtained from the $\text{Fe}_{0.5}\text{-950}$ following the control procedure. The XPS exhibits the same pyridinic, pyrrolic, graphitic, and oxidized N peaks seen in the as prepared sample. Fig. 3.15C shows the XPS obtained from the modified sample. The growth in intensity of the peak at 405 eV (pink) is associated with the presence of the 4-nitrobenzene moiety.⁵⁷ N1s XPS obtained from XC72 carbon subjected to the 4-nitroaniline modification procedure showed the presence of the 405 eV and 399 eV bands (Fig. 3.17).^{73, 86}

Fig. 3.16A, B, and C show the N1s XPS obtained from the as prepared, 'control', and modified PANIFeC catalysts. The XPS is similar to that found for the $\text{Fe}_{0.5}\text{-950}$ material thus showing that both materials incorporate 4-nitrobenzene during modification.

7. Electrochemical Activity

Fig. 3.18 presents staircase voltammograms obtained from a RDE (rotating disk electrode) coated with different catalyst materials. Fig. 3.18A shows the effect of the modification procedure on the $\text{Fe}_{0.5}\text{-950}$ catalyst measured in 0.1 M HClO_4 . The as prepared catalyst exhibits an $E_{1/2}$ of 0.77 ± 0.01 V vs. RHE, consistent with prior reports.¹⁵ RRDE measurements (Fig. 3.19) show that the reduction consumes $3.96 \pm 0.02 e^-$ with $2 \pm 1\%$ H_2O_2 produced, which is also consistent with prior reports.²³ The red line in Fig. 3.18A shows the effect of the ‘control’ protocol on the $\text{Fe}_{0.5}\text{-950}$ catalyst. This material exhibits an $E_{1/2}$ of 0.78 ± 0.01 V vs. RHE, not statistically different from the as prepared material. The control measurement used 6 M HCl to acid wash the catalyst in the same way as the modification procedure; the performance of the ‘control’ measurement in fact

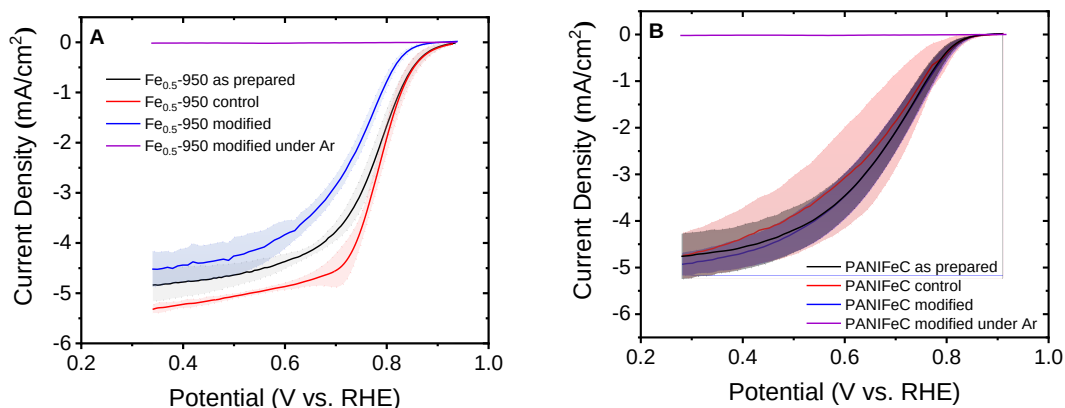


Figure 3.18. Effects of modification and control procedures of (A) $\text{Fe}_{0.5}\text{-950}$ and (B) PANiFeC as shown by staircase voltammetry in 0.1 M HClO_4 . The shaded areas represent $\pm$ one standard deviation in the current obtained from multiple measurements.

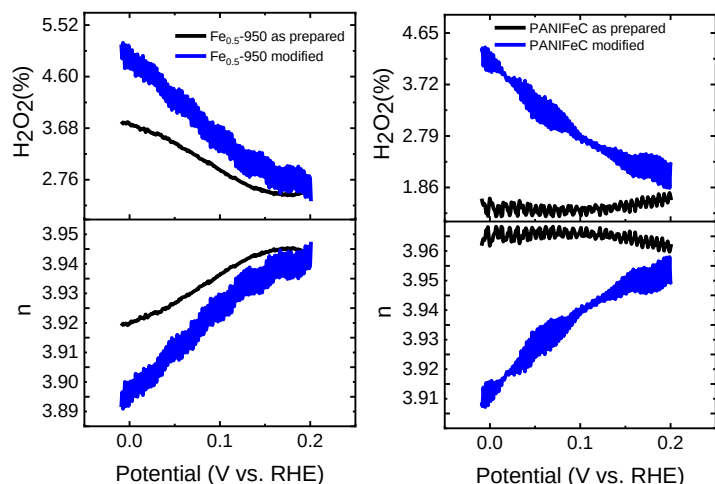


Figure 3.19. Representative %H₂O₂ produced and number of electrons transferred (n) over the limiting current region as determined by RRDE as measured in 0.1 M HClO₄.

rules out acid washing as a contributor to a loss in activity. The blue line in Fig. 3.18A shows the effect of the modification. The material exhibits an $E_{1/2}$ of 0.74 ± 0.01 V vs. RHE. RRDE measurements (Fig. 3.19) show that the reduction consumes $3.96 \pm 0.03 e^-$ with $2 \pm 1\%$ H₂O₂ produced.

Absent O₂, there is no reduction current from the modified sample (purple line, Fig. 3.18A, B). Thus, the half-wave potential of the modified material is substantially reduced (30 mV) relative to the as prepared sample.

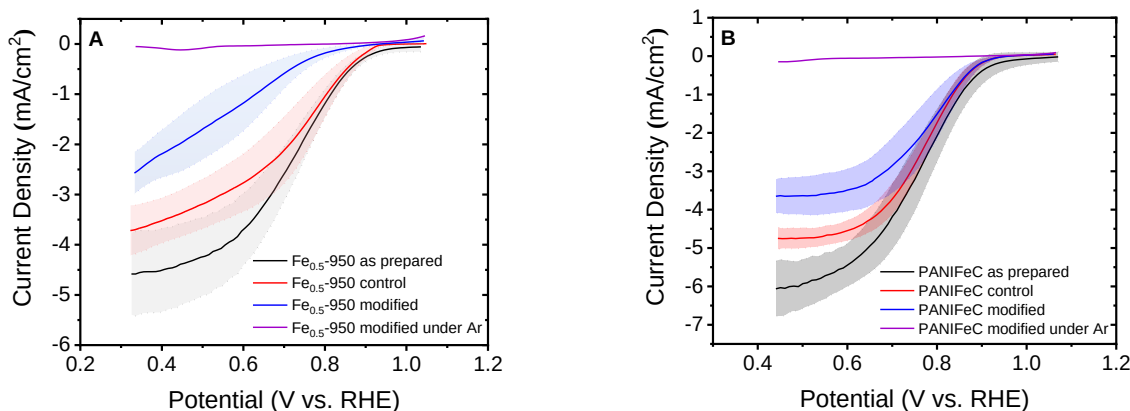


Figure 3.20. Effects of modification and control procedures of (A) Fe_{0.5}-950 and (B) PANiFeC as shown by staircase voltammetry in 0.1 M NaOH.

Fig. 3.18B shows the effect of the modification procedure on the PANiFeC catalyst measured in 0.1 M HClO₄. Without modification the catalyst exhibits an $E_{1/2}$ of 0.63 ± 0.03 V consistent with previous reports.¹⁶ RRDE measurements (Fig. 3.19) show that the

reduction consumes $3.97 \pm 0.01 e^-$ with $1.6 \pm 0.4\%$ H_2O_2 produced again consistent with prior reports.¹⁶ The red line represents PANiFeC after the control procedure. This material exhibits an $E_{1/2}$ of 0.66 ± 0.08 V. The blue line represents the modified PANiFeC catalyst. This material has an $E_{1/2}$ of 0.68 ± 0.03 V. RRDE measurements (Fig. 3.19) show that the reduction consumes $3.96 \pm 0.04 e^-$ with $2 \pm 2\%$ H_2O_2 produced. Absent O_2 , there is no reduction current. Thus, the half-wave potential is not altered within error for the PANiFeC material as a function of 4-nitroaniline exposure.

Fig. 3.20 presents staircase RDE voltammograms obtained from different catalyst materials in the alkaline electrochemical environment. Fig. 3.20A shows the effect of the modification procedure on the $Fe_{0.5}$ -950 catalyst in 0.1 M NaOH. In contrast to the acid case, the ORR measured here does not necessarily achieve limiting current at negative potentials. The origin of this behavior is likely associated with the enhanced production of peroxide (*vide infra*) seen with this material. $E_{1/2}$ values in this case are measured at the potential where the current is one half of the average of the last 100 mV of reported

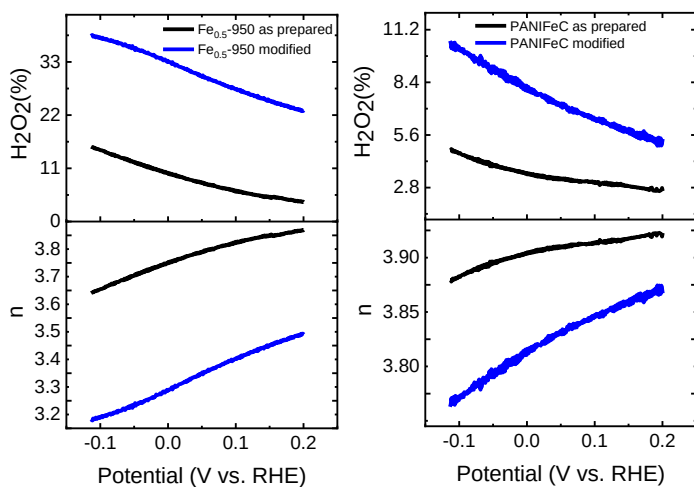


Figure 3.21. Representative %H₂O₂ produced and number of electrons transferred (n) over the limiting current region as determined by RRDE as measured in 0.1 M NaOH.

current values. Without modification, $Fe_{0.5}$ -950 exhibits an $E_{1/2}$ of 0.72 ± 0.03 V vs. RHE. RRDE measurements (Fig. 3.21) show that the reduction consumes $3.83 \pm 0.05 e^-$ with $8 \pm 2\%$ HO_2^- produced again consistent with prior reports.²³ The red line in Fig. 3.20A shows the effect of the

'control' protocol on the Fe_{0.5}-950 catalyst. This material exhibits an $E_{1/2}$ of 0.73 ± 0.06 V vs. RHE. The blue line in Fig. 3.20A shows the effect of the modification treatment described above. The material exhibits an effective $E_{1/2}$ of 0.58 ± 0.09 V vs. RHE. RRDE measurements (Fig. 3.21) show that the reduction consumes 3.4 ± 0.2 e⁻ with $28 \pm 11\%$ HO₂⁻ produced. The effect of the modification treatment then is to decrease the apparent $E_{1/2}$ and increase the amount of peroxide produced at the electrode surface.

Fig. 3.20B shows the effect of the modification procedure on the PANiFeC catalyst as measured in 0.1 M NaOH. Without modification PANiFeC exhibits an $E_{1/2}$ of 0.76 ± 0.03 V vs. RHE. RRDE measurements (Fig. 3.21) show that the reduction consumes 3.93 ± 0.02 e⁻ with $3 \pm 1\%$ HO₂⁻ produced. The red line represents PANiFeC after the control procedure. This material exhibits an $E_{1/2}$ of 0.77 ± 0.02 V vs. RHE. The blue line represents the modified PANiFeC catalyst. This material has an $E_{1/2}$ of 0.78 ± 0.04 V vs. RHE. RRDE measurements (Fig. 3.21) show that the reduction consumes 3.7 ± 0.2 e⁻

with $13 \pm 8\%$ HO₂⁻ produced. The modification slightly increases the amount of peroxide produced by the material while the apparent $E_{1/2}$ is unchanged.

We note that with modification of bare carbon (XC72) the oxygen reduction capabilities change when measured in basic media. At -0.7 V vs. RHE XC72 produces 17% HO₂⁻ and

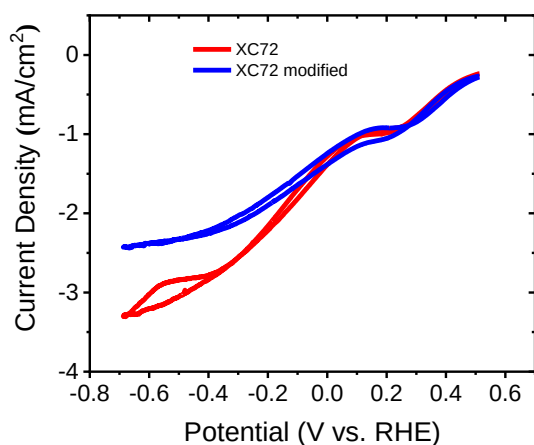


Figure 3.22. Effects of modification on ORR activity of XC72 carbon as shown by background subtracted cyclic voltammetry in 0.1 M NaOH.

modified XC72 produces 29% HO_2^- . This increase in the $2e^-$ reduction pathway decreases the overall current density obtained as shown in Figure 3.22.

8. Discussion

The structure of the active site(s) for ORR on NPM materials is a subject of substantial debate.^{15-18, 22} A number of techniques including, Mössbauer spectroscopy, XPS, TEM, x-ray absorption spectroscopy, x-ray diffraction, and BET surface area analysis have been utilized to interrogate the NPM materials. Mössbauer spectroscopy in particular has been used to evaluate speciation around Fe centers in NPM catalysts. Here, we utilize magnetometry to help resolve issues relating to the amount of non-paramagnetic Fe in these active sites. Surface modification is used to provide further insight into the relationship between these active sites and reactivity.

Magnetometry

The magnetometry shows that both the $\text{Fe}_{0.5}$ -950 and PANIFeC materials are heterogeneous and both contain non-paramagnetic material as shown in Table 3.3. Interestingly, the $\text{Fe}_{0.5}$ -950 exhibits more non-paramagnetic Fe relative to the PANIFeC. By way of contrast, carbon-supported Fe phthalocyanine (FePc) exhibits neither hysteresis nor sigmoidal behavior; this sample has no non-paramagnetic Fe. The presence of non-paramagnetic Fe in both the $\text{Fe}_{0.5}$ -950 and PANIFeC samples is unequivocal given the hysteretic, sigmoidal behavior seen in the magnetometry.

Mössbauer spectroscopy

We next consider what this non-paramagnetic material might be. The Mössbauer obtained from the PANIFeC material does show signals assigned to the presence of Fe_3S_4 and $\text{Fe}(0)$ (Fig. 3.6). Based on the appearance of the absorption near $\delta = 0$, it is

likely that the presence of superparamagnetic Fe(0) is a source of the non-paramagnetic behavior in the as prepared PANiFeC sample. Indeed, we showed previously that superparamagnetic Fe was present in a modified PANiFeC.¹⁶

The situation for the Fe_{0.5}-950 material is more complicated (Fig. 3.5A). The as prepared Fe_{0.5}-950 sample does not show the presence of either a sextet or a singlet that could be assigned to more reduced or non-paramagnetic Fe species. Alternatively, a singlet near $\delta = 0$ is seen in both the Fe_{0.5}-950 control and modified samples (Fig 3.5B, C). The presence of the $\delta = 0$ signal is strong support for the presence of superparamagnetic Fe(0) in the Fe_{0.5}-950 material. We note that EXAFS obtained from Fe_{0.5}-950 exhibits features that have been associated with an Fe-Fe bond.²³

As mentioned, there is no $\delta = 0$ signal in the as prepared Fe_{0.5}-950 sample. We suggest that Mössbauer spectroscopy does not necessarily provide a full picture of all the Fe species present in the material. Mössbauer spectroscopy relies on a recoilless transition in the gamma ray absorption process.⁸⁷⁻⁸⁸ It is likely that different Fe species in the material do not all exhibit the same recoilless fraction. A much smaller recoilless fraction among certain species could mean that they either appear in the Mössbauer with a signal strength not proportional to their concentration in the sample or are completely missing in the spectrum. Indeed, Mössbauer examining goethite-hematite mixtures yielded signals not proportional to concentration.⁶⁹ Thus, without clear understanding of the value of the recoilless coupling constant for each Fe species in the catalyst, *a priori* determination of the nature of the active site(s) in the material cannot be made from this technique alone.

There are several ways in which Mössbauer-absent species might be made to appear. Low temperature and/or the presence of a magnetic field can enhance particular Mössbauer signals. For example, recent work examining pyrolyzed Fe-porphyrins showed enhanced Mössbauer signals under low temperature/magnetic field conditions.⁸⁹ We also conducted 5 K Mössbauer spectroscopy on the Fe_{0.5}-950 as prepared sample but did not see any changes in the Mössbauer spectroscopy relative to the room temperature data. (data not shown).

A second way in which a Mössbauer-absent species might be made to appear is through chemical modification of the sample.⁹⁰ In the case here, modification of the sample by acid washing apparently increases the Fe(0) response in the Mössbauer. Table 3.3 shows definitively that substantial non-paramagnetic Fe is present even in the as prepared sample.

Thus, Mössbauer and magnetometry shows that both the Fe_{0.5}-950 and PANIFeC samples are heterogeneous, containing both paramagnetic and non-paramagnetic Fe. While relative percentages are not available, the non-paramagnetic Fe is likely present as both superparamagnetic Fe and ferromagnetic Fe. The as prepared Fe_{0.5}-950 contains 40% non-paramagnetic Fe, but signals associated with this material are not seen in the Mössbauer, likely due to a decreased recoilless fraction relative to the other (paramagnetic) Fe species in this material.

EPR

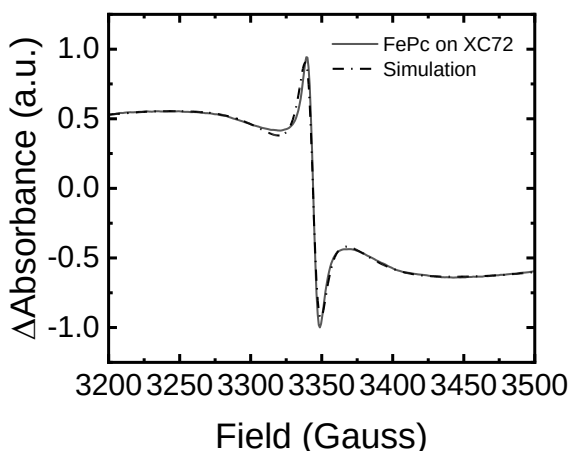


Figure 3.23. EPR spectrum of FePc on XC72 in ethanol at 5K.

a system with an $E/D \approx 0.33$ where D and E/D are the axial and rhombic zero-field splitting parameters, respectively.⁴⁵ An $E/D \approx 0.33$ is associated with a rhombic, high spin Fe(III) center.^{45, 89, 91} By way of contrast, EPR obtained from a Fe(III) porphyrin complex evinces a $g = 6$ signal and no $g = 4.3$. We note that our samples also show a small $g = 6$ signal. The ratio of the $g = 6$ signal to $g = 4.3$ signal is small suggesting that the $g = 6$ signal is from a minor species. Interestingly, samples of pyrolyzed porphyrins exhibit a large $g = 6$ to $g = 4.3$ ratio.⁸⁹ The relative $g = 6$ to $g = 4.3$ ratio and the position of the EPR signal at $g = 4.3$ is unaffected by the modification procedure, suggesting that the symmetry of the

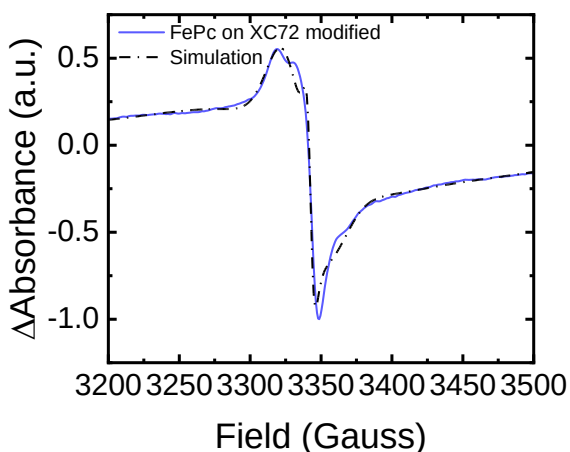


Figure 3.24. EPR spectrum of FePc on XC72 modified in ethanol at 5K.

EPR spectroscopy addresses paramagnetic materials, the presence of which in both the Fe_{0.5}-950 and PANIFeC samples is confirmed by the Mössbauer. EPR spectroscopy obtained from all materials examined here exhibits a $g = 4.3$ signal. For Fe(III) species, the $g = 4.3$ signal is typically interpreted to arise from

paramagnetic Fe(III) center is unaffected by the modification.

The EPR also shows signals around $g = 2$. A $g = 2$ signal can arise from ferric high spin porphyrins and/or paramagnetic species on the carbon (Fig. 3.11). In all materials studied here, the $g =$

2 signal changes with the 4-nitrobenzene modification procedure. The simulations suggest that the $g = 2$ signal becomes axial (Table 3.4).⁷⁶ We note that EPR obtained from XC72 subjected to the modification procedure did not show increased axially relative to non-modified XC72 (Fig. 3.12). When the modification procedure was performed, however, on FePc on XC72 catalyst, the same axial features as seen in the EPR of the modified Fe_{0.5}-950 and PANiFeC are present (Fig 3.23, 3.24). This observation suggests that the modification procedure is affecting the paramagnetic Fe center because the 4-nitrobenzene molecule is bound either directly to Fe or on a nearby carbon center.

Reactivity

Both the Fe_{0.5}-950 and PANiFeC materials are heterogeneous, exhibiting both paramagnetic and non-paramagnetic Fe centers. Interestingly, the 4-nitrobenzene modification procedure decreases the half-wave potential of the Fe_{0.5}-950 material, but not that of the PANiFeC when measured in either acid or base. This fact shows that the active site(s) or the active site weightings between the two materials are likely different.

The second point of distinction between Fe_{0.5}-950 and PANiFeC materials is the different percentage of peroxide production when measured in basic electrolyte. Both catalysts show increases in peroxide production after the 4-nitrobenzene modification, but the increase is greater for the Fe_{0.5}-950 (8% to 28%) relative to PANiFeC material (3% to 13%). Increased peroxide production in base is typically associated with greater exposure of 2-electron ORR active sites.⁹² These 2-electron active sites could be those formed by the 4-nitrobenzene modification. Indeed, modification of the bare XC72 with the 4-nitrobenzene results in 29% peroxide production at -0.4 V vs. RHE, comparable to

the 28% peroxide found in the modified Fe_{0.5}-950 material. The modified PANiFeC generates less peroxide, suggesting the effect of the 4-nitrobenzene is different.

The increased peroxide formation on the modified Fe_{0.5}-950 relative to modified PANiFeC suggests that the active site of the Fe_{0.5}-950 behaves more like carbon encapsulated Fe than that of the PANiFeC. This may suggest that the Fe_{0.5}-950 site is occluded by a carbon sheet or otherwise in proximity to carbonaceous species. We note there is substantially more non-paramagnetic Fe in Fe_{0.5}-950 relative to PANiFeC. It is possible that the active carbon sites in the Fe_{0.5}-950 are manifested as carbon that is wrapped around the small Fe particles or carbon near FeN₄-like moieties. The modification apparently alters these carbon-based active sites making them less active for the 4-electron pathway.

The PANiFeC material is much less affected by the 4-nitrobenzene modification, particularly with regard to half-wave potential. At the same time, EPR spectroscopy shows that the $g = 2$ region becomes more axial, which would be consistent with 4-nitrobenzene decoration near an active FeN₄ species. Indeed, the EPR seems similar to that found with the modified FePc on XC72. Consistent with the insensitivity of the PANiFeC material to poisons such as CO, this modification would not directly occupy the active site, but would still have proximity to change the $g = 2$ region. The exact reason that neither 4-nitrobenzene nor CO poison the PANiFeC is still an open question.

9. Conclusions

The major outcome of this work is to introduce magnetometry as an important characterization tool for NPM ORR catalysts. The catalysts studied here are heterogeneous with many different species present. Different preparations yield different species in different relative amounts in the as prepared materials. Interestingly, the Fe_{0.5}-950 material exhibits more non-paramagnetic Fe than the PANIFeC. Characterization of heterogeneous materials must include techniques that are sensitive to all the species present. Mössbauer spectroscopy can be problematic for evaluating all the species in heterogeneous materials due to the *a priori* unknown recoilless fraction of each component especially if the Mössbauer is obtained with the sample at room temperature and/or without an applied magnetic field. Alternatively, SQUID magnetometry reports directly on the presence of non-paramagnetic Fe. SQUID magnetometry is a powerful technique for characterizing Fe-containing materials, particularly those with low, but important Fe content.

Modification of the Fe_{0.5}-950 and PANIFeC yield different changes in activity toward the ORR. This different result suggests the active site(s) or the relative amounts of different active sites vary between the two materials. The observed differential poisoning provides an additional handle to categorize the differences in active sites between similarly prepared materials. We show that a carbon modification scheme can inhibit the ORR in some but not all NPM ORR materials. The degree of inhibition is related to the amount of non-paramagnetic Fe present in the sample as determined by magnetometry, with samples containing more non-paramagnetic Fe being more

susceptible to ORR inhibition using the surface modification scheme. Thus, this paper shows definitively there are different types of Fe-containing NPM ORR active sites.

Chapter 4 Using Magnetometry to Understand the Relative Role of Magnetic Particles in Co-based Catalysts for the Oxygen Reduction Reaction

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1. Introduction

A technique not widely used in the characterization of Co-based ORR materials is superconducting quantum interference device (SQUID) magnetometry. This technique can quantify the amount of non-paramagnetic material in the catalyst. This quantification is important in determining the nature of active material(s) present in the catalyst that is also magnetically active, including superparamagnetic and ferromagnetic Co nanoparticles, both of which may be present in catalysts.³⁴ Magnetometry has been utilized to evaluate Fe-containing ORR catalysts⁴² but has not yet been applied to those containing Co. Alternatively, there are many papers investigating the magnetic properties of Co nanoparticles and related materials.⁹³⁻⁹⁵

2. Electrochemical Activity

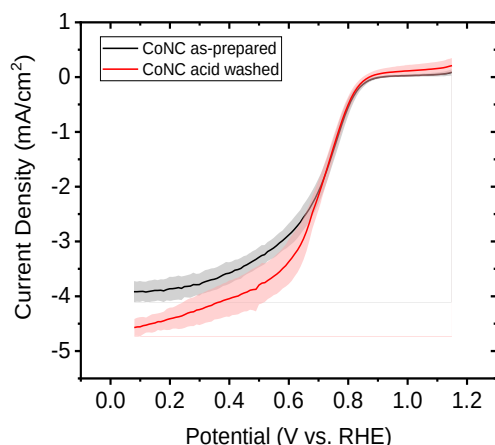


Figure 4.1. Effects of acid wash of CoNC on ORR performance as shown by staircase voltammetry in 0.1 M HClO₄. The shaded areas represent +/- one standard deviation in the current obtained from multiple measurements.

Figure 4.1 shows the staircase voltammograms obtained from the different CoNC materials measured in 0.1 M HClO₄ into which O₂ is sparged. All catalysts exhibit reduction current associated with the ORR. The $E_{1/2}$ was determined by the voltage at which half the limiting current was reached; the limiting current was determined for each individual staircase voltammogram

measurement. The CoNC as-prepared catalyst exhibits an $E_{1/2}$ of 0.71 ± 0.01 V. The acid washed CoNC catalyst exhibits an $E_{1/2}$ of 0.69 ± 0.02 V, not statistically different from the as-prepared catalyst. The RRDE measurements show that the CoNC as-prepared catalyst transfers 3.8 ± 0.1 e⁻, producing $8 \pm 6\%$ H₂O₂. The RRDE measurements show that the acid-washed CoNC catalyst transfers 3.78 ± 0.06 e⁻, producing $5 \pm 2\%$ H₂O₂. The ring and disk current as well as the calculated n-values and %H₂O₂ are shown in Figure 4.3. There are no significant electrochemical differences between the CoNC as-prepared and acid washed materials. The $E_{1/2}$ and n-value are consistent with other Co-based ORR catalysts as-measured in acidic electrolyte.⁹⁶⁻⁹⁸

Table 4.1. Summary of half-wave potentials and number of electrons transferred for all materials as measured in 0.1 M HClO₄.

Sample	E _{1/2} (V)	n	%H ₂ O ₂
CoNC as-prepared	0.71 ± 0.01	3.8 ± 0.1	8 ± 6
CoNC acid washed	0.69 ± 0.02	3.78 ± 0.06	5 ± 2
CoNC-CTAB as-prepared	0.59 ± 0.04	3.8 ± 0.1	12 ± 5
CoNC-CTAB acid washed	0.68 ± 0.03	3.70 ± 0.07	15 ± 4

Figure 4.2 shows the staircase voltammograms obtained from the different CoNC-CTAB materials in a 0.1 M HClO₄ solution into which O₂ was sparged. The CoNC-CTAB as-prepared catalyst exhibits an E_{1/2} of 0.59 ± 0.04 V. The acid washed CoNC-CTAB catalyst exhibits an E_{1/2} of 0.68 ± 0.03 V, statistically different from the as-prepared catalyst. The RRDE measurements show that the as-prepared CoNC-CTAB transfers 3.8 ± 0.1 e⁻, producing 12 ± 5% H₂O₂. The acid washed CoNC-CTAB transfers 3.70 ± 0.07 e⁻, producing 15 ± 4% H₂O₂. The ring and disk current as well as the calculated n-values and %H₂O₂ are shown in Figure 4.4. There are no significant differences in the product formation between the CoNC-CTAB as-prepared and acid washed materials. We note

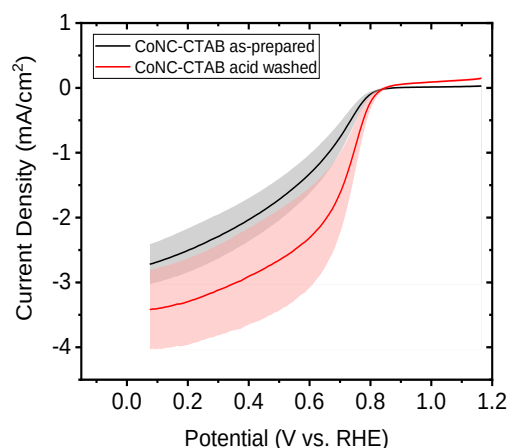


Figure 4.2. Effects of acid wash of CoNC-CTAB on ORR performance as shown by staircase voltammetry in 0.1 M HClO₄. The shaded areas represent +/- one standard deviation in the current obtained from multiple measurements.

that the error of the CoNC as-prepared %H₂O₂ yields is somewhat larger than the CoNC acid washed. We believe this larger error is due to the uncertainty in uptake of

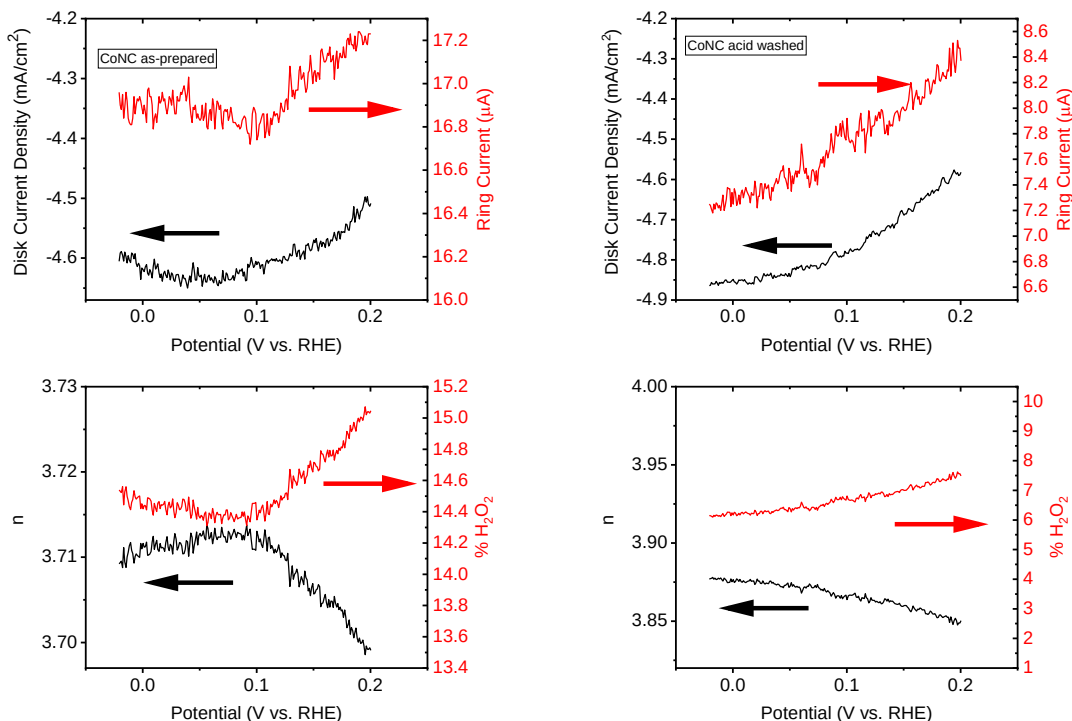


Figure 4.3. Representative disk and ring current collected for the CoNC as-prepared and CoNC acid washed materials measured in 0.1 M HClO₄. Bottom graphs are the calculated n and %H₂O₂ values for the potential regions shown.

Co⁺² ions during the CoNC precursor synthesis which results a larger range of results both in the H₂O₂ production and Co wt.% (Table 4.1, Table 4.3). The E_{1/2} and n-value of the CoNC-CTAB acid washed catalyst are consistent with other Co-based ORR catalysts as-measured in acidic electrolyte.⁹⁶⁻⁹⁸ The E_{1/2} and the amount of H₂O₂ produced for all catalysts as measured in 0.1 M HClO₄ are summarized in Table 4.1.

Figure 4.5 shows the staircase voltammograms of the CoNC materials as measured in 0.1 M NaOH. The as-prepared CoNC catalyst exhibits an E_{1/2} of 0.74 ± 0.01 V. The acid washed CoNC catalyst exhibits an E_{1/2} of 0.77 ± 0.02 V, a slight improvement from the as-prepared catalyst. The RRDE measurements show that the CoNC as-prepared catalyst transfers 3.76 ± 0.08 e⁻, producing 12 ± 4% OH₂⁻. The RRDE measurements show that the CoNC acid washed catalyst transfers 3.2 ± 0.1 e⁻, producing

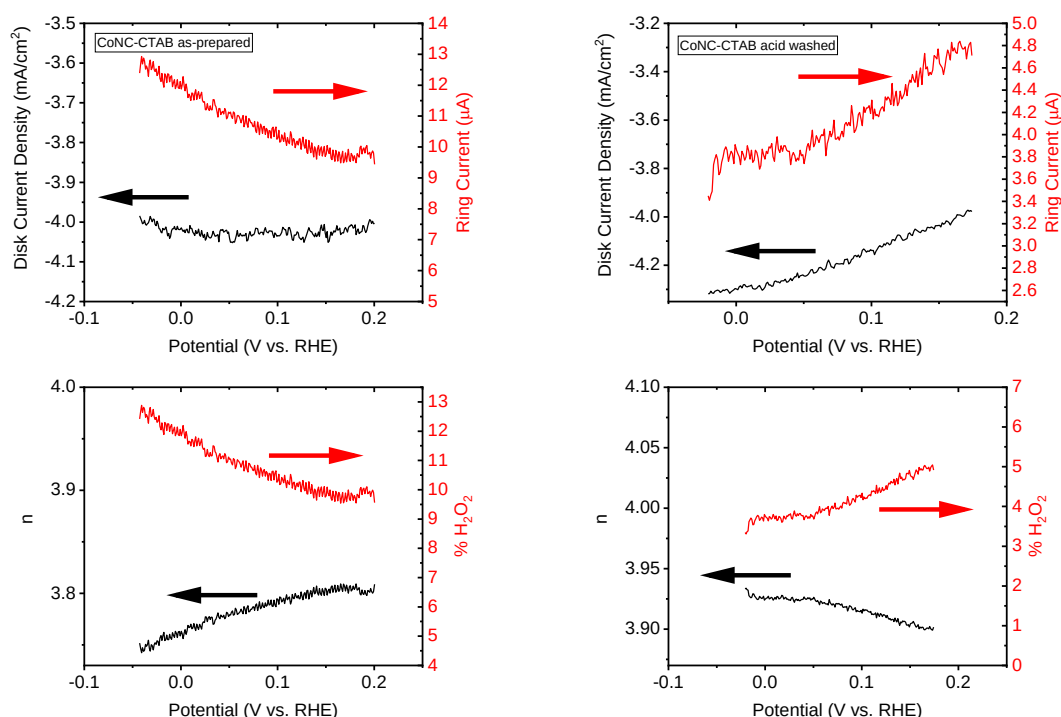


Figure 4.4. Representative disk and ring current collected for the CoNC-CTAB as-prepared and CoNC-CTAB acid washed materials measured in 0.1 M HClO₄. Bottom graphs are the calculated n and %H₂O₂ for the potential regions shown.

$39 \pm 7\%$ OH₂⁻. The ring and disk current as well as the calculated n -values and %OH₂⁻ are shown in Figure 4.7. After acid washing the CoNC catalyst there is significantly less

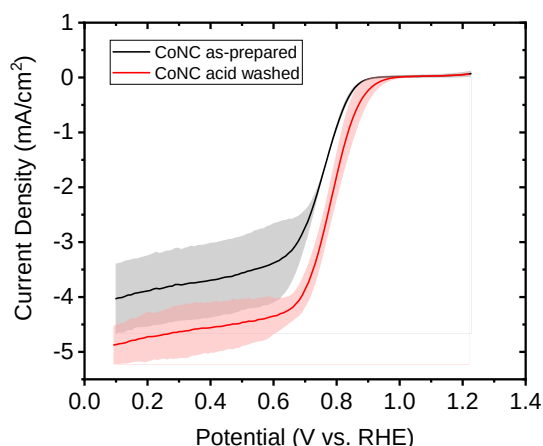


Figure 4.5. Effects acid wash procedures of CoNC as shown by staircase voltammetry in 0.1 M NaOH. The shaded areas represent +/- one standard deviation in the current obtained from multiple measurements.

electrons transferred (Table 4.2). The $E_{1/2}$ of the acid washed CoNC catalyst is consistent with other Co-based ORR catalysts as measured in basic electrolyte.^{30, 97, 99}

Figure 4.6 shows the staircase voltammograms of the different CoNC-CTAB

Table 4.2. Summary of half-wave potentials and number of electrons transferred for all materials as measured in 0.1 M NaOH.

Sample	$E_{1/2}$ (V)	n	%OH ₂ ⁻
CoNC as-prepared	0.74 ± 0.01	3.76 ± 0.08	12 ± 4
CoNC acid washed	0.77 ± 0.02	3.2 ± 0.1	39 ± 7
CoNC-CTAB as-prepared	0.71 ± 0.04	3.7 ± 0.2	16 ± 8
CoNC-CTAB acid washed	0.77 ± 0.01	3.7 ± 0.1	13 ± 5
Co NPs + XC72	0.73 ± 0.03	3.3 ± 0.2	36 ± 12

materials as measured in 0.1 M NaOH. The as-prepared CoNC-CTAB catalyst exhibits an $E_{1/2}$ of 0.71 ± 0.04 V. The acid washed CoNC-CTAB catalyst exhibits an $E_{1/2}$ of 0.77 ± 0.01 V, an improvement from the as-prepared catalyst. The RRDE measurements show that the CoNC-CTAB as-prepared catalyst transfers 3.7 ± 0.2 e⁻, producing $16 \pm 8\%$ H₂O₂.

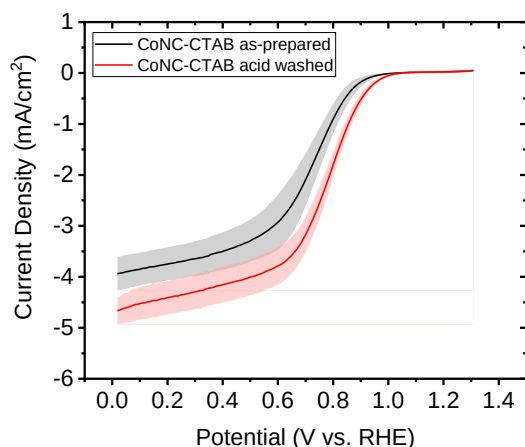


Figure 4.6. Effects of acid wash procedures of CoNC-CTAB as shown by staircase voltammetry in 0.1 M NaOH. The shaded areas represent +/- one standard deviation in the current obtained from multiple measurements.

The RRDE measurements show that the CoNC-CTAB acid washed catalyst transfers 3.7 ± 0.1 e⁻, producing $13 \pm 5\%$ H₂O₂. The ring and disk current as well as the calculated n-values and %OH₂⁻ are shown in Figure 4.8. The $E_{1/2}$ of the CoNC-CTAB acid washed catalyst is consistent with other Co-based ORR catalysts as measured in basic electrolyte.^{30, 97, 99}

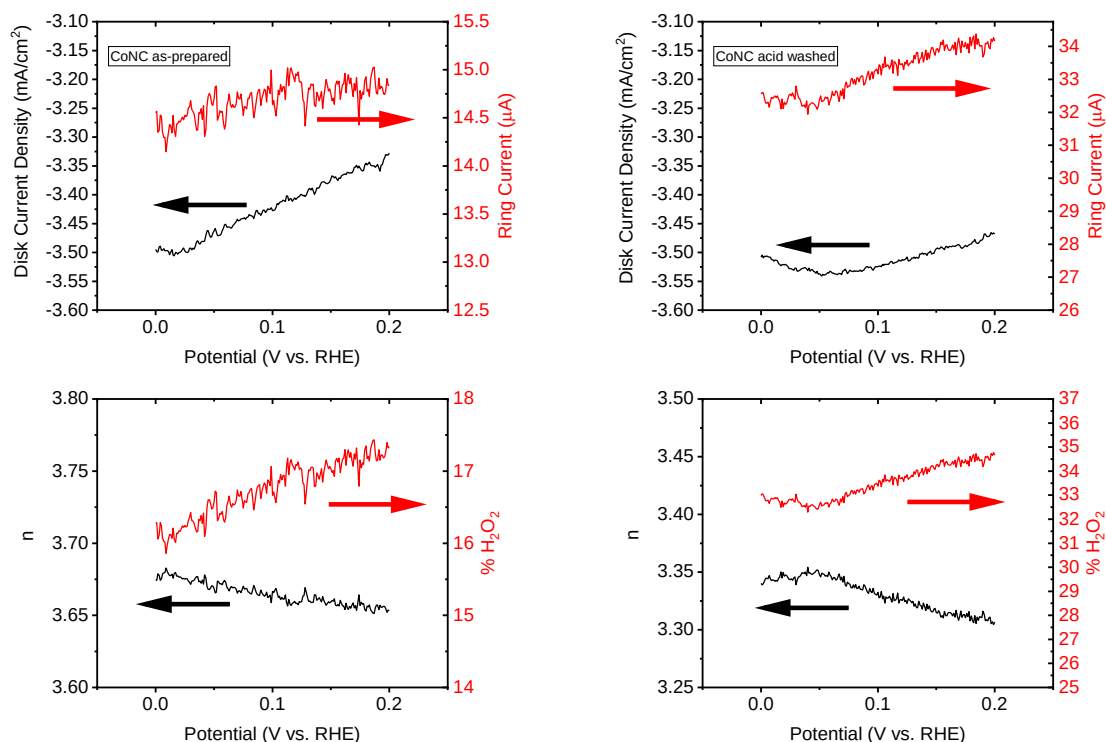


Figure 4.7. Representative disk and ring current collected for the CoNC as-prepared and CoNC acid washed materials measured in 0.1 M NaOH. Bottom graphs are the calculated n and $\%H_2O_2$ values for the potential regions shown.

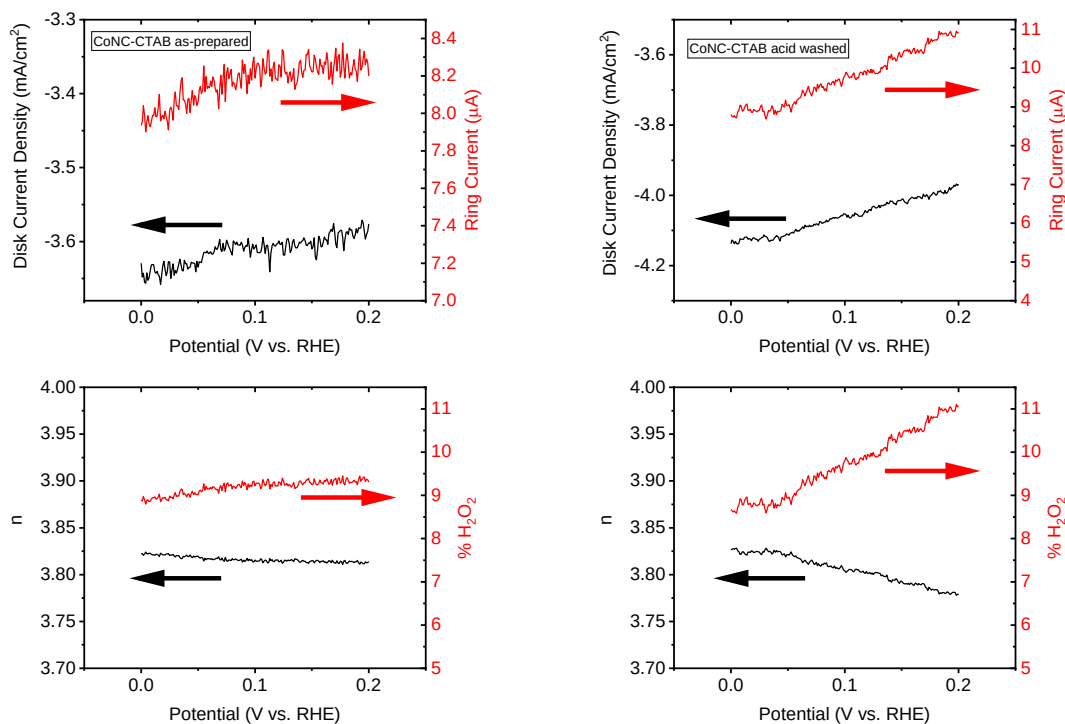


Figure 4.8. Representative disk and ring current collected for the CoNC-CTAB as-prepared and CoNC-CTAB acid washed materials measured in 0.1 M NaOH. Bottom graphs are the calculated n and $\%H_2O_2$ values for the potential regions shown.

3. XPS Analysis

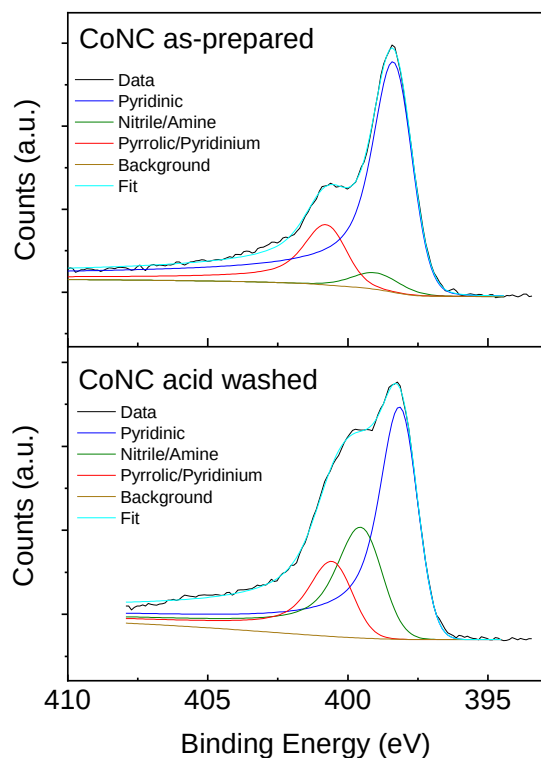


Figure 4.9. N 1s XPS scan of CoNC samples: as-prepared (top) and acid washed (bottom).

Figures 4.9 and 4.10 show the N 1s XPS spectra for the CoNC and CoNC-CTAB catalyst materials. Figure 4.9 shows the N 1s spectrum obtained from the CoNC as-prepared catalyst. The spectrum is fit with three peaks at 398, 399, and 400 eV corresponding to pyridinic, nitrile or amine groups, and pyrrolic N, respectively.^{28, 30, 85} Figure 4.9 also shows the N 1s spectrum obtained from the acid washed CoNC sample. The ratio of pyridinic to pyrrolic N changes from 4.4 in the as-prepared sample to 2.7 in the acid-washed sample. Acid

washing also changes the pyridinic/pyrrolic ratio in other N-containing carbon materials.¹⁰⁰ Thus, we speculate that acid washing the CoNC materials converted some of the pyridinic N to pyridinium N. We note the peak position of pyridinium N overlaps with pyrrolic N and thus it is not possible to distinguish between these two species.¹⁰¹⁻¹⁰² The XPS shows an additional peak at 399 eV which is assigned to nitrile or amine groups.⁸⁵ This peak is present in a previous publication of this synthesis, which presents the XPS of the materials after acid washing. However, their assignment for a peak at 399 eV is for a N bonded to Co.²⁸ We note that Co phthalocyanine XPS only contains a single nitrogen XPS peak at 398 eV.³⁹ Other publications on Co-N-C materials assign this peak as nitrile

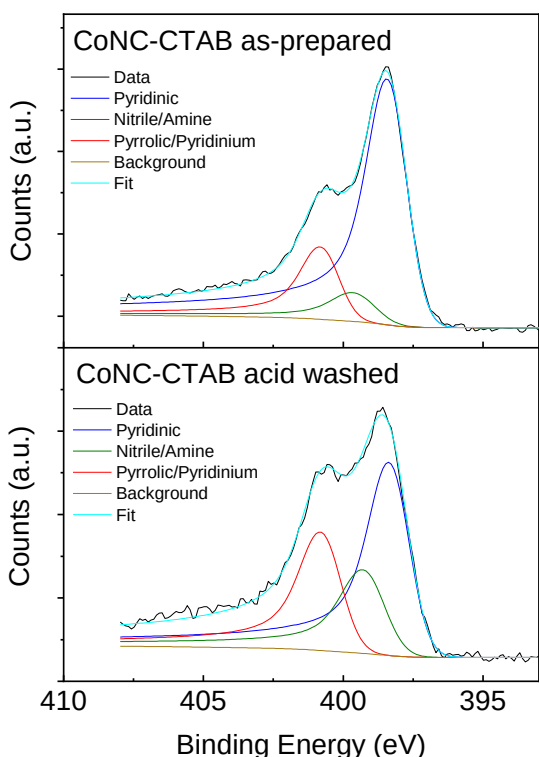


Figure 4.10. N 1s XPS scan of CoNC-CTAB samples: as-prepared (top) and acid washed (bottom).

The pyridinic/pyrrolic N ratios are 3.6 and 1.6 for the as-prepared and acid washed CoNC-CTAB samples, respectively.

Figures 4.11 and 4.12 are the Co 2p spectra for all catalyst materials. Figure 4.11 shows the Co 2p spectrum for the CoNC as-prepared catalyst. The spectrum is fit with two main peaks for Co 2p_{3/2} and Co 2p_{1/2} at 780.1 and 795.6 eV, respectively, and their corresponding

or amino groups.^{33, 99} The nitrile/amino N was likely always present but too low in intensity to be seen in the CoNC as-prepared XPS.

Figure 4.10 shows the N 1s spectra for the CoNC-CTAB catalyst materials. The XPS in Fig. 4.10 is similar to that found for the CoNC material, including changes in the pyridinic/pyrrolic N ratio upon acid washing and the changes associated with modification.

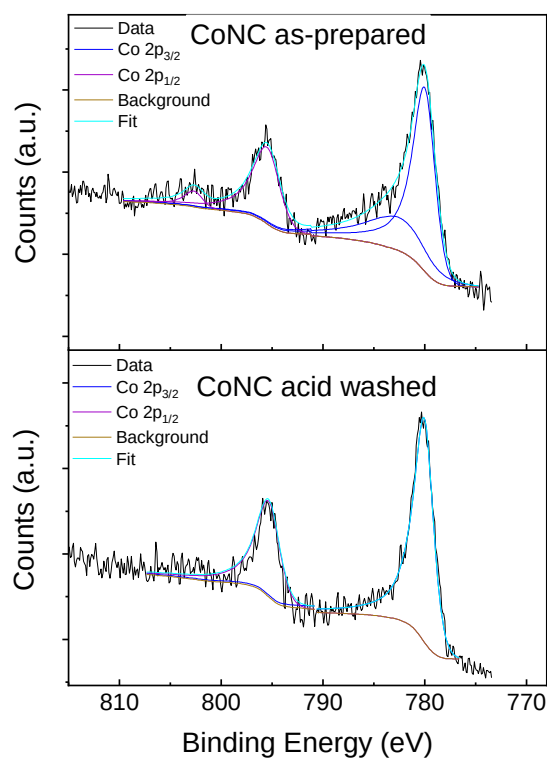


Figure 4.11. Co 2p X-ray photoelectron spectroscopy of CoNC as-prepared and acid washed.

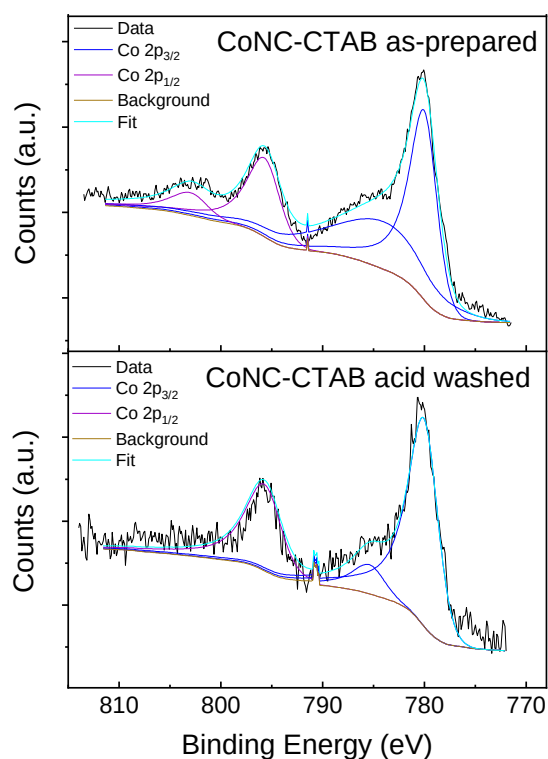


Figure 4.12. Co 2p X-ray photoelectron spectroscopy of CoNC-CTAB as-prepared, and acid washed.

satellites. The positions of these peaks and their satellites are consistent with the presence of Co^{2+} species.^{28, 40, 103} Figure 4.11 shows the Co 2p spectrum for the acid washed CoNC sample. The peak assignments and positions in Fig. 4.11 are the same as for the as-prepared sample. The satellite intensity for both the Co $2p_{3/2}$ and Co $2p_{1/2}$ peaks decreases with acid washing. This decrease is likely due to the reduced total Co content (Table 4.3). Figure 4.12 shows the Co 2p spectra for the CoNC-CTAB as-prepared and acid

washed. The XPS is similar to that found for the CoNC material.

4. SQUID Magnetometry and TEM

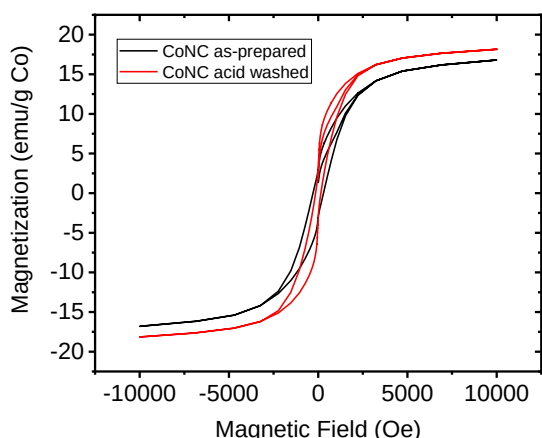


Figure 4.13. Representative plot of the effect of an applied magnetic field on magnetization of CoNC materials.

SQUID magnetometry was used to determine the percentage of non-paramagnetic Co in the CoNC and CoNC-CTAB materials. The magnetization was corrected for the mass of Co in the sample using the weight of catalyst in the capsule and the percentage of the Co as determined by ICP-OES (Table 4.3).

Figure 4.13 shows the magnetization of CoNC at 300 K under an applied magnetic field. To estimate the percentage of non-paramagnetic Co as compared to paramagnetic Co in the catalyst samples, the saturation magnetization was compared to the saturation magnetization of nanosized metallic Co (Figure 4.14).¹⁰⁴ We used nanosized metallic Co as the reference material because it is a superparamagnetic material in contrast to Co_3O_4

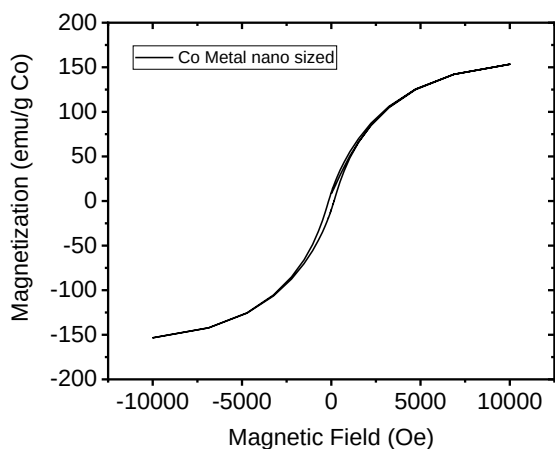


Figure 4.14. The effect of an applied magnetic field on magnetization of nanosized Co metal particles.

and CoO which do not exhibit a sigmoidal lineshape.^{93-94, 105} We note that the hysteretic behavior seen in figures 4.13 and 4.17 indicate that we have ferromagnetic particles, but the presence of superparamagnetic particles cannot be ruled out. For this reason, we refer to the material leading

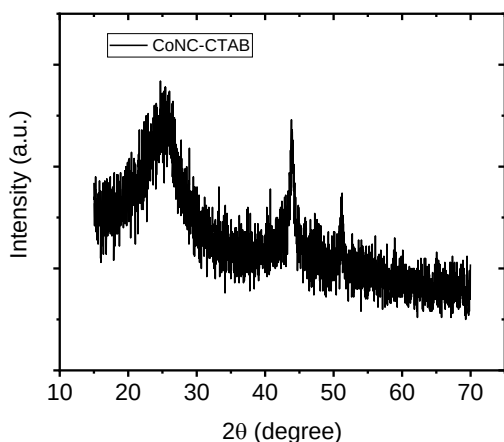


Figure 4.15. The XRD pattern for CoNCCTAB as-prepared.

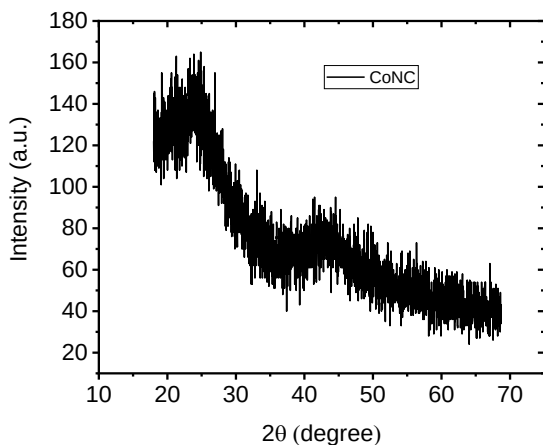


Figure 4.16. The XRD pattern for CoNC as-prepared.

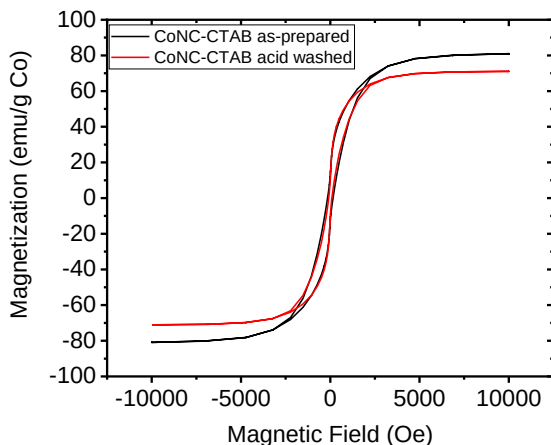


Figure 4.17. A representative plot of the effect of an applied magnetic field on magnetization of CoNC-CTAB materials.

to this sigmoidal SQUID magnetometry behavior as non-paramagnetic. Additionally, the XRD spectrum (Figure 4.15) of CoNC-CTAB includes peaks for metallic Co as well as for graphitic carbon and no peaks for Co oxides. The XRD pattern (Figure 4.16) for the CoNC catalyst only includes peaks for graphitic carbon.¹⁰⁶⁻¹⁰⁸

Figure 4.17 shows the magnetization data at 300 K under an applied magnetic field for the CoNC-CTAB-based materials. The hysteretic and sigmoidal lineshape present in both spectra are indicative of the presence of ferromagnetic materials. The average saturation magnetization for all materials is summarized in Table 4.3. Interestingly, the magnetization for the CoNC-CTAB samples is substantially larger than that found for

Table 4.3. Average Co weight percent for all catalyst materials as determined by ICP-OES. Average saturated magnetization and percentage ferromagnetic Co as determined by SQUID magnetometry.

Material	wt% Co	M_{sat} (emu/g Co)	Percentage Non-Paramagnetic Co
CoNC	5 ± 1	7 ± 7	5 ± 5
CoNC acid washed	2.7 ± 0.6	12 ± 9	8 ± 6
CoNC-CTAB	10 ± 1	74 ± 23	49 ± 16
CoNC-CTAB acid washed	5.6 ± 0.5	68 ± 10	46 ± 7

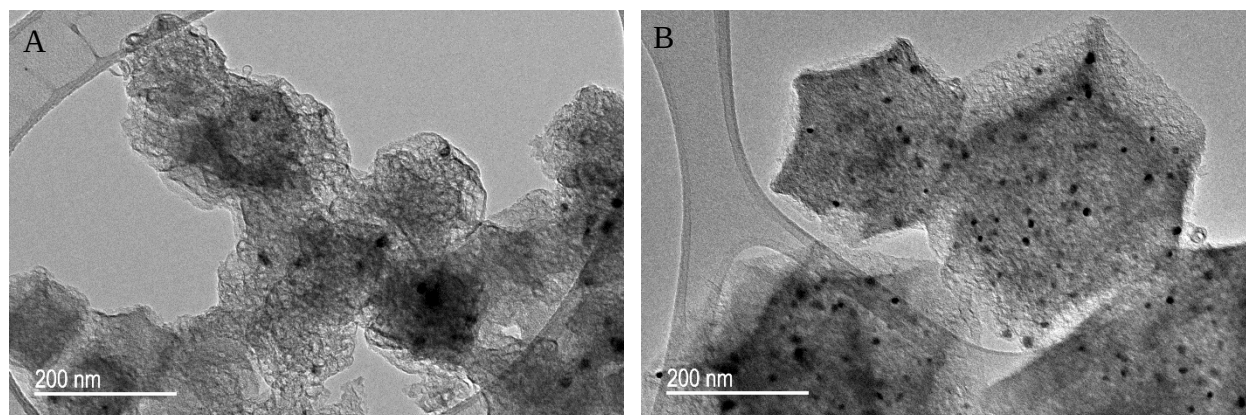


Figure 4.18 TEM images of (a) CoNC and (b) CoNC-CTAB as-prepared materials.

the CoNC samples. This indicates the presence of substantially more ferromagnetic material in the CoNC-CTAB samples relative to the CoNC samples.

The presence of nanoparticles in the CoNC and CoNC-CTAB materials can be confirmed with TEM images. As shown in Figure 4.18A, B, nanoparticles are present in both catalysts. In the areas examined, there are more (ca. 3 times) nanoparticles present in the CoNC-CTAB material as shown in the TEM image, which is consistent with the higher saturation magnetization of CoNC-CTAB as measured by SQUID magnetometry.

5. Understanding the Role of CTAB

The CoNC-CTAB as-prepared and acid washed materials exhibit more total Co relative to the comparable CoNC materials (Table 4.3). We wanted to determine if this difference in Co weight percentage in the catalyst material originates in the precursor

synthesis. ICP-OES was used to determine the total Co and Zn weight percentage in the catalyst precursors.

As summarized in Table 4.4, the CoNC-CTAB precursor material contains significantly more Co as compared to the CoNC precursor material. This is a significant increase in the amount of Co retained in the MOF precursor especially considering the additional C and N content expected (in the form of CTAB) in the CoNC-CTAB MOF precursor. We note that the C, H, and N content of both precursors are identical.

Table 4.4. Average C, H, N, Zn, Co weight percentage for catalyst precursor materials as determined by ICP-OES and CHN analysis.

Material	CoNC Precursor	CoNC-CTAB Precursor
C	42.14 $\pm$ 0.09%	42.3 $\pm$ 0.2%
H	4.3 $\pm$ 0.1%	4.3 $\pm$ 0.1%
N	23.98 $\pm$ 0.07%	24.0 $\pm$ 0.3%
Zn	22.2 $\pm$ 0.2%	20.6 $\pm$ 0.1%
Co	3.1 $\pm$ 0.2%	4.3 $\pm$ 0.6%

In order to further understand the role of CTAB in the precursor synthesis, we synthesized another catalyst material, starting with only $\text{Co}(\text{NO}_3)_2$ and CTAB. CTAB has been used previously to assist in the formation of Co-containing nanoparticles.^{32, 109-110} We then mixed the resulting product with XC72 to make the catalyst conductive. Based on fitting of the SQUID magnetometry data (see Calculation 2), the radius of the Co NPs in the Co NPs + XC72 material is 1.57 ± 0.02 nm. After pyrolysis, we were able to produce a catalyst with activity similar to that of the CoNC and CoNC-CTAB catalysts as measured

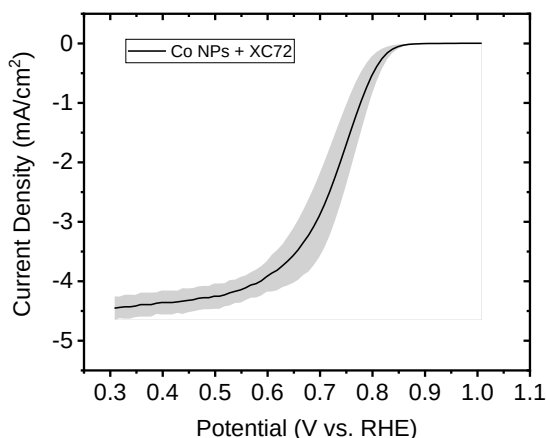


Figure 4.19. Staircase voltammogram of Co NPs + XC72 catalyst as measured in 0.1 M NaOH. The shaded areas represent +/- one standard deviation in the current obtained from multiple measurements.

in 0.1 M NaOH (Figure 4.19). The average $E_{1/2}$ of the Co NPs + XC72 catalyst as measured in 0.1 M NaOH is 0.73 ± 0.03 V. Based on ICP-OES analysis, the Co NPs + XC72 catalyst contains $51 \pm 5\%$ Co. The RRDE measurements show that the Co NPs + XC72 catalyst transfers $3.3 \pm 0.2 e^-$, producing $36 \pm 12\%$ H_2O_2 . Thus, this catalyst transfers significantly less

electrons compared to the CoNC or CoNC-CTAB as-prepared catalysts in 0.1 M NaOH.

The XRD pattern of the Co NPs + XC72 material includes peaks for metallic Co as well as for graphitic carbon (Figure 4.20), identical to the pattern for CoNC-CTAB, albeit with much greater intensity. This increased intensity is consistent with the increased percentage of Co in Co NPs + XC72 as determined by ICP-OES. The SQUID magnetometry of the Co NPs + XC72 material (Figure 4.23) also shows a significant

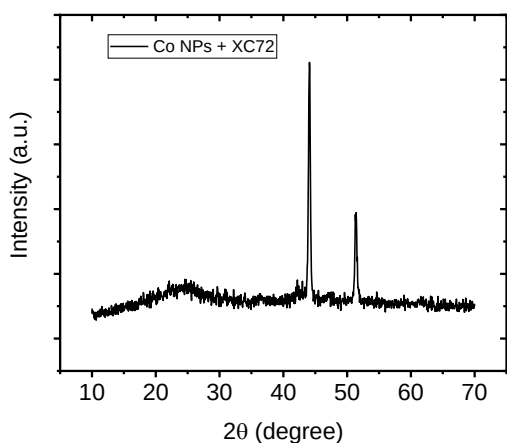


Figure 4.20. The XRD pattern for Co NPs + XC72 catalyst.

amount of non-paramagnetic Co material indicated by the high average

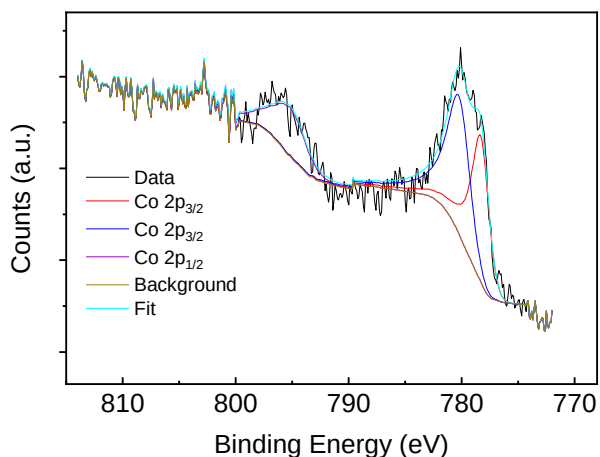


Figure 4.21. The Co 2p XPS of Co NPs + XC72.

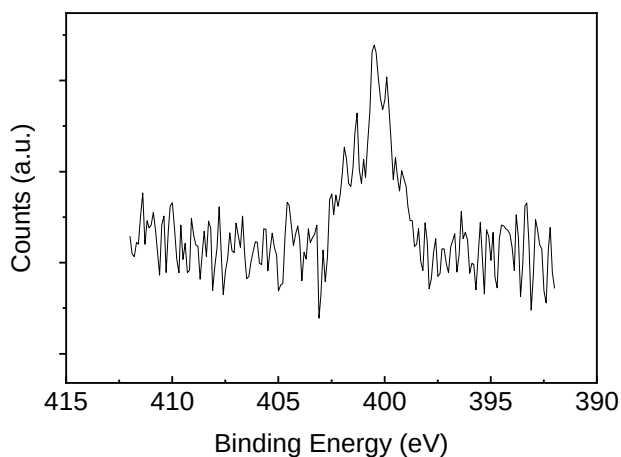


Figure 4.22. The N 1s XPS of Co NPs + XC72.

M_{sat} (150 ± 30). At 100% non-paramagnetic Co, the Co NPs + XC72 catalyst contains a greater percentage of non-paramagnetic Co as compared to CoNC-CTAB (49%). The coercivity of the Co NPs + XC72 material is smaller, (62 Oe) compared with CoNC-CTAB (155 Oe). The narrower hysteresis is indicative of more superparamagnetic domains rather than ferromagnetic domains in the Co NPs + XC72 material.⁶⁴ The Co 2p and N 1s XPS are shown in figure 4.21 and 4.22, respectively. The Co 2p spectrum is fit with three peaks, at, 778.4, 780.4, and 795.4 eV. The peak at 788.4 eV is

consistent with the presence of Co^0 species and the other peaks are consistent the presence of with Co^{+2} species.^{28, 40, 103, 111} The Co $2p_{1/2}$ peak for the Co^0 species is likely present, but too small to fit.

We have developed two catalysts that are primarily Co nanoparticles (Co NPs + XC72) and Co^{+2} (CoNC) as determined by SQUID magnetometry. We can now compare their respective rate constants for the ORR by using a Koutecky-Levich analysis

Table 4.5. Summary of the reaction rate constant (k_f) of materials as measured in 0.1 M NaOH at 0.720 V vs. RHE.

^aCalculated for surface atoms of the particle only

Material	Rate Constant ($10^{-6} \text{ cm s}^{-1}$)	Rate Constant/atom (10^{-23})	Rate Constant/Particle (10^{-23})	Tafel Slope (mV/dec)
CoNC	1.1 ± 0.5	1.9 ± 0.9	NA	60 ± 9
Co NPs + XC72	0.9 ± 0.5	0.5 ± 0.2^a	228 ± 116	54 ± 6

(Calculation 1).^{60, 112-113} The k_f for oxygen reduction of the Co NPs + XC72 catalyst is determined to be $0.9 \pm 0.5 \times 10^{-6} \text{ cm s}^{-1}$ while the k_f for oxygen reduction of the CoNC catalyst is determined to be $1.1 \pm 0.5 \times 10^{-6} \text{ cm s}^{-1}$ (Table 4.5) at 0.720 V vs. RHE. The rate constants for the two catalysts at this potential are not statistically different. By way of comparison, the overall rate constant for the ORR on Pt in 0.1 M NaOH at 0.7 V is

$$0.015 \text{ cm s}^{-1}.^{113}$$

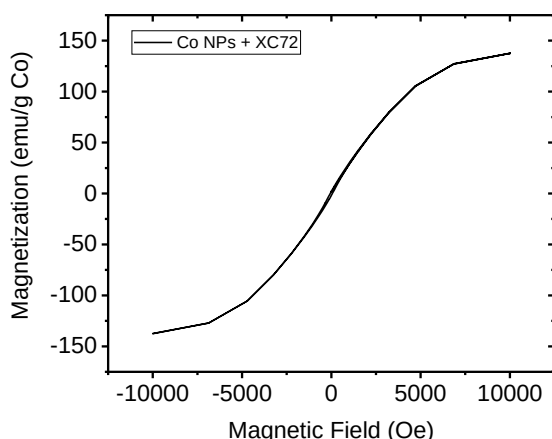


Figure 4.23. The effect of an applied magnetic field on magnetization of Co NPs + XC72.

We also determined the Tafel slope for the CoNC and Co NPs + XC72 in 0.1 M NaOH (Table 4.5). The Tafel slope is $60 \pm 9 \text{ mV/dec}$ for the CoNC as-prepared catalyst and $54 \pm 6 \text{ mV/dec}$ for the Co NPs + XC72 catalyst, similar to what has been reported previously for both Co-based

ORR catalysts and Pt in 0.1 M NaOH.^{97, 114-115} Equal Tafel slopes have been suggested to correlate to similar reaction mechanisms.⁹⁷ We note, however, that Pt catalysts do not involve a proton coupled electron transfer (PCET) as determined by kinetic isotope analysis when reducing O_2 in acidic or basic media.¹¹⁶ While to our knowledge there is

no report as to whether or not Co-based pyrolyzed catalysts involve a PCET, Fe-based catalysts do involve a PCET.¹¹⁶⁻¹¹⁷

6. Discussion

The CoNC as-prepared and CoNC acid washed catalysts do not exhibit significantly different activity in 0.1 M HClO₄ as determined by the $E_{1/2}$ or the number of electrons transferred (n , Table 4.1). The CoNC-CTAB as-prepared catalyst is significantly less active as compared to the CoNC-CTAB acid-washed catalyst and the CoNC catalysts in 0.1 M HClO₄ as determined by the $E_{1/2}$ value (Table 4.1).

The CoNC acid washed catalyst has a slightly greater $E_{1/2}$ as compared to the CoNC as-prepared catalyst as measured in 0.1 M NaOH. However, the CoNC acid washed catalyst has a significantly lower n value (Table 4.2). Catalysts with low Co loading will exhibit greater OH₂⁻ production in basic electrolyte.¹¹⁸ Generally, the $E_{1/2}$ increases after acid washing as measured in 0.1 M NaOH. The amount of Co is significantly diminished after acid washing as determined by ICP-OES results, and the SQUID magnetometry remains unchanged (Table 4.3), which may suggest that the acid washing is removing inactive oxidized Co species, leading to a more active catalyst.^{17, 119-}

120

The results presented above show that both the CoNC and CoNC-CTAB materials exhibit some ferromagnetic character. The CoNC-CTAB materials, however, are significantly more ferromagnetic, exhibiting an average saturation magnetization of 71 emu/g Co over all materials as compared to only 8 emu/g Co for CoNC. Thus, the CoNC-CTAB exhibits SQUID consistent with a substantial (47%) presence of metallic Co, while the CoNC has much less metallic Co (6%). These results suggest the inclusion of CTAB

in the precursor prior to pyrolysis play a role in directing speciation of the Co before and during the pyrolysis.

We next address the role of CTAB. The addition of CTAB to the precursor mixture leads to an increased percentage of Co in the precursor MOF (Table 4.4) as well as the final catalyst (Table 4.3). CTAB has been used previously to assist in the formation of Co-containing nanoparticles,^{32, 109-110} which may explain its role in the synthesis of CoNC-CTAB.

We speculate the amount of non-paramagnetic Co in the CTAB-based preparation relates to the degree of agglomeration of the Co during synthesis. In the CTAB-based preparation the 2-methylimidazole has two roles: 1) it serves as the ligand of the MOF which can form with both Co and Zn and 2) it makes the methanolic solution slightly less acidic. Prior to addition of 2-methylimidazole the pH of precursor solution is 3, but the solution exhibits a pH of 5 following 2-methylimidazole addition. Indeed, addition of base is commonly used in CTAB-syntheses of Co nanoparticles.¹⁰⁹⁻¹¹⁰ With addition of 2-methylimidazole the solution becomes basic enough to form nanoparticles, competing with the MOF formation. The addition of base is necessary for the formation of Co oxides (likely the form of the metallic Co nanoparticle prior to pyrolysis) because of the metathesis reaction between the $\text{Co}(\text{NO}_3)_2$ and base.¹²¹⁻¹²⁴ The critical micelle concentration (CMC) for CTAB is reported to be between 0.7-1 mM.¹²⁵⁻¹²⁷ The concentration of CTAB in the solution for CoNC-CTAB preparation is 27 mM, well above the CMC. Consequently, the CTAB likely forms micelles enhancing Co particle formation in the colloidal synthesis step and retention during pyrolysis.

To investigate the role of CTAB further, we synthesized another catalyst material, Co NPs + XC72, as a model to understand the role of CTAB in the CoNC-CTAB synthesis. The XRD (Figure 4.15, 4.20) results show that Co nanoparticles consistent with those formed in the CoNC-CTAB catalyst are also formed by using the Co NP + XC72 method. This result suggests that CTAB is incorporating more Co in the final MOF via the formation of Co oxide aggregates, which are then converted to Co nanoparticles in the final catalyst following pyrolysis. Indeed, Co NP + XC72 forms non-paramagnetic Co exclusively as shown by the SQUID magnetometry (Figure 4.23). We conclude that the addition of CTAB allows for the agglomeration of Co oxides in the precursor solution and the formation of metallic Co nanoparticles in the final pyrolyzed catalyst.

The Co NPs + XC-72 catalyst exhibits similar ORR activity relative to the as-prepared CoNC catalyst as measured in 0.1 M NaOH. Since the Co NPs + XC-72 catalyst consists nearly exclusively of Co nanoparticles, this result suggests that Co nanoparticles are the active centers for ORR as measured in 0.1 M NaOH. This conclusion is consistent with results for other Co-based ORR catalysts.^{99, 118}

We can compare the ORR rate constant of the CoNC and Co NPs + XC72 catalysts. These rate constants are particularly interesting to discuss because the CoNC catalyst contains primarily Co^{+2} while the Co NPs + XC72 contains primarily Co^0 nanoparticles. While the rate constants are the same for each catalyst as measured in 0.1 M NaOH, we can also consider the rate per Co atom. For the CoNC catalyst, the rate constant is $1.9 \pm 0.9 \times 10^{-23} \text{ cm s}^{-1} (\text{Co atom})^{-1}$. We used the Langevin fit of the SQUID magnetometry data to determine the number of particles present in the Co NPs + XC72 catalyst and the number of surface Co atoms (for details see Calculation 2). On this basis,

the Co NPs + XC72 catalyst the rate constant is $0.5 \pm 0.2 \times 10^{-23} \text{ cm s}^{-1} (\text{surface Co atom})^{-1}$ and the rate constant per particle for the Co NPs + XC72 is much larger at $2 \pm 1 \times 10^{-21} \text{ cm s}^{-1} (\text{Co nanoparticle})^{-1}$. Interestingly, the rate per surface Co atom for the Co NPs + XC72 catalyst is approximately a factor of four lower than the rate per Co atom in the CoNC catalyst. Of course, the calculation of the number of surface Co atoms is only approximate.

In conclusion, different preparations of Co ORR catalysts yield differing relative amounts of paramagnetic vs. non-paramagnetic Co species. In the systems studied here, the non-paramagnetic (metallic Co) material exhibits ORR activity similar to that found from a catalyst composed from a primarily paramagnetic Co. Magnetometry is a facile method to determine general Co speciation and further understand the species that lead to active catalysts.

Chapter 5 Effect of High Temperature Reductive Treatments on Fe-containing ORR Catalysts

1. Introduction

Speciation of the pyrolyzed Fe-based ORR material has long been a controversial topic. On the basis of the presence of corresponding Mössbauer spectroscopy signals, many authors suggest that a FeN_4 or related oxidized species forms the active site.^{23, 36, 52, 128} Alternatively, other authors suggest that reduced species, such as Fe^0 or Fe_3C are the active site.^{27, 129-130} The absence of poisoning of NPM materials by CO slightly implicates the latter species,¹³ but in situ NO exposure has been found to decrease ORR activity suggesting again the presence of FeN_4 .²⁴

Post-processing of pyrolyzed materials involving a second pyrolysis and/or acid washing has long been known to increase NPM ORR activity.¹² Some of the most effective post-processing treatments involve the use of NH_3 -treatment at high temperatures,^{20, 23, 49, 52} which yields more active materials relative to the use of inert gases.^{42, 52} Various origins of this increased activity have been suggested, including, increased basicity of the N groups on the catalyst surface,²³ increased surface areas leading to more efficient O_2 and electrolyte transport to active sites,^{52, 129, 131} changes in N speciation favoring the formation of pyridinic N groups,¹³²⁻¹³³ and active site speciation changes associated with the increased presence of FeN_4 species.⁵² Alternatively, reductive treatments usually result in the presence of reduced species and changes in Fe speciation to Fe^0 and iron nitrides (determined by XRD) have also been reported.⁵²⁻⁵³ H_2 heat treatments have also been used in the synthesis of non-precious metal, Fe-based,

ORR catalysts,^{12, 16, 42, 54} but there has not significant analysis on the resulting changes to the catalyst.

In this chapter we use magnetometry, XRD, XPS, N₂ physisorption, NO poisoning, ICP-OES, CHN analysis, TEM, and electrochemistry to examine the effect of two different reductive gas treatments on pyrolyzed ORR catalysts. We find that reductive gas treatments yield more superparamagnetic/ferromagnetic Fe species, and that some of the catalysts exhibiting large percentages of superparamagnetic/ferromagnetic materials also exhibit high activities for ORR catalysis.

2. Electrochemistry

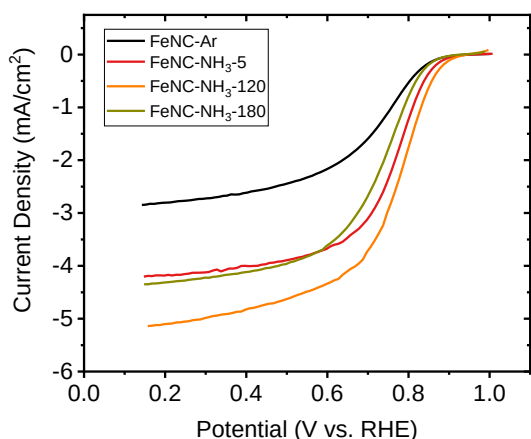


Figure 5.1. Average SCVs for FeNC-Ar, FeNC-NH₃-5, FeNC-NH₃-120, and FeNC-NH₃-180 catalysts as measured in 0.1 M HClO₄ at 1600 rpm.

Figure 5.1 shows average SCVs for the FeNC-Ar and NH₃-treated catalysts as measured in 0.1 M HClO₄ electrolyte. Two effects are seen in Fig. 5.1. First, the current density measured at 0.8 V (a potential chosen in the kinetic region for facile comparison between different

catalysts here and in the literature) from the FeNC-Ar catalyst is -0.5 ± 0.2 mA/cm² and, based on RRDE measurements (Figure 5.2), 3.8 ± 0.1 electrons are transferred. This electrochemical activity is consistent with previous reports for the FeNC-Ar catalyst.²³ The ORR current density from the FeNC-NH₃-5 catalyst at 0.8 V is -1.3 ± 0.2 mA/cm² and 3.9 ± 0.1 electrons are transferred. This electrochemical activity is again consistent with previous reports for the FeNC-NH₃-5 catalyst.¹⁰⁸ The ORR current density from the FeNC-

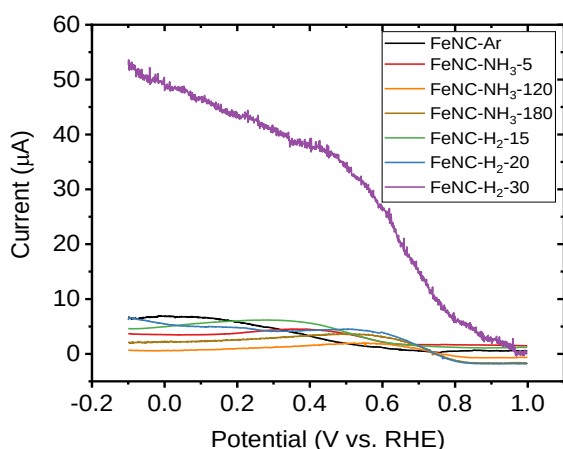


Figure 5.2. Representative Pt ring current from RRDE experiments for all catalyst materials at 1600 rpm.

NH₃-5 is significantly greater than the ORR current density from the FeNC-Ar catalyst at 0.8 V. The ORR current density from the FeNC-NH₃-120 catalyst at 0.8 V is -1.8 ± 0.4 mA/cm² and 3.9 ± 0.1 electrons are transferred. The ORR current density from the FeNC-NH₃-180 catalyst at 0.8 V is -0.7 ± 0.1 mA/cm² and 3.9 ± 0.1 electrons are transferred. The ORR current density from the FeNC-NH₃-180 catalyst is significantly lower than the current density from the FeNC-NH₃-5 catalyst as determined at 0.8 V. Overall, increasing NH₃ heat treatment time results in increased activity up to 120 min. By 180 min of NH₃ treatment, the activity decreases, but is still greater than that from the FeNC-Ar catalyst.

The second trend seen in Fig. 5.1 is a change in the steady state current density (measured at 0.2 V, a potential chosen in the mass transfer region) as a function of treatment time. In planar metallic electrodes, this increase in steady state current density is usually associated with a change in *n* value.¹³⁴⁻¹³⁵ In the materials here, however, the *n* value (measured using RRDE) changes from 3.8 in FeNC-Ar to 3.9 in all other NH₃-treated materials. Thus, changes in *n* value are not the origin of the increased current

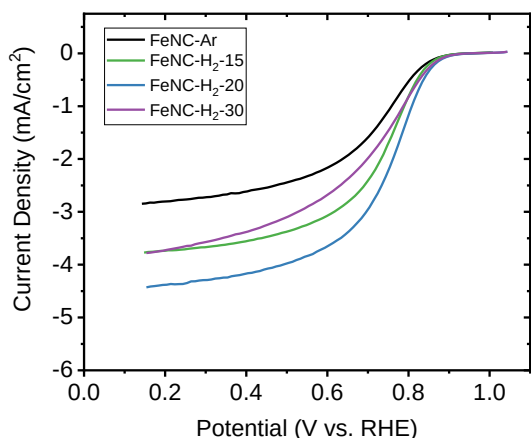


Figure 5.3. Average SCVs for FeNC-Ar, FeNC-H₂-15, FeNC-H₂-20, and FeNC-H₂-30 catalysts as measured in 0.1 M HClO₄ at 1600 rpm.

density. A second possibility for the increased steady state current density is a change in number (or type) of active sites exposed to O₂ and the electrolyte. This exposure may involve increased porosity in the carbon support or exposure (increased loading) of Fe sites at the surface.

Figure 5.3 shows average SCVs for FeNC-Ar and the H₂-treated catalysts as measured in 0.1 M HClO₄ electrolyte. The ORR current density at 0.8 V from the FeNC-H₂-15 catalyst is -0.7 ± 0.2 mA/cm² and 3.9 ± 0.1 electrons are transferred. The ORR current density at 0.8 V from the FeNC-H₂-20 catalyst is -1.0 ± 0.2 mA/cm² and 3.9 ± 0.1 electrons are transferred. The ORR current density from FeNC-H₂-20 is significantly greater than the ORR current density from the FeNC-Ar catalyst as determined at 0.8 V. The ORR current density at 0.8 V from the

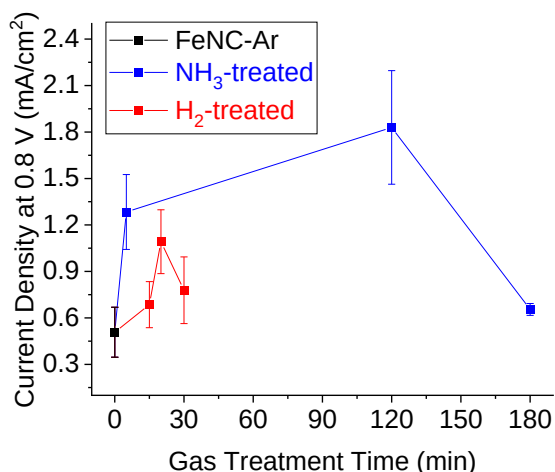


Figure 5.4. Average and standard deviation of the current density at 0.8 V for all catalyst materials. Line is a guide for the eye.

FeNC-H₂-30 catalyst is -0.8 ± 0.2 mA/cm² and 3.5 ± 0.1 electrons are transferred. The number of transferred electrons from the FeNC-H₂-30 has decreased significantly as compared to all other catalysts. An increase in the limiting current density at 0.2 V is also observed from the H₂-treated catalysts.

Table 5.1. Summary of the j_k , Tafel slope, current density, n value, %H₂O₂ and limiting current for all catalysts.

Catalyst	j_k at 0.8 V (mA/mg catalyst)	Tafel Slope (mV/dec)	Current Density at 0.8 V (mA/cm ²)	n (e ⁻)	H ₂ O ₂ production (%)	Limiting Current at 0.2 V (mA/cm ²)
FeNC-Ar	0.5 ± 0.3	93 ± 19	-0.5 ± 0.2	3.8 ± 0.1	9 ± 2	-2.8 ± 0.6
FeNC-NH ₃ -5	2.3 ± 0.7	84 ± 36	-1.3 ± 0.2	3.9 ± 0.1	5 ± 3	-4.2 ± 0.2
FeNC-NH ₃ -120	7 ± 1	76 ± 10	-1.8 ± 0.4	3.9 ± 0.1	6 ± 5	-4.9 ± 0.6
FeNC-NH ₃ -180	2.5 ± 0.6	94 ± 23	-0.7 ± 0.1	3.9 ± 0.1	4 ± 2	-4.3 ± 0.6
FeNC-H ₂ -15	2 ± 1	83 ± 11	-0.7 ± 0.2	3.9 ± 0.1	6 ± 2	-3.7 ± 0.3
FeNC-H ₂ -20	3 ± 1	80 ± 18	-1.1 ± 0.2	3.9 ± 0.1	5 ± 3	-4.4 ± 0.2
FeNC-H ₂ -30	2 ± 1	77 ± 19	-0.8 ± 0.2	3.5 ± 0.1	25 ± 7	-3.7 ± 0.3

Overall, the activity of the FeNC catalysts increases with increased H₂ treatment at 950 °C. However, when the H₂ treatment time is increased to 30 min, the activity decreases. The ORR current density measured at 0.8 V from the NH₃-treated and H₂-treated catalysts is illustrated in Figure 5.4.

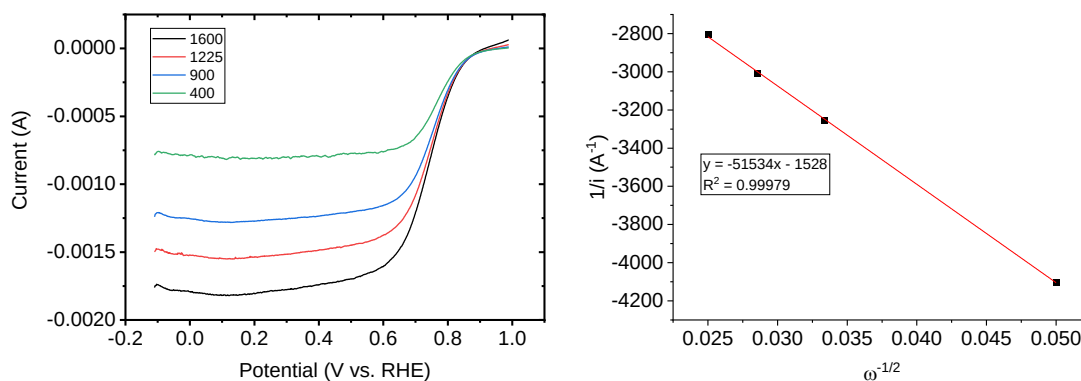


Figure 5.5. Representative Ar-subtracted CVs for the FeNC-NH₃-5 catalyst and the linear fit of $1/i$ vs. $\omega^{-1/2}$ at 0.8 V.

Table 5.1 reports j_k values at 0.8 V obtained using Eq. 2.1. Figure 5.5 shows representative Ar-subtracted CVs and the linear fit of $1/i$ vs. $\omega^{-1/2}$ at 0.8 V. Table 5.1 shows the j_k value for the FeNC-Ar catalyst is relatively low and consistent with previous reports.²³ Table 5.1 also shows that reductive gas treatment improves the j_k from that found for the untreated catalyst. The FeNC-NH₃-120 catalyst exhibits the highest j_k value at 7 ± 1 mA/mg catalyst at 0.8 V. This j_k value is consistent with other catalysts subjected to a long NH₃ treatment time.⁵² Figure 5.6 shows the average Tafel plots for each catalyst material. Table 5.1 shows that the Tafel slopes for all treated catalysts are similar. The Tafel slopes are again consistent with those from other reports examining Fe-based NPM ORR catalysts.^{17, 52, 136}

Table 5.3 compares the j_k value obtained at 0.8 V from the FeNC-NH₃-120 catalyst

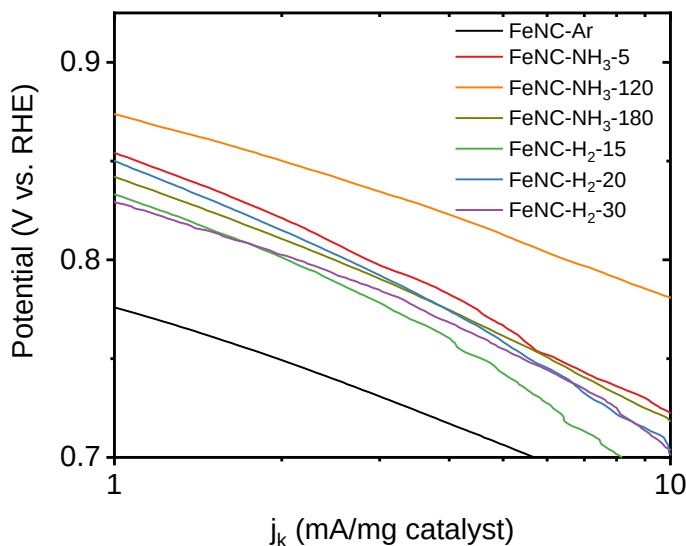


Figure 5.6. Average kinetic current density (mA/mg catalyst) plotted for potentials in the kinetic region for all catalyst materials.

to others reported in the literature. The table shows that the j_k value for FeNC-NH₃-120 is comparable to other reported j_k values obtained from Fe-based NPM ORR catalysts.

We note that other publications studying Fe-based ORR catalyst

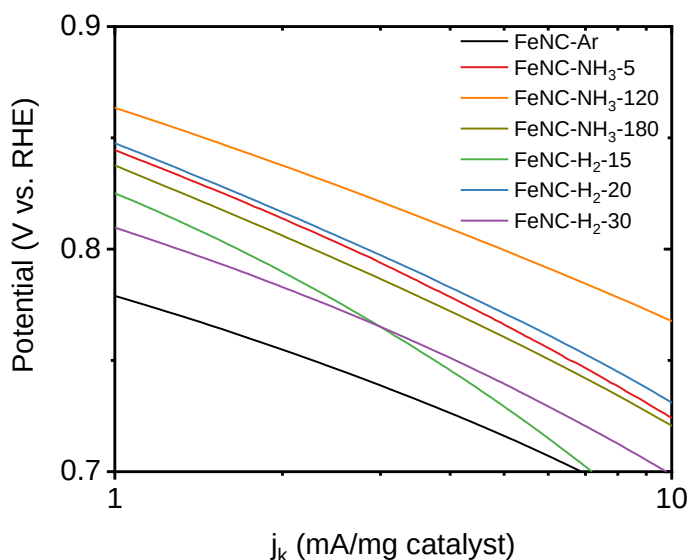


Figure 5.7. Average kinetic current density (mA/mg catalyst) plotted for potentials in the kinetic region for all catalyst materials determined using $1/i - 1/i_D = 1/i_k$. A rotation rate of 1600 rpm was used for the CVs from which this data was calculated.

materials use a slightly different method to

calculate j_k values.^{48, 137-139}

Instead of a linear fit of $1/i$ vs. $\omega^{-1/2}$ (Eq. 2.1, used here), Eq. 5.1 is used:

$$\frac{1}{j} = \frac{1}{j_D} + \frac{1}{j_K} \quad (5.1)$$

where j_D is the limiting current density at a particular rotation rate.

Table 5.2 shows the j_k

values determined using Eq. 5.1. The j_k values are similar to those determined from Eq. 2.1 (Table 5.1). In particular, the FeNC-NH₃-120 again has the highest j_k value (5.0 ± 0.4 mA/mg catalyst) at 0.8 V. Fig. 5.7 shows the average Tafel plots for each catalyst material determined using Eq. 5.1.

Table 5.2. Summary of the j_k values determined using Eq. 5.1 for all catalysts.

Catalyst	j_k at 0.8 V (mA/mg)
FeNC-Ar	0.5 ± 0.2
FeNC-NH ₃ -5	2.7 ± 0.4
FeNC-NH ₃ -120	5.0 ± 0.4
FeNC-NH ₃ -180	2.3 ± 0.4
FeNC-H ₂ -15	1.7 ± 0.7
FeNC-H ₂ -20	2.8 ± 0.5
FeNC-H ₂ -30	1.3 ± 0.3

Table 5.3. Summary of reported j_k values in literature for similar Fe-N-C based ORR catalysts.

^aEstimated from figure

Material	NH ₃ treatment?	j_k calculation method	Proposed Active Site	j_k at 0.8 V vs. RHE (mA/mg)	Reference
FeNC-NH ₃ -120	Yes, 120 min	Eq. 2.1	Fe ₄ N	7 ± 1	This work
FeNC pre-CO	Does not say	Eq. 5.1	FeN ₄	2.4 ^a	140
Fe _{0.5} -N/CDC-2	No	Eq. 5.1	FeN _x C _y	8.0	137
Fe _{0.5} -950	Yes, 5 min	Eq. 5.1	FeN ₄	>10 ^a	23
PANI-Fe-C	No	Eq. 5.1	FeN ₄	2 ^a	17
1.5Fe-ZIF	No	Eq. 5.1	FeN ₄	45.0	36
Fe _{0.5} -NH ₃	Yes, 5 min	Eq. 5.1	FeN ₄	5	141
Fe ₃ C@N-C-900	No	Eq. 5.1	Fe ₃ C	2.5 ^a	129
E	Yes, 60 min	Eq. 5.1	FeN ₄	8 ^a	52

3. ICP-OES and CHN Analysis

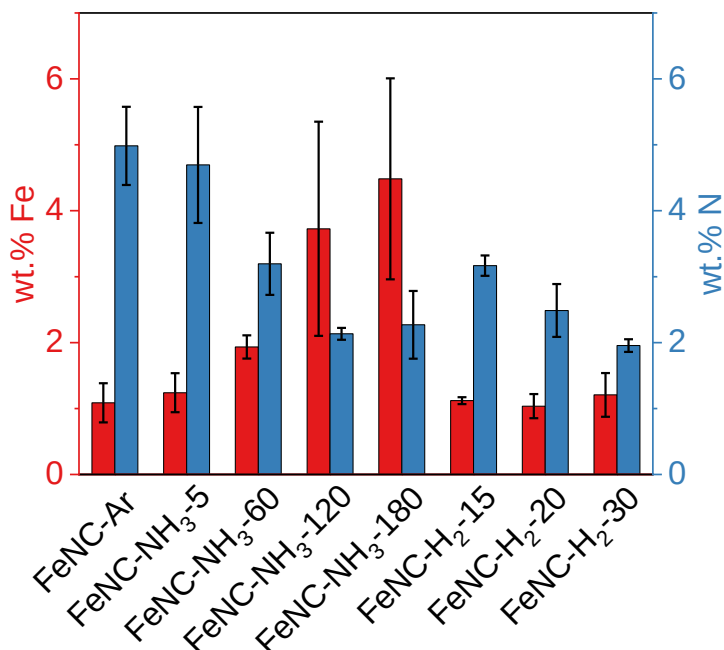


Figure 5.8. Fe and N wt.% determine by ICP-OES and CHN Analysis for all catalyst materials. (A) NH₃-treated catalysts and (B) H₂-treated catalysts.

We also determined changes in Fe and N content following the NH₃ or H₂ treatments (Figure 5.8). With increasing NH₃ treatment time the wt.% Fe increases from 1% to 4%. There is no significant change in the wt.% Fe following H₂ treatments.

The changes in wt.% Fe can be explained by the overall loss of mass during the heat

treatments (Figure 5.9). The FeNC-NH₃-5 and all the H₂-treated catalysts exhibit ca. 30% mass loss and show no significant increases in the wt.% Fe as compared to the FeNC-

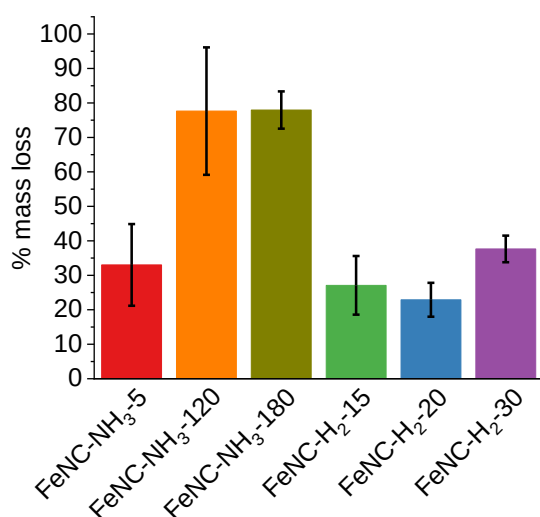


Figure 5.9. % mass loss from FeNC-Ar starting material for all treated catalysts.

Ar catalyst. The FeNC-NH₃-120,180 catalysts both exhibit and ca. 78% mass loss and an increase in wt.% Fe from 1% to 4%. The wt.% N decreases significantly from 5% to 2% with longer NH₃ and H₂ treatments.

4. XRD

The XRD of the NH_3 -treated catalysts are shown in Figure 5.10A. The FeNC-Ar and FeNC- NH_3 -5 catalysts have small XRD peaks consistent with the presence of α -Fe, and Fe_3C .¹⁴²⁻¹⁴³ With longer NH_3 treatment time (120, 180 min), there is a significant intensity increase for peaks consistent with γ - Fe_4N and γ -Fe.¹⁴⁴⁻¹⁴⁶ With long NH_3 treatment times the formation of γ - Fe_4N has been reported for NPM ORR catalysts.^{52, 147} Fe_3C and α -Fe peaks also have greater intensity as compared to the FeNC- NH_3 -5 catalyst.

The XRD of the H_2 -treated catalysts are shown in Figure 5.10B. The FeNC- H_2 -15 catalyst has XRD peaks consistent with α -Fe, γ -Fe and Fe_3C . With longer H_2 treatment

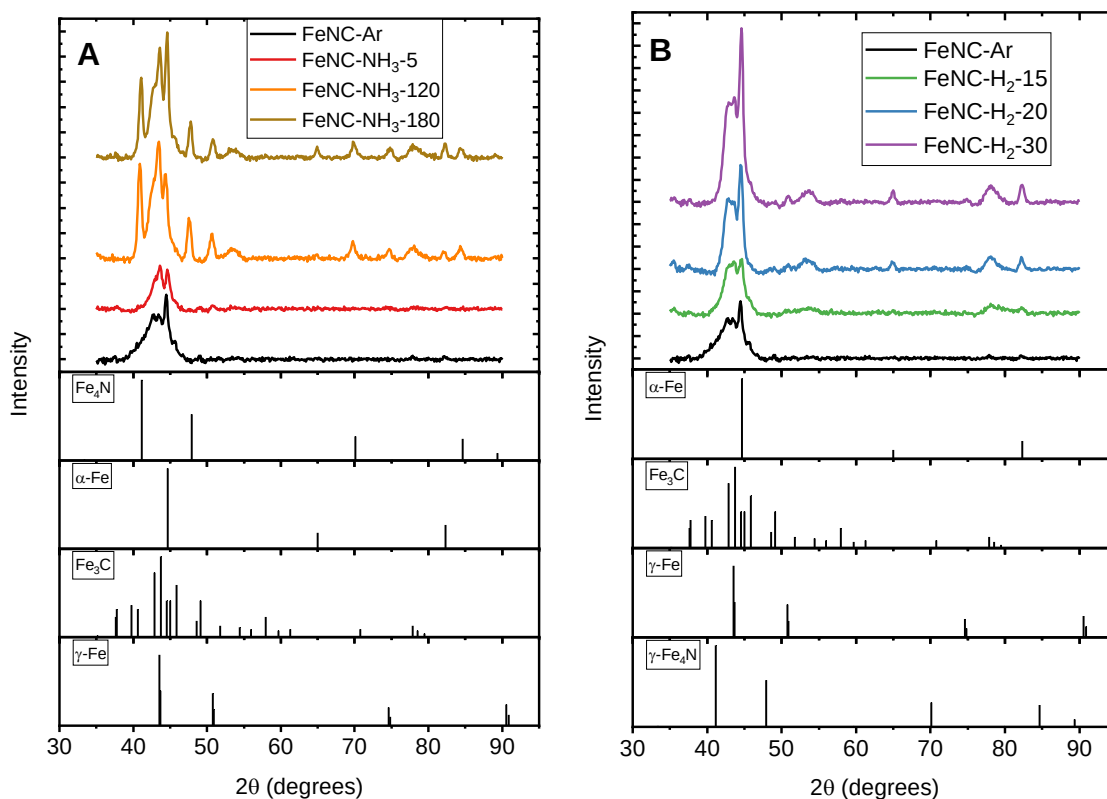


Figure 5.10. The background subtracted XRD pattern for (A) NH_3 -treated catalysts and (B) H_2 -treated catalysts. All catalyst materials shown are offset in y for clarity.

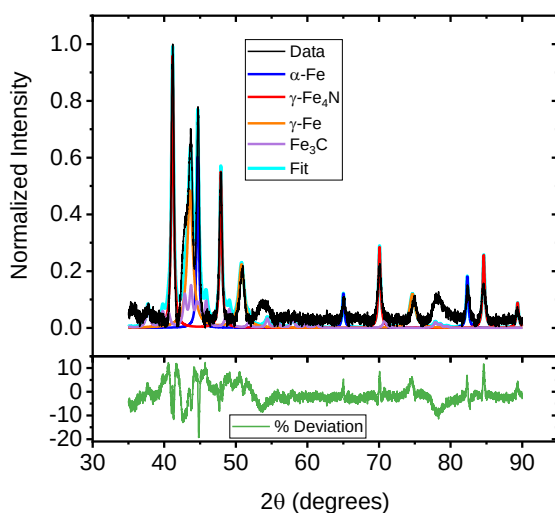


Figure 5.11. Data and fits for the FeNC-NH₃-120 catalyst. Lower spectrum is the %difference between data and total fit.

time, peaks associated with α -Fe and Fe₃C grow significantly. Unlike the NH₃-treated catalysts there are no significant XRD peaks associated with γ -Fe₄N.

By fitting the XRD spectra we determined the relative peak intensity ratios for the species present in the FeNC-NH₃-120, FeNC-NH₃-180, FeNC-H₂-20, and FeNC-H₂-30

catalysts. An example fit is shown in Fig. 5.11. Table 5.4 reports ratios of different species obtained from the fit. The peak intensity ratio of γ -Fe₄N to all other species decreases from 0.78 to 0.36 between the FeNC-NH₃-120 catalyst and the FeNC-NH₃-180 catalyst. This ratio change indicates a significant conversion of γ -Fe₄N species to α -Fe, γ -Fe, and Fe₃C species with the longer exposure to NH₃. For the H₂-treated catalysts, the peak intensity ratio of α -Fe to all other species increases from 0.92 to 1.4 between the FeNC-H₂-20 and the FeNC-H₂-30 catalyst. This ratio change indicates a significant increase in

Table 5.4. XRD peak fit ratios for the FeNC-NH₃-120, FeNC-NH₃-180, FeNC-H₂-20, and FeNC-H₂-30 catalysts.

Catalyst	γ -Fe ₄ N/all other species	α -Fe/all other species γ -Fe
FeNC-NH ₃ -120	0.78	0.38
FeNC-NH ₃ -180	0.36	0.5
FeNC-H ₂ -20	N/A	0.91
FeNC-H ₂ -30	N/A	1.4

the amount of α -Fe present in the catalyst relative to other species. Of course, this fitting cannot report on absolute amounts of the different Fe-containing species.

5. SQUID Magnetometry

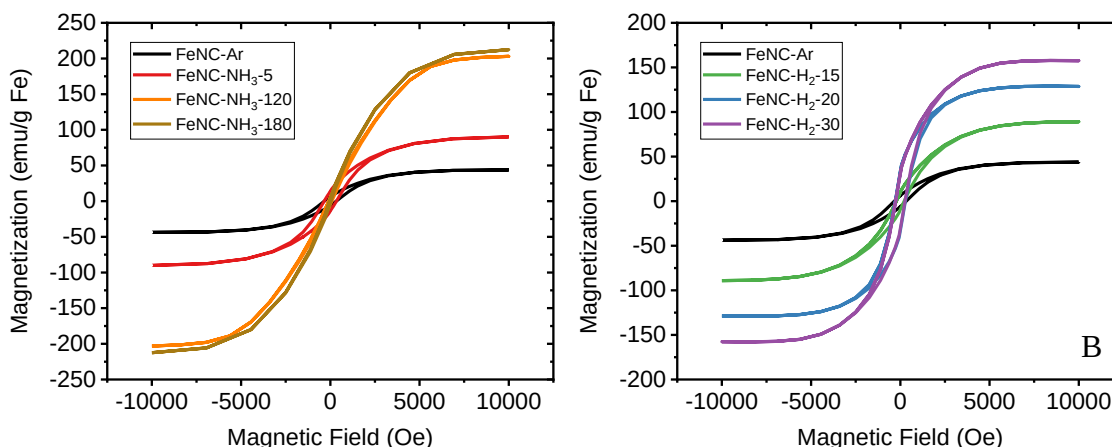


Figure 5.12. Representative plots of magnetization with applied magnetic field for the FeNC-Ar catalyst and the (A) NH₃-treated catalysts and (B) H₂-treated catalysts.

SQUID magnetometry was used to evaluate the relative content of ferromagnetic/superparamagnetic species as compared to paramagnetic species in all catalyst materials. To normalize the magnetization to the mass of Fe in the catalysts we used the mass of catalyst in the sample holder and the wt.% Fe obtained from ICP-OES measurements (Figure 5.8). For reference, the saturation magnetization for pure Fe⁰, γ -Fe₄N, and Fe₃C are 221 emu/g, 188 emu/g, and 83 emu/g, respectively.^{72, 144, 148-149}

Representative magnetization plots for the FeNC-Ar and NH₃-treated catalysts are shown in Figure 5.12A. As the NH₃ treatment time increases, the saturation magnetization increases up to 120 min of treatment. The total saturation magnetization derives from a convolution of the susceptibilities of all the magnetic species present in the catalyst (Fe⁰, γ -Fe₄N, and Fe₃C). The saturation magnetization of the FeNC-Ar catalyst is 33 ± 8 emu/g Fe. This relatively low saturation magnetization is consistent with the XRD for the FeNC-Ar catalyst which has small peaks for α -Fe and Fe₃C. The saturation magnetization of FeNC-NH₃-120 (198 ± 17 emu/g Fe) is consistent with a sample containing reduced

species such as Fe^0 , $\gamma\text{-Fe}_4\text{N}$ which are species determined to be present by XRD. The saturation magnetization of the FeNC-NH₃-180 catalyst is 195 ± 59 emu/g Fe which is not significantly different from the FeNC-NH₃-120 material. This result indicates that we have converted nearly all the available Fe to magnetic species. We also note that the FeNC-NH₃-120 and the FeNC-NH₃-180 catalysts do not exhibit the hysteretic behavior associated with ferromagnetic species^A. This suggests that the catalyst is composed of superparamagnetic material.

Representative magnetization plots for the FeNC-Ar and H₂-treated catalysts are shown in Figure 5.12B. As H₂ treatment time increases, the saturation magnetization also increases. For the FeNC-H₂-20 catalyst, the saturation magnetization has reached 141 ± 11 . Assuming all the saturation magnetization contribution is from Fe^0 , the percentage of ferromagnetic/superparamagnetic species is $64 \pm 5\%$. For the FeNC-H₂-30 catalyst, the saturation magnetization has reached 175 ± 15 . Assuming all the saturation

Table 5.5. Summary of the saturation magnetization for all the catalyst materials as determined by SQUID magnetometry.

Catalyst	Saturation Magnetization (emu/g Fe)	Fe species present based on XRD
FeNC-Ar	33 ± 8	Fe^0 , Fe_3C
FeNC-NH ₃ -5	80 ± 16	Fe^0 , Fe_3C
FeNC-NH ₃ -120	198 ± 17	Fe^0 , Fe_3C , $\gamma\text{-Fe}_4\text{N}$
FeNC-NH ₃ -180	195 ± 59	Fe^0 , Fe_3C , $\gamma\text{-Fe}_4\text{N}$
FeNC-H ₂ -15	89 ± 9	Fe^0 , Fe_3C
FeNC-H ₂ -20	141 ± 11	Fe^0 , Fe_3C
FeNC-H ₂ -30	175 ± 15	Fe^0 , Fe_3C
Fe^0	221	-
Fe_4N	188	-
Fe_3C	88	-
Iron phthalocyanine (FeN ₄)	0.4	-

magnetization contribution is from Fe^0 , the percentage of ferromagnetic/superparamagnetic species is $79 \pm 7\%$. A summary of the saturation magnetization and the Fe species present for all catalyst materials is shown in Table 5.5. The increases in saturation magnetization from the FeNC-Ar catalyst are consistent with increased Fe^0 / $\gamma\text{-Fe}_4\text{N}/\text{Fe}_3\text{C}$ nanoparticles in the treated catalysts. Indeed, TEM images show significantly more nanoparticles in NH_3 and H_2 treated catalysts compared to the FeNC-Ar catalyst (Figure 5.13).

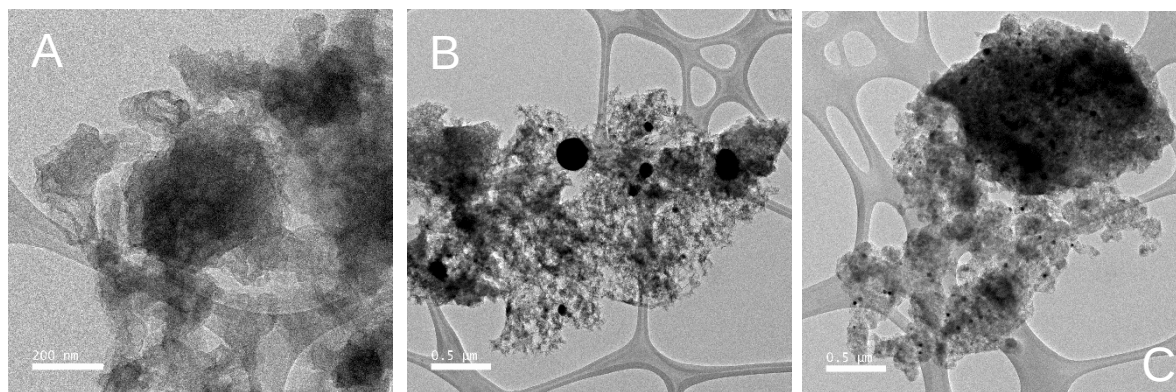


Figure 5.13. TEM images of (A) FeNC-Ar, (B) FeNC-NH₃-120, and (C) FeNC-H₂-20.

Acid washing is typically used in NPM catalyst preparation.^{22, 150} The analyses reported above were obtained prior to immersion in the acid electrolyte. To evaluate the effect of immersion into 0.1 M HClO_4 electrolyte we immersed 300 mg of the FeNC-NH₃-120 catalyst into 250 mL of 0.1 M HClO_4 for 1 hr in air. Following drying at 90 °C overnight, we obtained the magnetization from this material under an applied magnetic field. The saturation magnetization from the acid-immersed catalyst was 218 emu/g Fe which is similar to that from the as-prepared FeNC-NH₃-120 catalyst (198 emu/g Fe). This measurement shows that acid immersion does not significantly alter speciation in the FeNC-NH₃-120 catalyst and the material still consists nearly entirely of

superparamagnetic Fe species. Electrochemical measurements show ORR reactivity identical with that reported for the FeNC-NH₃-120 catalyst prior to acid washing.

6. XPS

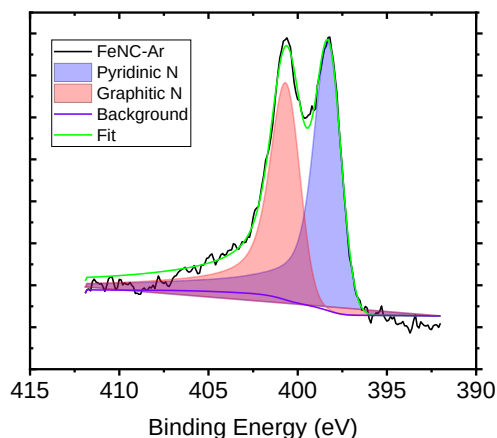


Figure 5.14. N1s XPS of the FeNC-Ar catalyst

Figure 5.15 shows N 1s XPS obtained from the NH₃ and H₂ treated catalyst materials. The N 1s XPS from the FeNC-Ar catalyst is shown in Figure 5.14. Each spectrum is fit with 2 peaks for pyridinic and graphitic N at 398 and 401 eV, respectively.¹⁵¹ With increasing NH₃ or H₂ treatment time, the graphitic/pyridinic N peak area ratio increases. Table 5.6

summarizes the graphitic/pyridinic peak area ratios. The increasing graphitic/pyridinic ratio is consistent with prior results from NH₃ and H₂ heat treatment on carbon/nitrogen materials.¹⁵¹⁻¹⁵² The change in the area ratio may indicate the removal of surface pyridinic

Table 5.6. Peak area ratios determined from fits of N 1s and C 1s spectra.

Catalyst	Graphitic/Pyridinic N Peak Area Ratios
FeNC-Ar	0.9
FeNC-NH ₃ -5	1.1
FeNC-NH ₃ -120	2.3
FeNC-NH ₃ -180	3.1
FeNC-H ₂ -15	1.2
FeNC-H ₂ -20	2.0
FeNC-H ₂ -30	2.3

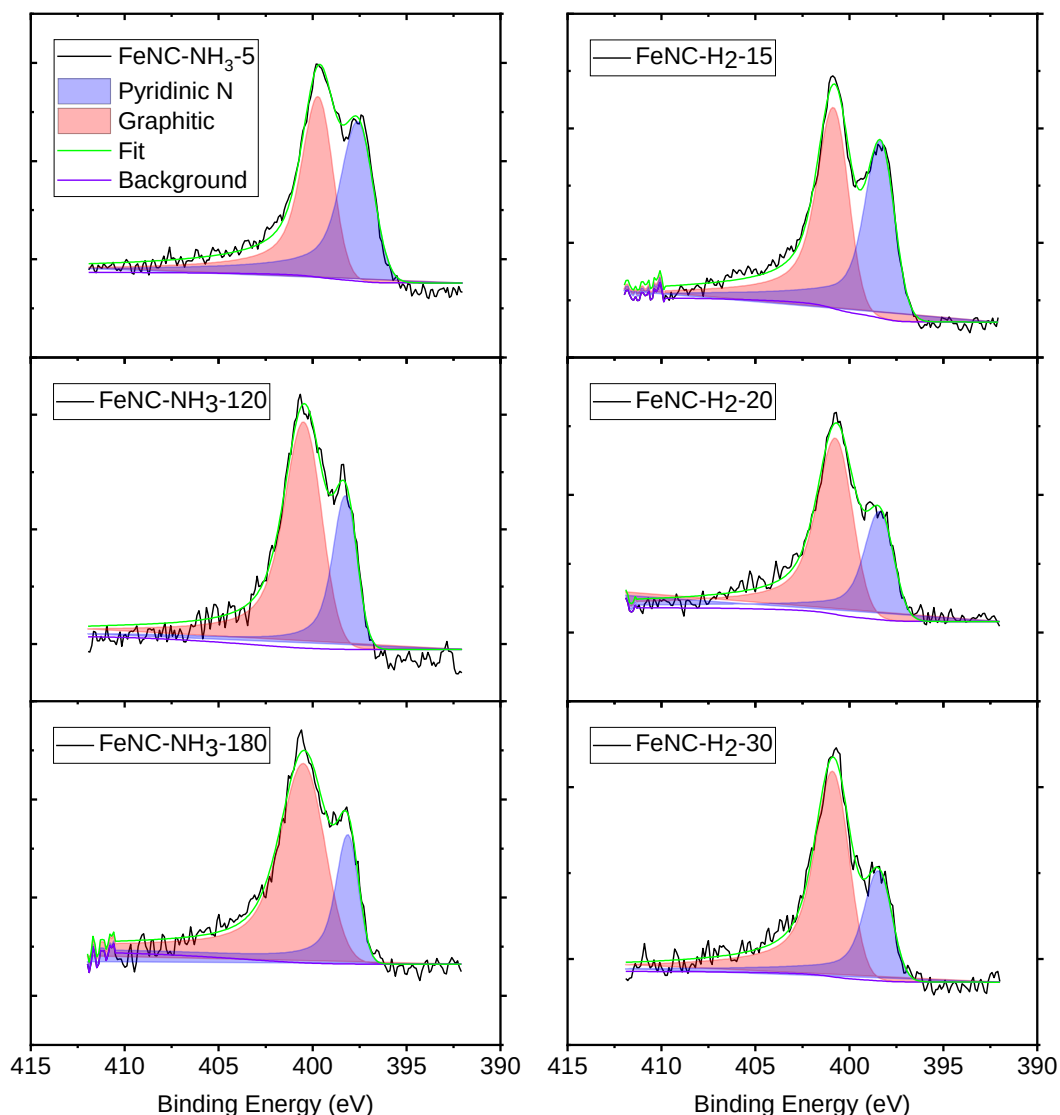


Figure 5.15. The N 1s XPS for catalyst materials. The legend in the top left applies to all plots.

N, consistent with the decrease in the wt.% N determined by CHN measurements (Figure 5.8). Consistent with prior literature, Fe 2p XPS exhibits a low S/N ratio (ca. 2) and consequently speciation is difficult to evaluate (data not shown).^{42, 153}

We conducted potentiometric titrations on all catalyst materials to investigate putative changes to the functional groups on the C of the catalyst as a function of reductive gas treatment. The data show acid functionalities on the order of 0.1-0.2

mmol/g. Unmodified carbons exhibit acidic functionalities on the order of 0.05-0.1 mmol/g. Modified carbons often exhibit acidic functionalities on the order of 1-10 mmol/g.¹⁵⁴⁻¹⁵⁵ Thus, there are no significant changes in the functional groups on the surface as compared to unmodified C (data not shown).

7. N₂ Physisorption

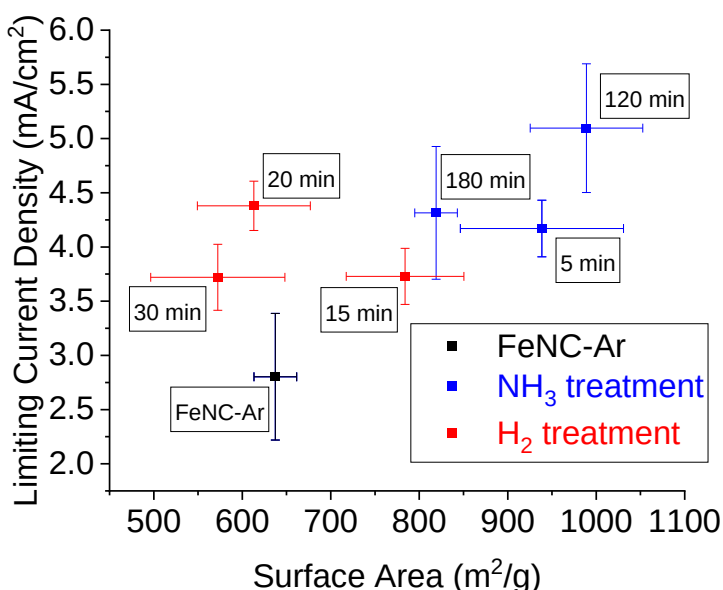


Figure 5.16. Relationship between the surface area and the current density at 0.2 V for NH₃- and H₂-treated catalysts.

N₂ physisorption

measurements were used to determine the surface area of the catalyst materials. Surface areas were found to range between 500 and 1050 m²/g, consistent with prior literature.^{15, 53, 129, 131}

Figure 5.16 illustrates the relationship between

surface area and limiting current density. The figure shows that the NH₃ treatment generally yields catalysts exhibiting higher surface areas which is correlated with increased limiting current density, as has been found previously.^{47, 129, 131} The FeNC-NH₃-120 catalyst exhibits the largest limiting current density and exhibits the largest surface area. The H₂ treatment leads to generally lower surface areas as compared to the NH₃ treatment. The increased surface area from the NH₃ treated catalysts relative to those

treated with H_2 is likely associated with $C + NH_3$ redox reactions yielding N_2 and CH_4 .^{53, 156-158} H_2 does not significantly change the C surface area during C material treatment.¹⁵⁹

8. NO poisoning

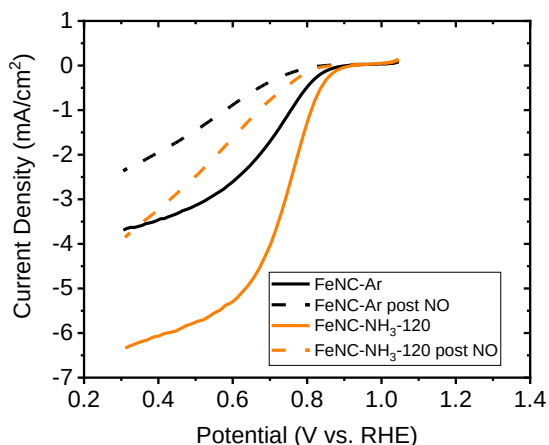


Figure 5.17. Effect of NO poisoning on ORR activity in 0.1 M $HClO_4$ at a rotation rate of 1600 rpm.

NPM ORR catalysts are poisoned by NO generated in situ during ORR.^{24, 160} The existence of this poisoning behavior has been suggested to be evidence that the NPM ORR active site are of the FeN_4 type as stand-alone Fe porphyrins are also poisoned by NO.^{24, 160} Figure 5.17 shows the effect of NO poisoning,

performed using the procedure described in the literature²⁴, on the ORR activity of the FeNC-Ar and FeNC-NH₃-120 catalysts. The solid lines in Fig. 5.17 show the ORR activity of the catalysts prior to NO exposure. Following NO exposure, both materials exhibit a decrease in ORR activity. In particular, the FeNC-Ar catalyst exhibits a -140 mV shift in the ORR $E_{1/2}$. This negative shift is consistent with previous literature, which reported shifts between -50 mV and -200 mV.²⁴ We also note the lack of limiting current density for the NO-exposed FeNC-Ar catalyst, again consistent with the literature. The FeNC-NH₃-120 material exhibits -180 mV shift in the ORR $E_{1/2}$, a greater decrease than that found for the untreated FeNC-Ar catalyst. This activity decrease indicates that the active sites formed from NH₃ treatment are sensitive to NO poisoning.

9. Discussion

It has long been known that reductive treatments to pyrolyzed NPM materials yield more active ORR catalysts.^{16, 52} The origins of this increased activity have been associated with changes in Fe and N speciation in the material. Prior work using NH_3 gas treatments suggested that NH_3 resulted in an increased amount of FeN_4 -type active sites.^{16, 52, 161} Increased surface area, deriving from NH_3 decomposition and CH_4 formation has also been proposed to yield greater activity.⁵³

Measurements show that the NH_3 -based reductive treatments yield more active catalysts up to 120 min treatment time. If the treatment time is extended, however, the activity of the NPM material is decreased. This decrease – as seen in the j_k values – is not necessarily associated with either increased peroxide production, or a substantial decrease in catalyst surface area. Similar to the NH_3 treatment, H_2 treatment also results in increased activity at intermediate treatment times. At long times, however, the activity again decreases as seen in the increased $\%\text{H}_2\text{O}_2$ production.

Effect of NH_3 and H_2 treatments

The XRD and SQUID magnetometry measurements show that all the materials subjected to either the NH_3 or H_2 the reductive treatments contain ferromagnetic/superparamagnetic Fe species. The presence of these species is not surprising, as procedures to produce materials like $\gamma\text{-Fe}_4\text{N}$, encapsulated Fe^0 , or Fe_3C all feature a reductive step at temperatures similar to those used here.^{149, 162-163} The magnetometry obtained from both the $\text{FeNC-NH}_3\text{-120}$ and $\text{FeNC-NH}_3\text{-180}$ materials suggests that almost all of the Fe in the sample has converted to superparamagnetic species as saturation magnetizations are consistent with those obtained from $\gamma\text{-Fe}_4\text{N}$ and

Fe⁰.^{72, 144, 148-149} Notably, the presence of oxidized Fe species, such as FeN₄, would substantially lower the saturation magnetization. The XRD from the FeNC-NH₃-120 and FeNC-NH₃-180 indicates that speciation in these samples is a mixture of Fe⁰, γ-Fe₄N, and Fe₃C. While the magnetization in the H₂ treated samples is lower, increased H₂ treatment time also results in increased saturation magnetization relative to the untreated samples. This increased saturation magnetization is also reflected in the XRD, where peaks associated with Fe₃C and Fe⁰ species increase significantly in intensity.

N speciation also changes significantly with NH₃ or H₂ treatment time. The N 1s XPS shows that the graphitic/pyridinic ratio increases significantly with increased treatment time (Table 5.6). The CHN analysis indicates that with increased treatment time the wt.% of N decreases significantly (Figure 5.8). These results indicate that surface pyridinic N species are likely being removed. The increasing graphitic/pyridinic ratio also indicates that increased pyridinic N content is not necessary to improve catalyst activity.

There are significant changes in catalyst surface area with increased NH₃ treatment time. With even short (5 min) NH₃ treatment times the surface area increases significantly. However, at long treatment times (180 min) the surface area decreases, likely due to consumption of the catalyst as 80% of the original material has been removed. These surface area changes are also seen in the H₂ treated catalysts although the effect is not as significant as that seen with NH₃.

Comparison of NH₃ and H₂ treatments

There are two major differences in catalyst properties between the NH₃ and H₂ treatments. First, the catalyst surface area does not increase significantly over the untreated sample when treated with H₂ but nearly doubles with NH₃ treatment. NH₃ at

high temperatures decomposes into H_2 and N_2 . However, when flowing through a hot zone sufficiently quickly (as in our case), full decomposition does not occur.¹⁵⁷⁻¹⁵⁸ C is known to react with NH_3 gas to form N_2 and CH_4 .¹⁵⁶ This reaction is likely the source of the dramatic increase in surface area with the NH_3 treatment.

The second change between treatments relates to Fe speciation. The saturation magnetization obtained from the FeNC- H_2 -20 catalyst is only ca. 60% as high as that obtained from the FeNC- NH_3 -120 catalyst. Additionally, XRD-based speciation shows that only Fe_3C and Fe^0 are found with the H_2 treatment while the NH_3 treatment yields additionally $\gamma-Fe_4N$. The FeNC- H_2 -30 material contains more superparamagnetic/ferromagnetic species – as shown by magnetometry – but does not contain $\gamma-Fe_4N$. The generally increased presence of superparamagnetic Fe species with the NH_3 treatment may relate to the increased treatment time used here, or the reductive activity associated with NH_3 . Longer reductive gas treatment times yield greater saturation magnetization values.

Correlation between speciation and reactivity

In this paper we utilized NH_3 or H_2 heat treatment to yield catalysts with improved activity, to a point. The best performing catalyst presented here is the FeNC- NH_3 -120 catalyst, based on the overall current density and j_k value (7 ± 1 mA/mg catalyst). This j_k value is on the upper end in comparison with other Fe-based NPM ORR catalysts. By way of contrast, the FeNC- NH_3 -180 also contains a similar amount of superparamagnetic species but exhibits lower activity. We focus here on the FeNC- NH_3 -180 and FeNC- NH_3 -120 materials as their very high saturation magnetization essentially excludes the

presence of FeN₄ sites. Higher saturation magnetization has previously been reported for catalysts with higher activity.⁴⁸

Both the FeNC-NH₃-180 and FeNC-NH₃-120 exhibit saturation magnetization consistent with the presence of Fe⁰ and γ -Fe₄N but the FeNC-NH₃-120 is substantially more active for ORR. XRD obtained from these materials shows that the shorter NH₃ treatment yields a material with lower relative intensity associated with Fe⁰ and higher intensity associated with γ -Fe₄N. This result – correlating increased activity with the increased presence of γ -Fe₄N – suggests that γ -Fe₄N is contributing to ORR activity. This result is also consistent with prior suggestions in the literature that the formation of Fe_xN species yields an improved ORR catalyst.^{52, 147} In particular, density functional theory calculations have shown that the addition of Fe₄N to a graphene sheet with an embedded FeN₄ improves the calculated onset potential for the ORR.¹⁶⁴

We also showed that NO poisons the FeNC-Ar and FeNC-NH₃-120 catalysts. The NO poisoning scheme has been shown to poison other ORR catalysts and proposed to bind to an FeN₄-type site.¹⁶⁰ The FeNC-NH₃-120 catalyst, however, contains nearly all superparamagnetic Fe species. The strong NO poisoning of the FeNC-NH₃-120 catalyst by NO indicates that active ORR species outside of FeN₄ are poisoned by NO.

This paper shows that different Fe-containing species can all exhibit ORR activity. Species found here include Fe⁰, Fe₃C, and γ -Fe₄N. FeN₄ is also a commonly proposed active site for pyrolyzed NPM catalysts, based on Mössbauer spectroscopy.^{21-22, 52, 137, 165} Unpyrolyzed FeN₄ catalysts also exhibit activity for the ORR.^{11, 166} In this paper we used reductive gas treatments to make ORR catalysts exhibiting different activities. Indeed, all of these species are implicated, particularly in those catalysts, such as the FeNC-H₂-20

and FeNC-NH₃-5, containing both paramagnetic and superparamagnetic/ferromagnetic Fe species, as determined by SQUID magnetometry. The presence of Fe⁰ and Fe₃C has also been reported in active ORR catalysts.^{16, 27} Interestingly, the FeNC-H₂-30 catalyst also contains nearly all superparamagnetic/ferromagnetic Fe species yet exhibits relatively poor ORR activity and, in particular, generates substantial peroxide. XRD shows that this catalyst contains more Fe⁰ relative to the more active FeNC-H₂-20 which suggests that Fe⁰ is less active for the ORR as compared to Fe₄N.

10. Conclusions

Pyrolyzing Fe – N – C based precursors leads to complex materials. Speciation in these materials can be simplified through the use of a reductive gas treatment. Extensive reductive treatment by using NH₃ leads to materials exhibiting magnetometry consistent with the nearly exclusive presence of superparamagnetic Fe species such as Fe⁰, Fe₃C, and γ-Fe₄N. Longer reductive treatments using either NH₃ or H₂ leads to the presence of more superparamagnetic/ferromagnetic Fe species. The most active materials for ORR obtained here were found from those exhibiting only superparamagnetic Fe species. Comparison of materials obtained using different treatment times implicates γ-Fe₄N as a particularly active ORR catalyst.

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